AD-A180 273

DTIC FILE COPY

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER

2. GOVT ACCESSION NO.

3. RECIPIENT'S CATALOG NUMBER

4. TITLE (and Subtitle)
Nitrolysis of the CN Single Bond and Related Chemistry of Nitro and Nitroso Groups

5. TYPE OF REPORT & PERIOD COVERED
Annual
1/1/86 - 12-31-86

6. PERFORMING ORG. REPORT NUMBER

DTIC
ELECTE
MAY 1 8 1987
S D
D

7. AUTHOR(s)
Joseph H. Boyer

8. CONTRACT OR GRANT NUMBER(s)
N00014-85-K-0896

9. PERFORMING ORGANIZATION NAME AND ADDRESS
University of New Orleans
Lakefront
New Orleans, LA 70148

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS

11. CONTROLLING OFFICE NAME AND ADDRESS

12. REPORT DATE
March 1987

13. NUMBER OF PAGES

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)
Department of the Navy
Office of Naval Research Code 432
Arlington, Virginia

15. SECURITY CLASS. (of this report)
Unclassified

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)
Reproduction in whole or in part is premitted for any purpose of the United States Government.

DISTRIBUTION STATEMENT A
Approved for public release
Distribution Unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Tert-Amines
Nitrosamines
Nitramines
α-Substitution in Nitrosamines
Nitrocyanocarbenes
Electron transfer
Barrelene derivatives

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A. Nitrosolyses of tertiary piperidines, piperazines, bisdimethylaminoalkanes, and functionalized methyldialkylamines were effected by dinitrogen tetroxide in carbon tetrachloride at 0 - 45°. The method has now been widely applied to the conversion of tertiary amines to nitrosamines.

B. 1,2-Dinitrocyclohexene was prepared. This is the first example of a 1,2-dinitrocycloalkene.

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-LF-014-6601

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

20. Abstract, continued:

C. Formation of 2-methyl-6-nitroindazole during the nitration of 4-nitro-N,N-dimethylbenzylamine was explained on the basis of an initial intramolecular charge transfer.

D. Trityl chloride and silver phenylcyanomethane nitronate gave trityl phenylcyanomethane nitronate, an unstable ester that rearranged and fragmented to a 1-triphenylmethoxy-4,5-diphenyl-1,2-3-triazole, carbon dioxide, α,α'-bis(triphenylmethaneazo)stilbene, benzonitrile-N-oxide, and trityl isocyanate.

E. Alkylation of nitroacetonitrile was investigated. The anion of benzylcyanonitromethane displaced a nitro group in dibenzylnitroacetonitrile to give tribenzylnitrosuccinonitrile, an example of a Kornblum reaction.

F. Dibromonitroacetonitrile brominated certain aromatic compounds. In the presence of copper it reacted with benzene to give benzoyl cyanide.

G. Formal nitrocyanocarbene adducts and brominations from nitrodibromoacetonitrile were realized.

H. α-Aminoacids were converted to α-amino derivatives of nitrosamines and nitramines. This begins to develop a general method for α-functionalization in nitrosamines.

I. Dinitrodibromomethane afforded both formal adducts of dinitrocarbene and also adducts from nitrosyl bromide.

J. Ligand transfer from iodobenzene ditrifluoroacetate afforded the conversion of phenacyl iodide to phenacyl alcohol.

Accesion For
NTIS CRA&I ☒
DTIC TAB ☐
Unannounced ☐
Justification
By
Distribution/
Availability Codes
Dist | Avail and/or Special
A-1

QUALITY INSPECTED 4

Contents

A. Nitrosolysis of Tertiary Amines: Piperidines, Piperazines, Bisdimethylaminoalkanes, and Functionalized Methyldialkylamines

J. CHEM. SOC PERKIN TRANS 1 1986

Joseph H. Boyer * and Govindarajulu Kumar, and T. Perumal Pillai
Chemistry Department, University of Illinois at Chicago, Chicago, Illinois 60680, U.S.A.

Preparative amounts of mono- and di-nitrosamines were obtained from aliphatic cyclic and acyclic tertiary monamines and diamines by treatment with dinitrogen tetraoxide in carbon tetrachloride at 0—45 °C. *N*-Methyl- and *N*-ethyl-piperidines (1) and (2) gave *N*-nitrosopiperidine (15), but *N*-isopropyl- and *N*-t-butyl-piperidines (3) and (4) did not. *N*-Methyl-, *N*-ethyl-, *N*-isopropyl- and *N*-t-butyl-*N'*-methylpiperazines (5)—(8) gave *N,N'*-dinitrosopiperazine (22) (in 90%, 81%, 55%, and 8% yields, respectively) and the diamine (8) also gave *N*-t-butyl-*N'*-nitrosopiperazine (23) (45%). The *N'*-nitroso and the *N'*-nitro derivatives of *N*-methylpiperazine were similarly converted into *N,N'*-dinitroso- and *N*-nitroso-*N'*-nitropiperazines (22) (45%) and (30) (53%). Bisdimethylaminoalkanes $(Me_2N)_2(CH_2)_n$ (10)—(14) gave bismethylnitrosaminoalkanes $[MeN(NO)]_2(CH_2)_n$ (24)—(27) and dimethylnitrosamine (28): n = 1(0%,90%); n = 2(68%,0%); n = 3(48%,43%); n = 4(41%,38%); n = 6(58%,35%). β-Dimethylaminopropionitrile (18), 1-methylnitrosamino-2-dimethylaminoethane (17), and α-dimethylaminoacetic acid (19) gave the corresponding nitrosoamines by replacement of an *N*-methyl group.

In earlier reports, nitrosamines were obtained from cyclic and acyclic tertiary amines which contained α-hydrogen on treatment with dinitrogen tetraoxide in carbon tetrachloride at 0–45 °C. Where competition existed, dealkylation was predominantly demethylation. The following steps [equation (1)] were proposed to account for this nitrosolysis.[1,2]

$$R_2NCH_2R \xrightarrow[-ONO_2]{N_2O_4} R_2\dot{N}(NO)CH_2R \xrightarrow{-NO} R_2\dot{N}CH_2R$$
$$a$$

$$2a \longrightarrow R_2\dot{N}{=}CHR + R_2\dot{N}HCH_2R \quad \left[\xrightarrow{H^{\cdot}} R_2NCH_2R \text{ for recycle} \right.$$
$$b \qquad \left. \xrightarrow{\dot{O}NO_2} R_2\dot{N}HCH_2R\ \bar{N}O_2 \text{ sometimes insoluble} \right]$$

$$\dot{O}NO_2 + N_2O_4 \rightleftharpoons ONO + N_2O_5$$

$$b \xrightarrow{ONO} R_2NCHR \longrightarrow R_2NNO + RCHO \qquad (1)$$
$$\quad\ ONO$$

Heterolytic dissociation of an intermediate nitrosammonium cation, enhanced by the greater stability of certain carbonium ions thus formed, was proposed to account for certain nitrosamine formations which did not involve α-hydrogen expulsion and co-formation of a carbonyl compound [equations (2) and (3)].[3,4]

$$R'_2NCR_3 \xrightarrow{NO^{\cdot}} R_2N(NO)CR_3 \longrightarrow R_2NNO + R_3C^{\cdot} \qquad (2)$$

$$(R_2N)_2CH_2 \xrightarrow{NO^{\cdot}} R_2\dot{N}(NO)CH_2NR_2 \longrightarrow R_2NNO + R_2NCH_2 \qquad (3)$$

We now report investigations into the *N*-methyl-, *N*-ethyl-, *N*-isopropyl-, and *N*-t-butyl-piperidines (1)—(4); the corresponding *N*-alkyl-*N'*-methylpiperazines (5)–(8) and 1,4-diazabicyclo-octane (9) (Dabco); the five bisdimethylaminoalkanes (10)–(14); and the five methyldialkylamines (17)–(21), each also containing an additional functional group.

Results

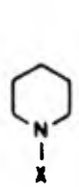
Piperidines.—Dinitrogen tetraoxide in carbon tetrachloride at 0—45 °C converted the *N*-methyl- and *N*-ethyl-piperidines (1) and (2) into the *N*-nitrosopiperidine (15) (80 and 72%), but failed to bring about similar conversions of the *N*-isopropyl- and *N*-t-butyl-piperidines (3) and (4) which were recovered unchanged (60 and 45%). Nitrosonium tetrafluoroborate also failed to replace the *N*-t-butyl group in the amine (4) with a nitroso group, and both nitronium tetrafluoroborate and nitric acid (90%) in concentrated sulphuric acid failed to convert the amine (4) into the nitramine (16).

Piperazines.—Similar treatment with dinitrogen tetraoxide converted Dabco (9) into its dinitrate salt (70%) [*cf.* equation (1)] and 1,4-dinitrosopiperazine (22) (15%), and the *N*-methyl-, *N*-ethyl-, *N*-isopropyl-, and *N*-t-butyl-*N'*-methyl-piperazines (5)–(8) into the same dinitrosamine (22) (90, 81, 55, and 8%). The latter amine (8) also gave the mononitrate salt (45%) of *N*-t-butyl-*N'*-nitrosopiperazine, (23).

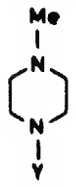
Dimethylaminoalkanes.—Of the five bis-dimethylaminoalkanes (10)–(14), the latter four gave the bis-methylnitrosaminoalkanes (24)—(27) (41–68%) by replacement of methyl groups during nitrosolysis with dinitrogen tetraoxide, and four of the amines, (10) and (12)—(14), gave dimethylnitrosamine

Copy available to DTIC does not permit fully legible reproduction

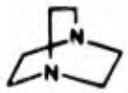
87 4 1 001



(1)–(4),(15),(16)



(5)–(8),(20),(21)



(9)

(1) X = Me
(2) X = Et
(3) X = Me_2CH
(4) X = Me_3C
(15) X = NO
(16) X = NO_2

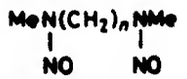
(5) Y = Me
(6) Y = Et
(7) Y = Me_2CH
(8) Y = Me_3C
(20) Y = NO
(21) Y = NO_2

$Me_2N(CH_2)_nNMe_2$ Me_2NCH_2Z

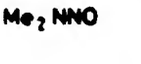
(10) n = 1
(11) n = 2
(12) n = 3
(13) n = 4
(14) n = 6

(17) Z = $CH_2N(NO)Me$
(18) Z = CH_2CN
(19) Z = CO_2H

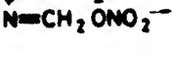
(22) Z = NO
(23) Z = Me_3C
(30) Z = NO_2



(24) n = 2
(25) n = 3
(26) n = 4
(27) n = 6



(28)



(29)

(31) (32)

(28) (35—90%) by replacement of methylene derivatives. When the reaction with bis(dimethylamino)methane (10) at −20 °C was interrupted after 15 min the only product isolated was dimethylmethyleneammonium nitrate (29), identified by comparison with an authentic sample prepared from Eschenmoser's salt $[Me_2N{=}CH_2]^+I^-$ and silver nitrate.

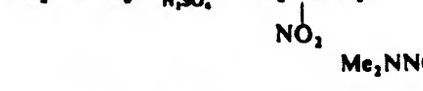
Functionalized Methyldialkylamines.—In comparison with the conversions (5)→(22) and (11)→(24), a β-nitrosamino group decreased the extent of conversion of *N*-methyl-*N'*-nitrosopiperazine (28) into the dinitrosamine (22) (45%), and that of 1-dimethylamino-2-methylnitrosaminoethane (17) into the dinitrosamine (24) (48%). Similarly, *N*-methyl-*N'*-nitropiperazine (21) gave *N*-nitroso-*N'*-nitropiperazine (30) (53%).

β-Dimethylaminopropionitrile (18) efficiently gave β-methylnitrosaminopropionitrile (31) (78%), and α-dimethylaminoacetic acid (19) gave α-methylnitrosaminoacetic acid (32) (24%).

Discussion

Key steps in an explanation for the formation of nitrosamines and aldehydes from reactions between certain tertiary aliphatic amines and dinitrogen tetraoxide required both the expulsion of an α-hydrogen and nitric oxide from a trialkylnitrosoammonium cation and the dissociation of a hemiaminalnitrite ester [equation (1)].

Results obtained from the *N*-alkylpiperidines (1)—(4) and the *N,N'*-dialkylpiperazines (5)—(9) showed that primary alkyl groups tended to be replaced easily by the nitroso group, the isopropyl group was less readily replaced, and the t-butyl group was replaced in low yield or not at all. Since replacement of a t-butyl group cannot proceed according to the process described in equation (1), it was assumed that a heterolytic dissociation of a nitrosammonium cation partially accounted for the formation of *N,N'*-dinitrosopiperazine (28) (8%) from *N*-t-butyl-*N'*-methylpiperazine (5), *cf.* equation (2). A similar explanation accounts for the formation of dimethylnitramine from t-butyldimethylamine in a mixture of nitric (90%) and concentrated sulphuric acid [equation (4)].[5]



$$Me_2NCMe_3 \xrightarrow[H_2SO_4]{HNO_3} Me_2\overset{+}{N}(NO_2)CMe_3 \longrightarrow Me_2NNO_2 + Me_3C^+ \quad (4)$$

Apparently the conversion of Dabco (9) into *N,N'*-dinitrosopiperazine (22) was blocked to a large extent by the formation

Table 1. Nitrosolysis of alkylpiperidines and dialkylpiperazines

Amine	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
Nitrosamine	(15)	(15)	(15)	(15)	(22)	(22)	(22)	(22)
Yield (%)	80	72	Trace[a]	Trace[b]	90	81	55	8[d]
M.p. (b.p.)/°C	(95—97/ 12 mmHg[c])				155—157[e]			

[a] 60% of starting material recovered. [b] 42% of starting material recovered. [c] 218 °C/760 mmHg. C. Parr, *J. Org. Chem.*, 1959, **24**, 1325. [d] The mononitrate salt of (23) was the main product (45%), m.p. 178—180 °C (d) (Found: C, 40.75; H, 7.65; N, 23.75. Calc. for $C_8H_{18}N_4O_4$: C, 41.02; H, 7.75; N, 23.92%). [e] M.p. 156—156.5 °C, reported by M. V. George and G. J. Wright, in reference 15.

Table 2. Nitrosolysis of dimethylaminoalkanes

Amine	(10)	(11)	(12)	(13)	(14)
Dinitrosamine		(24)	(25)	(26)	(27)
Yield (%)[a]		68 (50)	48 (40)	41 (35)	58 (53)
M.p./°C		53—55[c]	64—66[d]	68—70[d]	58—60[d]
Dimethylnitrosamine (%)[a,b]	90 (78)		43 (30)	38 (32)	35 (31)

[a] Yields determined by g.c. analysis of product mixtures; lower yields in parentheses represent isolation by chromatography on silica gel. [b] Identical with an authentic sample. [c] D. Seebach, R. Dach, D. Ender, B. Renger, M. Janssen, and G. Brachtel, *Helv. Chim. Acta*, 1978, **61**, 1622. [d] S. S. Brown, C. L. Leese, C. M. Timmis, and R. Wade, *J. Chem. Soc.*, 1963, 846.

Table 3. Nitrosolysis of functionalized methyldialkylamines

Amine	(17)	(18)	(19)	(20)	(21)
Nitrosamine	(24)	(31)	(32)	(22)	(30)
Yield (%)[a]	48	78	24	45	53
M.p./°C	53—55[b]	*c*	65—70[d]	155—157[e]	138—140[f]

[a] Isolated by column chromatography over silica gel. [b] Note *c*, Table 2. [c] Liq.: $\delta_H(CDCl_3)$ 2.6 (t), 2.9 (t), 3.1 (s), 3.8 (t), 3.9 (s), and 4.5 (t). [d] H. T. Nagasawa, P. S. Fraser, and D. L. Yuzo, *J. Med. Chem.*, 1973, **16**, 583. [e] Ref. 15. [f] (Found: C, 30.0; H, 5.05; N, 35.0. Calc. for $C_4H_8N_4O_5$: C, 30.00; H, 5.04; N, 34.99%).

Copy available to DTIC does not permit fully legible reproduction

of Dabco dinitrate which was insoluble in the medium and did not convert. It was separately shown that the dinitrate salt on heating gave compound (22) in low yield.

The diminished ability of dinitrogen tetraoxide in carbon tetrachloride to replace isopropyl and t-butyl groups at an amine nitrogen atom is in agreement with a previous report in which methylethylisopropylamine in acidified aqueous sodium nitrite gave low yields of methylisopropylnitrosamine (7—9%), ethylisopropylnitrosamine (7—10%), and a trace (1.3—1.5%) of methylethylnitrosamine; similar results were obtained with *N*,*N*-dimethylcyclohexylamine and *N*,*N*-dimethyl-2-(1,2,3,4-tetrahydro)naphthylamine, each of which gave dimethylnitrosamine in small amounts (2.1—5.9%) and the methylcycloalkylnitrosamine in yields of 59—73%.[6]

Since *N*,*N*′-dinitrosopiperazine (22) was obtained from *N*-nitroso-*N*′-methylpiperazine (20) in 45% yield it cannot be an intermediate in the conversion of *N*,*N*′-dimethylpiperazine (5) into the dinitrosodiamine (22) in 90% yield. In a similar reaction, *N*-nitro-*N*′-nitrosopiperazine (30) (53%) was obtained from *N*-nitro-*N*′-methylpiperazine (21) in a nitrosolysis reaction with dinitrogen tetraoxide. An explanation for this inhibition to nitrosolysis brought about by the presence of the nitrosamino or the nitramino group cannot be offered at this time.

An opposite effect was noted in the nitrolysis of certain *N*-t-butyl amines in which a nitro group attached at a β-carbon atom enhanced the formation of a nitramine by replacement of the t-butyl group. For comparison, the formation of dimethylnitramine from t-butyldimethylamine (devoid of nitro substituents) was much less efficient. Additional information will be sought to confirm and clarify this promotion in reactivity by a *C*-nitro group and a hindrance to reactivity by an *N*-nitroso or an *N*-nitro group.

A slight preference for the replacement of a methyl group rather than a methylene derivative was detected in a comparison of the formation of the dinitrosamine products (25)—(27) on the one hand and dimethylnitrosamine (28) on the other. It was of special interest to note that the latter was not produced in the reaction with 1,2-bis(dimethylamino)ethane (11) and was the only nitrosamine obtained from bis(dimethylamino)methane (10). The isolation of dimethylmethyleneammonium nitrate when the nitrolysis of the diamine (10) was interrupted before completion confirmed the proposed intermediacy of an aminium (radical cation) nitrate and its disproportionation to a methyleneammonium nitrate and a nitrate of the original amine. In a similar nitrosolysis, aqueous nitrous acid converted *N*-dimethylaminomethylpyrrole into dimethylnitrosamine.[6] Nitrosolysis of hexamethylenetetramine to R-Salt is, of course, a related reaction.

The failure of the nitrosolysis of 1,2-bis(dimethylamino)-ethane (11) to produce dimethylnitrosamine (28) was outstanding. Isolation of the intermediate diamine dinitrate when the nitrosolysis of the diamine (11) at 0 °C was interrupted after 30 min supported the previously proposed explanation for the conversion of a dimethylamino alkane into a methylnitrosaminoalkane. At the same time, it indicated that a 1,4-diradical dication was not present, insofar as the diradical would be expected to dissociate to the dimethyl methyleneammonium cation.

It was noted above that the formation of *N*,*N*′-dinitrosopiperazine (22) was considerably less efficient in the nitrosolysis of *N*-nitroso-*N*′-methylnitrosaminopiperazine than in the nitrosolysis of *N*,*N*′-dimethylpiperazine (5). A similar effect was noted in the efficiency of the formation of 1,2-bismethylnitrosaminoethane (24) which was lowered from 68% for conversion of the diamine (10) to 48% for conversion from 1-dimethylamino-2-methylnitrosaminoethane. The presence of the cyano group in β-dimethylaminopropionitrile had little, if any, adverse effect on the nitrosolysis to β-methylnitrosaminopropionitrile (78%). Nitrosolysis of α-dimethylaminoacetic acid gave α-methylnitrosaminoacetic acid.

Experimental

Instruments included Pye-Unicam SP200 (i.r.) Varian A-60 and T-60 (n.m.r.) Spectrometers. Elemental analyses were provided by Micro-Tech Laboratories, Inc., Skokie, Illinois. G.c. analyses were done in a HP-5790 instrument with a HP-3390-A integrator. (Column: 3% OV-17 on 80/100 Gas Chrom. Q Stainless Steel 6 ft. × 1/8 in.; carrier gas nitrogen; column temperature 100—200 °C with FID).

N-Methyl- and *N*-ethyl-piperidines (1) and (2), *N*-methyl-*N*′-methylpiperazine (5), 1,4-diazabicyclooctane (9), bis(dimethylamino)alkanes (10)—(14), β-dimethylaminopropionitrile (18), and α-dimethylaminoacetic acid (19) were commercially available.

N-Isopropyl- and *N*-t-butyl-piperidines (3)[7] and (4),[8] *N*-ethyl- and *N*-t-butyl *N*′-methyl-piperazines (6)[9] and (8),[10] 1-methylnitrosamino-2-dimethylaminoethane (17),[11] *N*-methyl-*N*′-nitrosopiperazine (20),[12] and *N*-methyl-*N*′nitropiperazine (21)[13] were prepared by literature procedures.

N-Isopropyl-*N*′-methylpiperazine (7)[14] was prepared from bis-(2-chloroethyl)-*N*-methylamine and isopropylamine (75%).

General Procedure.—Dinitrogen tetraoxide (excess) was added to a stirred solution of a tertiary amine (15 mmol) in carbon tetrachloride (15 ml), precooled to 0 °C. During the addition the temperature rose to 35—50 °C. The mixture was cooled to room temperature and stirring was continued overnight (14—16 h). Nitrogen oxides and solvent were removed under reduced pressure and the residue was partitioned between dichloromethane (50 ml) and saturated aqueous sodium chloride solution (50 ml). The aqueous layer was extracted with dichloromethane (2 × 25 ml). The combined extracts were dried (Na_2SO_4) and concentrated to give the products.

DABCO and Dinitrogen Tetraoxide.—Excess dinitrogen tetraoxide was added to 1,4-diazabicyclo-octane (9) (1.68 g, 15 mmol), suspended in carbon tetrachloride (15 ml), with cooling. During the addition, there was no rise in temperature. Stirring was continued overnight at room temperature. The reaction mixture was filtered to give a colourless solid (1.77 g, 70%). This was found to be the dinitrate salt of DABCO, m.p. 185—186 °C (decomp.).[1] The filtrate was concentrated to give (22) (0.33 g, 15%), m.p. and m.m.p. identical with authentic sample, 155—157 °C.[15]

t-Butylpiperidine (4) *and Nitronium Tetrafluoroborate.*—Nitroniumtetrafluoroborate, (1.32 g, 10 mmol) was added to a solution of compound (4) (1.41 g, 10 mmol) in absolute acetonitrile (20 ml) with stirring and cooling (ice-bath). After the addition, the reaction mixture was warmed slowly to 20 °C, stirred for 1 h and poured into water. The solution was extracted with dichloromethane (2 × 25 ml) and dried (Na_2SO_4) and the solvent evaporated under reduced pressure to give a liquid (0.49 g), t.l.c. and n.m.r. data of which showed it to be the starting amine (4) (35% recovery).

An experiment with nitrosonium tetrafluoroborate afforded similar results (32% recovery). In both cases there was no indication by t.l.c. comparison with authentic samples of the formation of either the *N*-nitro- or *N*-nitroso-piperidine.

t-Butylpiperidine (4) *with 90% Nitric Acid in Conc. Sulphuric Acid.*—The tertiary amine (4) (0.50 g, 3.6 mmol) was added to an excess of conc. sulphuric acid (18 ml) with cooling in ice.[5] To

Copy available to DTIC does not permit fully legible reproduction

this mixture was added at 0 °C a mixture of nitric acid (90%, 4.6 ml) and conc. sulphuric acid (7.5 ml). After the reaction had been stirred overnight at room temperature the solution was poured onto ice. Solid potassium carbonate was added to achieve pH 6. The mixture was extracted with dichloromethane, dried ($MgSO_4$), and concentrated. The residual liquid (0.19 g) was found to be the starting amine, (4) (38%), identified by t.l.c. and n.m.r. comparisons with authentic samples.

Acknowledgements

Financial support was received from DNR.

References

1 J. H. Boyer and T. P. Pillai, *J. Chem. Soc., Perkin Trans. 1*, 1985, 1661.
2 J. H. Boyer, T. P. Pillai, and V. T. Ramakrishnan, *Synthesis*, 1985, 677.
3 J. Glazier, E. D. Hughes, C. K. Ingold, A. T. James, G. T. Jones, and E. Roberts, *J. Chem. Soc.*, 1950, 2671.
4 W. Lijinsky and D. M. Singer, IRAC Science Publ., 1975(9), 111 (*Chem. Abstr.*, 1975, **83**, 109582f).
5 D. A. Cichra and H. G. Adolph, *J. Org. Chem.*, 1982, **47**, 2474.
6 R. N. Loeppky, W. Tomasik, J. Outram, and A. Feicht, IARC Sci. Publ. 1982, 41—45; (*Chem. Abstr.*, 1983, **99**, 37759).
7 A. Lattes and J. J. Perie, *Tetrahedron Lett.*, 1967, **51**, 5165.
8 A. T. Bottini and J. D. Roberts, *J. Am. Chem. Soc.*, 1958, **80**, 5203.
9 G. W. Gribble, J. M. Jasinski, J. T. Mellicone, and J. A. Penetta, *Synthesis*, 1978, 766.
10 J. L. Imbach, A. R. Katritzky, and R. A. Kolniski, *J. Chem. Soc. B*, 1966, 566.
11 Tara Singh, R. G. Stein, and J. H. Biel, *J. Med. Chem.*, 1969, **12**, 801.
12 M. Harfenist, *J. Am. Chem. Soc.*, 1954, **76**, 4991.
13 A. N. Gafarov, S. S. Novikov, G. T. Zakirova, N. P. Konovalova, and L. S. Vasileva, *Zh. Org. Khim.*, 1973, **9**, 51.
14 J. Reiter and L. Toldy, *Acta Chim. (Budapest)*, 1975, **87**, 69.
15 M. V. George and G. J. Wright, *J. Am. Chem. Soc.*, 1958, **80**, 1200.

Copy available to DTIC does not permit fully legible reproduction

B. 1,2-Dinitrocyclohexene

Org. Prep. and Proc., 1986, 18, 363

Joseph H. Boyer and Philip F. Pagoria

Department of Chemistry, University of New Orleans, New Orleans, LA 70148

Previously, only five examples of isolated 1,2-dinitroalkenes had been reported: 1,2-dinitroethene (1a),[1] 2,3-dinitro-2-butene (1b),[2] 3,4-dinitro-3-hexene,[2] dinitrostilbene (1c),[3] and tetranitroethene.[4,5] Mild to extensive thermal decomposition (25°C) has been noted for these 1,2-dinitroalkenes. We now describe the conversion of the oxime of α-nitrocyclohexanone (2)[6] to 1,2-dinitrocyclohexene (5), isolated as an unstable yellow oil; this is, to our knowledge the first example of a 1,2-dinitrocycloalkene.

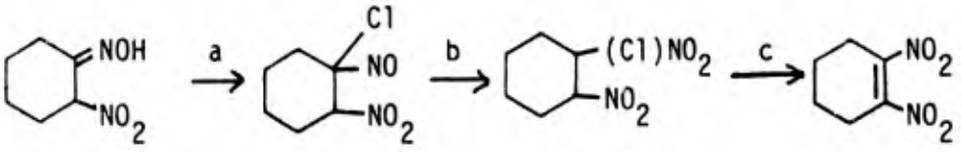
$O_2NC(R)=C(R)NO_2$ $\quad$ $K^+\ O_2N=C(CN)C(CN)=NO_2\ K^+ \longrightarrow O=C(CN)C(CN)=NO_2\ K^+$

5 $\quad$ 6 $\quad$ 7

a, R = H

b, R = CH_3

c, R = Ph



2 $\quad$ 3 $\quad$ 4 $\quad$ 5

a) Cl_2 b) O_3 c) NaOH

Recently bromine oxidation converted a dimetal salt of each of three 1,2-dinitroalkanes to the corresponding dinitroalkene 1a-c. A similar preparation of 1,2-dinitrocyclohexene (5) was cited.[7,8] Since experimental detail has not been reported for this dehydrogenation of 1,2-dinitrocyclo-

hexane, the olefin (5) was assumed to be unknown (it has not been listed in Chemical Abstracts). Halogen oxidation of a 1,2-dinitronate anion, has limited value as an olefin synthesis insofar as halogen addition to an olefinic linkage[1,9] and halogen replacement of a nitro group can also occur.[10] In a recent report, bromine converted the dipotassium salt of α,α'-dinitrosuccinonitrile (6) to the potassium salt of nitroketosuccinonitrile (7).[11] We rejected an investigation of a halogen oxidation of the dinitronate anion of 1,2-dinitrocyclohexane to the olefin (5) to avoid these complications. Moreover a mild alkaline conversion of 1,2-dinitrocyclohexane at 25° for 6 hours gave 1-nitrocyclohexene (82%)[12] and apparently did not afford the intermediacy of the dinitronate anion.

Although chlorine is recommended for converting the oxime (2) to a gem-chloronitroso compound (3), tetrabutylammonium hypochlorite[13] also effected the change insofar as the deep blue color characteristic of the nitroso compound (3) developed. The latter method was abandoned when an excess of the hypochlorite reagent failed to bring about oxidation to the nitro compound (4). Oxidation of a nitroso compound to a nitro compound (3) ⟶ (4) was effected by either ozone (preferred) or m-chloroperbenzoic acid (MCPBA); however, there was considerable difficulty in product isolation from the reaction with MCPBA. For the last step an elimination of the elements of hydrogen chloride to give the olefin (5) was brought about in a phase transfer operation with tetrabutylammonium bromide, aqueous sodium hydroxide, and benzene. The competitive alkaline elimination of nitrous acid to give 1-chloro-2-nitrocyclohexene (or isomeric olefins) was not detected.

Bromine at 25°C added slowly to the olefin (5) to give 1,2-dibromo-1,2-dinitrocyclohexane (stereoisomerism unspecified). The failure to obtain an adduct between (5) and either cyclopentadiene or anthracene was

unexpected insofar as both di-[2] and tetranitroethene[4,5] were highly reactive in additions with these dienes.

EXPERIMENTAL SECTION

Instruments included Perkin Elmer 237B and 521 grating IR, Varian A-60, Bruker WP-80 and A.E.I. MS 30 double beam mass spectrometers. Elemental analyses were provided by Micro-Tech Laboratories, Skokie, Illinois.

1-Chloro-1,2-dinitrocyclohexane (4). A general procedure for the conversion of an oxime to a gem-chloronitroalkane was followed.[14] Through 1.4 g (8.9 mmol) of oxime (2) dissolved in 50 ml of methylene chloride and cooled to ice-bath temperature, chlorine gas was bubbled in slowly for 5 min. (or until the green chlorine color persisted). Oxygen gas was then passed into the solution to remove the excess chlorine (the blue color of the nitroso compound was restored) and was followed by a stream of ozone for about 75 min. or until the blue color of the nitroso compound had dissipated. Oxygen was passed through the solution for 10 min. to remove the excess ozone. Removal of the solvent left a light blue oil. Separation by column chromatography [1:9 ethyl acetate/hexanes (250 ml) on silica gel 60 (3 X 18 cm column)] gave a fraction with an R_f = 0.49 from which a clear oil was obtained after solvent removal. Kugelrohr distillation (1 mm, 140-150°C) of the oil yielded 0.77 g (42%) of a diastereoisomeric mixture of 1-chloro-1,2-dinitrocyclohexane as oily colorless crystals, mp. 52-70°C. ^{1}HNmr ($CDCl_3$): δ 5.4 (t, 1H), 1.4-2.05 (m, 4H), 2.35 (m, 4H); IR (KBr): 3028, 2960, 2878, 1568, 1440, 1450, 1372, 1353, 1334 cm^{-1}.

Anal. Calcd for $C_6H_9ClN_2O_4$: C, 34.53; H, 4.32; N, 13.43; Cl, 17.03

Found: C, 34.57; H, 4.49; N, 13.26; Cl, 16.67

1,2-Dinitrocyclohexene (5). After 0.4 g (1.92 mmol) sample of 1-chloro-1,2-dinitrocycloxane (4) and 0.68 g (2.1 mmol) of tetra-n-butylammonium

bromide was dissolved in 6 ml of benzene 3.84 ml of 0.5 N sodium hydroxide diluted to 5 ml was added and the mixture was stirred for 1.25 h at room temperature until the aqueous solution was neutral to moist pH paper. The organic phase was separated, washed with 10 ml of water and dried over anhydrous magnesium sulfate. Removal of the solvent left an orange oil. A 5 ml portion of ether was added to remove residual tetra-n-butylammonium bromide, the mixture was filtered, and the solvent was removed to give 0.19 g (58%) of the olefin (5) as a light orange oil.
^{1}H-nmr ($CDCl_3$): δ 2.5-2.95 (m, 4H), 1.65-2.05 (m, 4H); ^{13}C-nmr ($CDCl_3$): δ 145.09 (C-NO_2), 26.28, 20.75 (-CH_2-); IR (KBr): 2958, 2879, 1534, 1437, 1456, 1350, 1339, 1370, cm^{-1}.

Attempts to purify further by distillation were unsuccessful; flash chromatographic separation from silica gel with mixtures of ethyl acetate and hexane (1:9) gave a light yellow oil.

Anal. Calcd for $C_6H_8N_2O_4$: C, 41.86; H, 4.65; N, 16.27

Found: C, 42.32; H, 4.66; N, 15.73

1,2-Dibromo-1,2-dinitrocyclohexane. After 0.19 g (1.1 mmol) of freshly prepared 1,2-dinitrocyclohexene (5) was dissolved in 6 ml of chloroform, 0.36 g (2.1 mmol) of bromine in 5 ml of chloroform was added dropwise. The solution was allowed to stand at room temperature for 14 days. The solvent and excess bromine were removed and a yellow solid mixture was taken up in 10 ml of methylene chloride. The solution was extracted with 10 ml of water and dried over magnesium sulfate. Solvent removal left a yellow gum. Recrystallization from hexane yielded 0.21 g (58%) of the dibromide as colorless needles, mp 199-200°C (dec.) (softening at 150° and shrinking at 190°C). This material was twice sublimed at 95-100°C at 0.5 mm to yield a white powder, mp 208-210°C (dec) (softened and yellowed slightly at 195°C).

^{1}H-nmr ($CDCl_3$): δ 3.0-2.5 (broad m, 4H), 2.1-1.55 (broad m, 4H); ^{13}C-nmr ($CDCl_3$): δ 95.63, 92.50, 39.35, 38.96, 22.18; IR (KBr): 2960, 2890, 1567, 1442, 1452, 1350, 1323 cm^{-1}.

Anal. Calcd for $C_6H_8N_2O_4Br_2$: C, 21.70; H, 2.41; N, 8.44

Found: C, 22.00; H, 2.47; N, 8.18

Acknowledgment. Financial assistance was received from ONR.

REFERENCES

1. E. S. Lipina, F. Z. Pavlova, and V. V. Perekalin, Zh. Org. Khim., 5, 1312 (1969); Eng. p. 1280.
2. E. M. Nygaard and T. T. Noland, U.S. 2,396,282; Chem. Abstr., 40, 3126 (1946).
3. H. Wieland and E. Blumich, Ann, 424, 86, 103 (1921); J. P. Freeman and W. D. Emmons, J. Am. Chem. Soc., 79, 1712 (1957).
4. T. S. Griffin and K. Baum, J. Org. Chem., 45, 2880 (1980).
5. K. Baum and D. Tzeng, ibid., 50, 2736 (1985).
6. I. Tanaka, H. Mera, and S. Ono, Japanese Patent, 7,505,188; Chem. Abstr., 83, 58266w (1975).
7. E. S. Lipina and V. V. Perekalin, Acta Phys. Chem., 19, 125 (1973).
8. V. V. Perekalin, Zh. Org. Khim., 21, 1111 (1985); Eng. p. 1011.
9. E. F. Witucki, W. Maya, and M. B. Frankel, Org. Prep. Procd. Int., 12, 197 (1980).
10. G. V. Nekrasova and E. L. Lupina, Metody Sint., Str. Khim. Prevrashah. Nitrosoedin., 23 (1980); Chem. Abstr., 95, 219724j (1981).
11. T. P. Pillai and J. H. Boyer, Org. Prep. Proc. Int., 15, 7 (1983).
12. A. T. Nielsen, J. Org. Chem., 27, 2001 (1962).
13. E. J. Corey and H. Estreicher, Tetrahedron Lett., 1117 (1980).
14. M. W. Barnes, J. Org. Chem., 41, 733 (1976).

C. Nitration of 4-Nitro-N,N-dimethylbenzylamine.

Formation of 2-Methyl-6-nitroindazole.

J. Chem. Res. (S), 1986, 416.

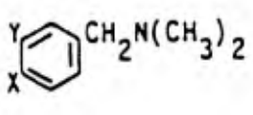
Joseph H. Boyer, P. F. Pagoria, and T. P. Pillai., Department of Chemistry, University of New Orleans, New Orleans, Louisiana 70148 and Department of Chemistry, University of Illinois at Chicago, Chicago, Illinois 60680

and

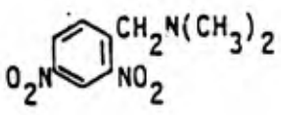
M. D. Pace and D. Stec., Polymers Materials Branch, Chemistry Division, Naval Research Laboratory, Washington D. C. 20375.

Examination of the nitrosolysis[1] of N,N-dimethylbenzylamine to N-methyl-N-nitrosobenzylamine revealed a mildly competitive nitration to 4-nitro-N,N-dimethylbenzylamine 1 and 2,4-dinitro-N,N-dimethylbenzylamine 2. The latter amine partially converted during isolation to 2-methyl-6-nitroindazole 4. Further examination of the formation of the indazole is reported here.

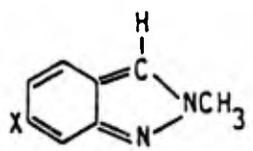
A red oil previously obtained from 4-nitro-N,N-dimethylbenzylamine 1 in



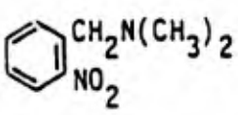
1 X = NO_2, Y = H
3 X = Y = NO_2
4 X = Y = H



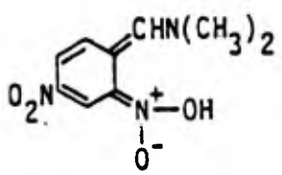
2



5 X = NO_2
7 X = H



6



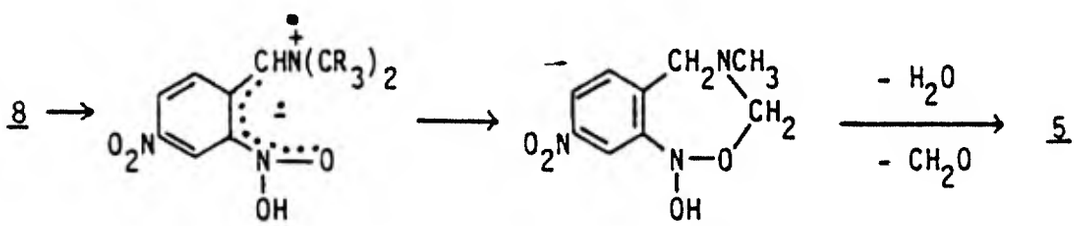
8

a mixture of fuming nitric and sulfuric acids (time, temperature, and reaction efficiency were not reported) and identified as 2,4-dinitro-N,N-dimethylbenzylamine 2[2] has now been shown by chromatographic separation (silica gel) to contain a mixture of the amine 2 (56%), the isomeric 3,4-dinitro-N,N-dimethylbenzylamine 3 (21%), and unidentified material. A more complex nature of the red oil was revealed by epr spectroscopic detection of the spontaneous generation and disappearance of three radicals.[3-7] Further purification by distillation was unsuccessful since the amine 2 slowly changed to 2-methyl-6-nitroindazole 5[2] and the amine 3 decomposed without distilling at 180°C (1 torr). Nitrate salts of the amines were prepared. The nitrate of amine 2 did not convert to the indazole 5.

Pure samples of the amine 2 were obtained as needed from the nitrate salt by treatment with base and extraction with ether. An epr spectroscopic examination of the amine 2, alone or in a prepared mixture with N,N-dimethylamine 4 or its 3,4-dinitro derivative 3, over a period of several days did not detect radical formation. Progress in the formation of the indazole 5 from the amine 2 stored in acetonitrile at 25°C was monitored by ^{1}H-nmr. In the second day the signal for the 2-methyl protons in the indazole 5 were first detected; after 6 days a precipitation of the indazole was noted and after 2 months the quantitative conversion was complete. The conversion was faster in the added presence of either N,N-dimethylbenzylamine 4 or its 3,4-dinitro derivative 3, in accordance with a previously observed base promotion by dimethylamine.[2] In the red oil mixture the amine 2 presumably converted more rapidly because of the presence of the amine 3 and, perhaps, other unidentified bases. Since a similar thermolysis of 2-nitro-N,N-dimethylbenzylamine 6 to 2-methylindazole 7 was not observed, it is proposed that the conversion 2 → 5 depended on a base promoted initial tautomerization to the nitronic acid 8, expected to be present in part as its amine salt as well as the zwitterionic form of the amino acid.

A dark red color in a solution of the amine 2 with either dichlorodicyanobenzoquinone or tetracyanoethylene (radical scavengers) was characteristic of an electron transfer. Storage of the solution, monitored by ^{1}H-nmr, for 12 days without further change to the amine (quantitatively recovered) revealed a requirement for a radical intermediate in the conversion 2 → 5.

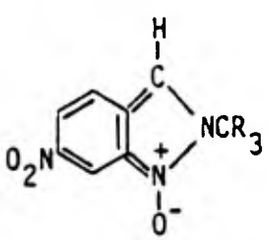
An explanation compatible with base catalysis, acid deceleration, and the intermediacy of one or more radicals, is based on an initial charge transfer within the nitronic acid 8 to give the zwitterion diradical 9.[8,9] This provided for α-hydrogen transfer from a radical cation centered at an amine nitrogen atom,[10] cyclization, and product formation with the formal expulsion of formaldehyde and water molecules. Although the order of these events remains unestablished they are accommodated by the proposed intermediacy of the tetrahydro-2,1,4-benzoxadiazepine 10.[11,12]



9 R = H

10

It was suggested that 6-nitro-2-methylindazole-1-oxide 11 was a precursor to the indazole 5.[2] This is unlikely since formation of the N-oxide 11,



11 R = H

expected to be stable under the experimental conditions, was not detected as the reaction 2 → 5 (over a 2 month period) was monitored by nmr and ir spectroscopy. It appears that α-hydrogen transfer in the charge transfer intermediate 9

allowed the formation of the indazole 5 but not the indazoleoxide 11 to follow. When ejection of an alkanol or its equivalent can be competitive with or replace an α-hydrogen transfer from an amine radical cation the formation of an N-oxide would be expected, e.g. 9 → 11, (R = H).

Experimental

An equivolume mixture (6 ml) of fuming sulfuric (30% sulfur trioxide) and nitric acid (90%) was kept at 0-5°C as 4-nitro-N,N-dimethylbenzylamine 1 (1.0 g, 5.6 mmol) was added slowly with stirring. The reaction mixture became a solution on gradually warming to 25°C. It was heated at 100°C for 4 h, cooled, treated with ice water (125 ml), neutralized (sodium carbonate) to pH 7-8, and extracted with ether (3 X 50 ml). The ether extracts were combined, washed with water (2 X 50 ml), dried over anhydrous magnesium sulfate, and concentrated to leave a red oil (1.0 g). Chromatographic separation of the oil from a column (46 X 2.2 cm, Davisil 62 silicagel) by elution with a 1:1 mixture (180 ml) of hexanes and ether gave 2,4-dinitro-N,N-dimethylbenzylamine 2 (0.7 g, 56%) as a yellow oil (Rf = 0.5) with ir and nmr data in agreement with the published values.[2] Further elution (370 ml) gave 3,4-dinitro-N,N-dimethylbenzylamine 3 (0.26 g, 21%) as an orange oil; ^{1}H-nmr ($CDCl_3$): δ 8.1-7.6 (3, aromatic), 3.5 (2, s, CH_2), 2.3 (6, s, CH_3); ir (KBr): 3100, 3060, 2978, 2940, 2895, 1600, 1550, 1537, 1460, 1360 cm^{-1}. Attempted distillation of the amine 3 was unsuccessful and brought about decompostion (180°C, 1.0 torr).

Nitrate salts were obtained by slowly adding an excess of fuming nitric acid to the amine 2 or 3 (0.3 g, 1.3 mmol) in ether (10 ml) at 0-5°C. Concentration left a yellow solid that recrystallized from ethanol as colorless needles. Amine nitrate 2·HNO_3 (0.31 g, 82%), mp 90-91°C; ^{1}H-nmr (D_2O): δ 9.2-8.2 (3, aromatic), 4.8 (2, s, CH_2), 3.1 (6, s, CH_3); ir (KBr): 3528, 3100, 3080,

2939, 2880, 2860, 1610, 1537, 1472, 1360, 1320 cm^{-1}; anal. calcd. for $C_9H_{12}N_4O_7$: C, 37.50; H, 4.17; N, 19.44; found: C, 37.10; H, 4.15; N, 19.28. 3,4-Dinitro-N,N-dimethylbenzylamine nitrate 3·HNO_3 (0.21 g, 57%), mp 127-128°C; ^{1}H-nmr (D_2O): δ 8.3-8.0 (3, aromatic), 4.6 (2, s, CH_2), 3.0 (6, s, CH_3); ir (KBr): 3100, 3070, 3030, 2895, 2660, 1550, 1540, 1478, 1390, 1365 cm^{-1}; anal. calcd. for $C_9H_{12}N_4O_7$: C, 37.50; H, 4.17; N, 19.44; found: C, 37.29; H, 4.20; N, 19.38. Each amine 2 and 3 in water was recovered from its nitrate salt by treatment with an excess of aqueous sodium bicarbonate followed by ether extraction.

The amine 2, neat or in acetonitrile, slowly converted quantitatively (25°C, 2 months) to 2-methyl-6-nitroindazole 5, mp 159-160°C.[2]

Acknowledgment: Financial support was received from ONR.

References

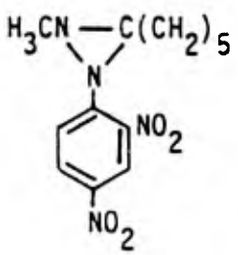
1. J. H. Boyer, T. P. Pillai, and V. T. Ramakrishnan, Synthesis 1985, 677.
2. A. L. Patey and N. M . Waldron, Tetrahedron Lett., 1970, 3375.
3. J. H. Boyer, M. D. Pace, P. Pagoria, T. P. Pillai, and D. Stec, NRL Memorandum Report 5736, Naval Research Laboratory, Washington, D.C. March 10, 1986. One radical (a^N = 15.6, 12.2 G) was identified as dimethylnitroxyl, $(CH_3)_2NO^{\bullet}$;[4] another (a^N = 28, 1.8 G) as a diazoxy radical, ArN = N O·;[5,6] the third (a^N = 20.8, 9.48, 3.06 G) appeared similar to the radical, 2-$RCOC_6H_4NHO^{\bullet}$.[7]
4. A. Joshi and G. C. Yang, Org. Magn. Reson., 1981, 17, 138.
5. W. A. Gibbons and A. M. Trozzolo, J. Am. Chem. Soc., 1966, 88, 173.
6. J. I. G. Cadogan, R. M. Paton, and C. Thompson, J. Chem. Soc. Perkin Trans. 2, 1971, 583.
7. E. G. Janzen, C. C. Lai, and R. V. Shetty, Tetrahedron Lett., 1980, 21, 1201.

8. Electron transfer to an undissociated nitronic acid group has been proposed.[9]

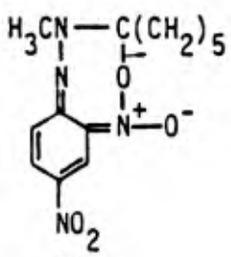
9. A. Nielsen, "Nitronic Acids and Esters," in H. Feuer, ed., "The Chemistry of the Nitro and Nitroso Groups," in S. Patai, ser. ed., "The Chemistry of Functional Groups," John Wiley, New York, 1969, pp 399, 400.

10. Y. L. Chow, W. C. Damen, S. F. Nelsen, and D. H. Rosenblatt, Chem. Rev., 1978, 78, 243.

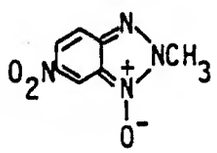
11. Similarly expulsion of cyclohexanone from an intermediate dihydro-2,1,4,5-benzoxatriazepine-1-oxide ii was proposed to explain the quantitative thermolysis of 1-(2,4-dinitrophenyl)-2-methyl-3,3-pentamethylenediaziridine i in toluene (110°C, 7.5 h) to 2-methyl-6-nitrobenzotriazole-1-oxide iii.[12]



i



ii



iii

12. H. W. Heine, P. G. Williard, and T. G. Rowe, J. Org. Chem., 1972, 37, 2980.

D. THE FORMATION AND FACILE CONVERSION OF TRITYL PHENYLCYANOMETHANE NITRONATE

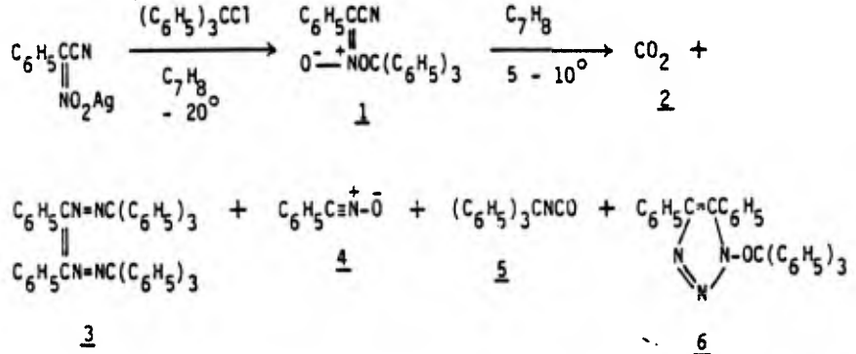
Heterocycles, 1986, 24, 2813.

Joseph H. Boyer and Thanikavelu Manimaran

Chemistry Department, University of New Orleans, New Orleans, La. 70148, U.S.A.

Abstract - Trityl chloride and silver phenylcyanomethane nitronate in toluene at -20°C gave trityl phenylcyanomethane nitronate 1, an unstable ester that rearranged and fragmented at 5-10°C to 1-triphenylmethoxy-4,5-diphenyl-1,2,3-triazole 6 with coproducts carbon dioxide, α,α'-bis(triphenylmethaneazo)stilbene 3, benzonitrile-N-oxide 4, and trityl isocyanate 5.

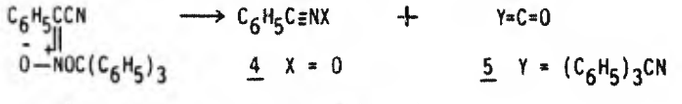
A product $C_{33}H_{25}N_3O$ obtained from an unexplained reaction[1] between silver phenylcyanomethane nitronate and trityl chloride in toluene at 0°C has been identified by X-ray crystallographic analysis as 1-triphenylmethoxy-4,5-diphenyl-1,2,3-triazole 6[2]. Coproducts included carbon dioxide 2, α,α'-bis(triphenylmethaneazo)stilbene 3, benzonitrile-N-oxide 4, and trityl isocyanate 5, eq(1)[1]. Trityl pnenylcyanomethane nitronate 1 has now been identified as the initial product of the reaction at -20°C by comparative infra-red spectroscopic analysis (-20°C) of the ester 1 and the related benzyl[3] and benzhydryl[4] phenylcyanomethane nitronates (decomposition at 25°C)[5]. The conversion, eq(1), is important as a rare example of a transfer at low temperature of the oxygen atoms in a nitronate group to a carbon atom and is pertinent to explosive reactions of nitro compounds in which carbon dioxide may be similarly produced.



eq(1)

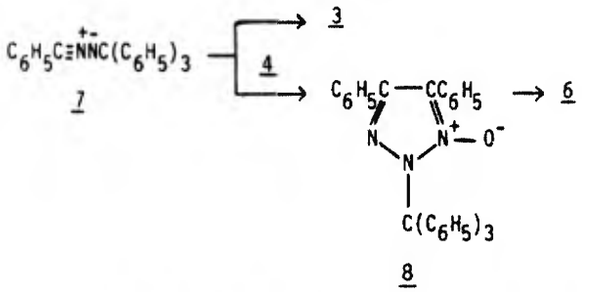
Product analysis revealed two fragmentation modes for the ester 1: one afforded benzonitrile-N-oxide 4 and trityl isocyanate 5, while the other differed by an interchange of oxo and tritylimino substituents (X, Y) to afford carbon dioxide 2 and benzonitrile-N-tritylimine 7, eq(2)[6,7]. The

intermediacy of the nitrilimine 7 accounted for the formation of the bisazostilbene 3 (18%) by dimerization[1,6,7] and the triazole 6 (24%) by a dipolar addition with benzonitrile oxide 4 to give 2-trityl-4,5-diphenyl-1,2,3-triazole-1-oxide 8 (unisolated) followed by migration of a trityl group from a nitrogen to an oxygen atom, eq(3)[8,9].



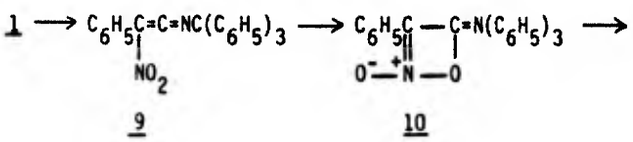
1 → 4 X = O + 5 Y = $(C_6H_5)_3CN$

1 → 7 X = $NC(C_6H_5)_3$ + 2 Y = O eq(2)

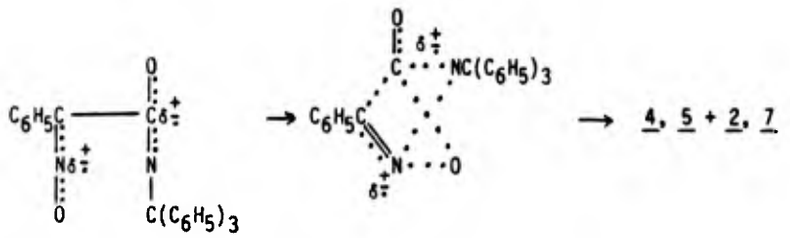


7 → 3 + 4 → 6 → 8 eq(3)

In a rationale for the dual fragmentation an initial isomerization of the ester 1 to the N-tritylimine 9 of phenylnitroketene,[10,11] ring-closure to the N-tritylimine 10 of 4H-3-phenyl-1,2-oxazet-4-one-2-oxide,[12,13] and ring opening by cleavage of a weak NO bond provided a model 11 as a precursor to compounds 4 and 5 by one fragmentation and to compounds 2 and 7 by another, eq(4). Further treatment of this complicated reaction will be dealt with in a longer report.



1 → 9 → 10



11 → 4, 5 + 2, 7 eq(4)

ACKNOWLEDGMENT

Financial support was received from ONR.

REFERENCES

1. D. Y. Curtin, R. J. Crawford, and D. K. Wedegaertner, J. Org. Chem., 1962, 27, 4300.

2. We are indebted to Dr. E. D. Stevens and Dr. C. L. Stevens for the X-ray analysis. The data will be published elsewhere.

3. J. T. Thurston and R. L. Shriner, J. Org. Chem., 1937, 2, 183.

4. R. L. Shriner and G. B. Brown, J. Org. Chem., 1938, 2, 561.

5. Since dual absorption bands near 1550 and 1350 cm^{-1}($-NO_2$) were absent at -20°C the formation of the nitronate esters predominated over the formation of the isomeric nitro compounds to be derived from C- and N-alkylation.

6. The nitrilimine 7 was previously abandoned as a precursor to the bisazostilbene 3 when benzonitrile-N-oxide 4 and trityl isocyanate 5 failed to give an adduct that might have fragmented to the nitrilimine 7 and carbon dioxide[7].

7. N. E. Alexandrou, J. Org. Chem., 1965, 30, 1335.

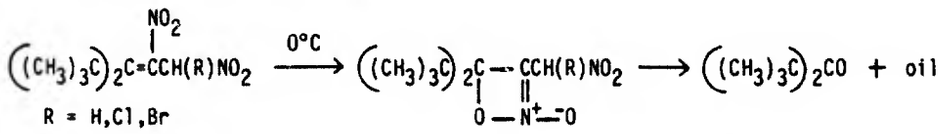
8. Attempts to realize independently a dipolar addition between benzonitrile-N-tritylimine 7 and benzonitrile-N-oxide 4 were abandoned when (a) tritylhydrazine and benzaldehyde failed to convert to the expected hydrazone (to be oxidized to the imine 7) and (b) N-tritylbenzohydrazidoyl chloride ($C_6H_5C(Cl)=NNHC(C_6H_5)_3$), to be dehydrochlorinated to the imine 7, was not obtained from β-N-tritylbenzohydrazide ($C_6H_5CONHNHC(C_6H_5)_3$) upon treatment with either thionyl chloride or phosphorus pentachloride.

9. The combined yield (42%) of compounds 3 and 6 is in good qualitative agreement with the yield (50%) reported for carbon dioxide[1].

10. The 1-5 sigmatropic isomerization 1 → 8 represented a formal change from O- to N-tritylation of a cyanomethane nitronate anion.

11. Attempts to prepare compound 8 by a reaction between trityl isocyanide and the sodium salt of phenylchloronitromethane were unsuccessful[7].

12. The formation of 4,4-di-t-butyl-3-methyl-4H-1,2-oxazete-2-oxide from 3-t-butyl-4,4-dimethyl-2-nitro-2-pentene on standing at 25°C was the first recognized example of an isomerization of an α,β-unsaturated nitro compound to a four-membered heterocycle. It underwent facile dissociation to give di-t-butyl ketone and an oil[13].



13. A. Berndt, Angew. Chem. Int. Ed. Eng., 1968, 7, 637; K. Wieser and A. Berndt, ibid., 1975, 14, 69, 70.

E. Alkylation of Nitroacetonitrile

JOSEPH H. BOYER, THANIKAVELU MANIMARAN and K. G. SRINIVASAN
Department of Chemistry, University of New Orleans
New Orleans, Louisiana 70148.

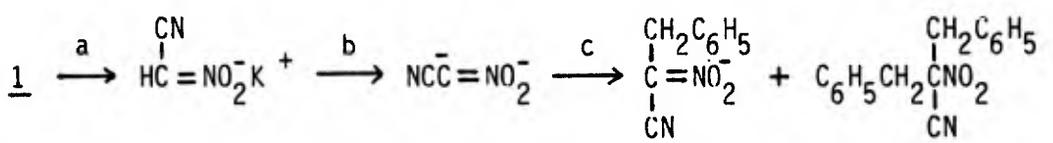
Alkylation of mono- and dianions of nitroacetonitrile 1, heretofore unknown, was briefly examined. A facile reaction between the nitrile 1 and acetone in the presence of triethylamine gave α,α'-dinitro-β,β'-dimethylglutaronitrile 3, eq(1). This result complemented the preparations of metal salts of α,α'-dinitro derivatives obtained by the nitration of homologous aliphatic dinitriles $(CH_2)_n(CN)_2$ (n = 0, 2 - 6), but not glutaronitrile (n = 1), eq(2).[1-3] Generally acidification of metal nitronates gave intractable oils in which corresponding nitro compounds (except for 1,4-dinitrobutane) were not detected.[2,3] Presumably the conversion of nitroacetonitrile, eq(1), proceeded by a condensation with acetone followed by a Michael addition of compound 1 to α-nitro-β,β-dimethylacrylonitrile 2 to give the glutaronitrile 3,[4,5] after acidification of its bistriethylammonium salt, an isolated derivative.

$$\underset{1}{O_2NCH_2CN} \xrightarrow[(CH_3)_2CO \\ -H_2O]{(C_2H_5)_3N} \underset{2}{(CH_3)_2C{=}C(NO_2)CN} \xrightarrow{1} \underset{3}{(CH_3)_2C(CHNO_2CN)_2} \qquad \text{eq(1)}$$

$$NC(CH_2)_nCN \xrightarrow[ROK]{RONO_2} \left[NCC(NO_2)(CH_2)_nC(NO_2)CN\right]^{=} 2K^+ \qquad \text{eq(2)}$$

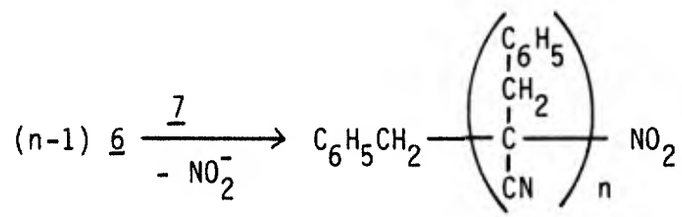
n = 0, 2 - 6

The dianion 5 of nitroacetonitrile was obtained from the potassium salt 4 and n-butyllithium.[6,7] When treated with two equivalents of benzyl bromide C-dialkylation gave dibenzylnitroacetonitrile 7 in very low yield. A different product, α,α,α'-tribenzyl-α'-nitrosuccinonitrile, 8, was obtained in low yield from the dianion 5 prepared by direct double deprotonation of the nitrile 1 when treated with two equivalents of n-butyllithium. Formation of the product 8 was considered to be an example of the displacement of a nitro group in an α-nitronitrile 7 by a nitronate anion 6, eq(4).[8,9] Since compound 8 is also an α-nitronitrile it is capable of further reaction with the nitronate anion 6 to give higher analogs of polycyanonitroalkanes 9, n > 2. The presence of these higher oligomers in the intractable mixture was not established. Products could not be isolated when benzyl bromide was replaced by methyl iodide, eq(3).



1 → (a) → 4 → (b) → 5 → (c) → 6 + 7 eq(3)

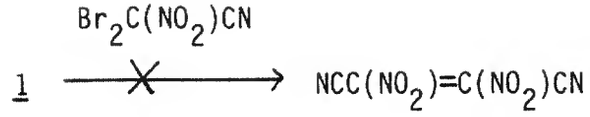
a = KOC_2H_5, b = n-C_4H_9Li, c = $C_6H_5CH_2Br$



(n-1) 6 —7, - NO_2^-→ $C_6H_5CH_2$—[C(C_6H_5)(CH_2)(CN)]$_n$—NO_2

7 - 9 n = 1, 2, >2 eq(4)

Attempts to combine nitroacetonitrile 1 and its dibromo derivative to obtain 1,2-nitro-1,2-dicyanoethylene 11 were unsuccessful, eq(5).



eq(5)

Experimental

Instruments included a Pye-Unicam SP 200 spectrophotometer, a Varian A-60 spectrometer, and an AEI Scientific Apparatus Limited MS30 mass spectrophotometer. Elemental analyses were obtained from Micro-Tech Laboratories, Skokie, Il. Tetrahydrofuran and hexamethylphosphoric triamide were freshly distilled from lithium aluminum hydride and calcium hydride.

α,α-Dinitro-β,β-dimethylglutaronitrile 3: To a stirred solution of nitroacetonitrile[11] (1.72 g, 20 mmol) in methanol (20 ml) triethylamine (4.04 g, 40 mmol) was added dropwise at 30°C. After 30 minutes the solvent was replaced with dry acetone (20 ml) and stirred (3 hours) as the triethylammonium salt of the glutaronitrile 3 precipitated as a colorless solid (1.85 g, 45%) mp 142-43°C (dec) after recrystallization from chloroform; ir (KBr): 3000, 2190 (CN), 1465, 1440, 1360, 1240 and 1045 cm^{-1}; nmr ($CDCl_3$): δ 3.05 (q, 12 H, CH_2, J = 7Hz), 1.53 (s, 6 H, $C(CH_3)_2$, 1.26 (t, 18 H, $-CH_2-CH_3$, J = 7 Hz); anal. calcd. for $C_{19}H_{38}N_6O_4$: C, 55.07; H, 9.17; N, 20.29; found: C, 55.05; H, 9.52; N, 20.26.

This nitronate salt (0.50 g, 1.2 mmol) was stirred with anhydrous ether (15 ml) saturated with dry hydrogen chloride for 10 minutes at 0-5°C. The solution after removal of triethylammonium chloride was concentrated at 5°C to give the glutaronitrile 3 (0.23 g, 90%), mp 118-19°C (dec); ir (KBr): 3000, 1565 (NO_2), 1360 (NO_2), 1285, 1010 cm^{-1}; anal. calcd. for $C_7H_8N_4O_4$: C, 39.63; H, 3.80; N, 26.41; found: C, 39.34; H, 3.80; N, 26.56. To avoid decomposition it was stored at 0°C.

Dibenzylnitroacetonitrile 7. The potassium salt[12] of nitroacetonitrile (1.25 g, 10 mmol) in a mixture of dry tetrahydrofuran (50 ml) and hexamethylphosphoric triamide (10 ml) cooled to -85°C by a liquid nitrogen and alcohol bath was treated with n-butyllithium (6.25 ml of a 1.6 M solution, 10 mmol) in hexane added dropwise under nitrogen with stirring (30 minutes) followed by a solution of benzyl bromide (3.42 g, 20 mmol) in tetrahydrofuran (10 ml) added slowly with stirring at -85°C for 3 hours. Stirring was continued overnight at room temperature, the mixture was treated with acetic acid (3 ml), and the solvent was removed. The residue dissolved in ether was washed with water and saturated sodium chloride solution and dried ($MgSO_4$). Ether was removed and the residue was chromatographed over neutral alumina. Hexane eluted dibenzylnitroacetonitrile (20 mg, 0.8%) as colorless needles, mp 152-53°C; ir (KBr): 3040, 1555, 1500 (NO_2), 1370 (NO_2), 1330, 745 and 705 cm^{-1}; nmr ($CDCl_3$): δ 7.46 (s, 10 H, aromatic), 4.63 (s, 4 H, CH_2); m/e (70 ev): 266 (M^+); anal. calcd. for $C_{16}H_{14}N_2O_2$: C, 72.17; H, 5.30; N, 10.52; found: C, 71.82; H, 5.32; N, 10.44.

Tribenzylnitrosuccinonitrile 8. To a stirred solution of nitroacetonitrile (0.86 g, 10 mmol) in dry tetrahydrofuran (50 ml) and hexamethylphosphoric triamide (10 ml) at -80°C under nitrogen n-butyllithium (12.50 ml of a 1.6 M solution, 20 mmol), followed by benzyl bromide (3.42 g, 20 mmol) in tetrahydrofuran (10 ml) was added. The mixture was stirred at -80°C for 3 hours and at room temperature overnight, treated with acetic acid and worked up as in the previous experiment to give the tribenzyl derivative 8 as colorless needles (80 mg, 2%) mp 129-30°C; ir (KBr): 3040, 2230 (CN), 1555 (NO_2), 1495, 1440, 1370 (NO_2), 1330, 745 and 700 cm^{-1}; nmr ($CDCl_3$): δ 7.26 (s, 15 H, aromatic), 3.83 (s, 2 H, C_6H_5-CH_2-C-NO_2), 3.50 (dd, 4 H, J = 14 Hz, $(C_6H_5CH_2)_2C$); anal. calcd. for $C_{25}H_{21}N_3O_2$: C, 75.93; H, 5.35; N, 10.63; found: C, 75.67; H, 5.47; N, 10.67.

Acknowledgment: Financial support was received from ONR.

References

1. T. P. Pillai and J. H. Boyer, Org. Prep. Procd. Int., 1983, 15, 7.

2. E. F. Witucki, W. Maya, and M. B. Frankel, Org. Prep. Procd. Int., 1980, 12, 197.

3. H. Feuer and C. Savides, J. Am. Chem. Soc., 1959, 81, 5826; H. Feuer, A. M. Hall, S. Golden, and R. L. Reitz, J. Org. Chem., 1968, 33, 622.

4. Michael additions of the anions of nitroalkanes to α,β-unsaturated esters, nitriles, or kektones were reported.[5]

5. G. A. Russell, M. Makosza, and J. Hershberger, J. Org. Chem., 1979, 44, 1195.

6. Treatment of potassium nitronates with n-butyllithium or treatment of the corresponding nitroalkane with two equivalents of n-butyllithium gave the dianions of nitroalkanes.[7]

7. D. Seebach and F. Lehr, Helv. Chim. Acta, 1979, 62, 2239.

8. Displacement of the nitro group of an α-nitronitrile by treatment with anions of nitroalkanes at 25°C to give β-nitronitriles was described as an electron transfer chain process.[9]

9. N. Kornblum, H. K. Singh, and S. D. Boyd, J. Org. Chem., 1984, 49, 358.

10. W. Steinkopf and L. Boehm, Ber., 1908, 41, 1044.

11. W. Ried and E. Kohler, Justus Liebigs Ann. Chem., 1956, 598, 145.

12. K. D. Grundermann and H. V. Alles, Angew. Chem. Internat. Edit., 1966, 5, 846.

F. Dibromonitroacetonitrile and Aromatic Compounds

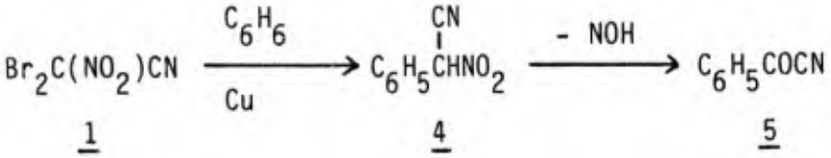
JOSEPH H. BOYER and THANIKAVELU MANIMARAN

Chemistry Department, University of New Orleans

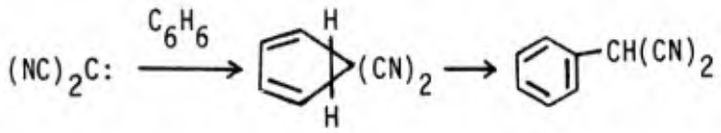
New Orleans, Louisiana 70148

It was previously reported that tetramethylethylene, two sulfides, and triethylamine were converted to adducts formally derived from nitrocyanocarbene by treatment with dibromonitroacetonitrile 1; co-products included the olefin dibromide and the amine hydrobromide.[1]

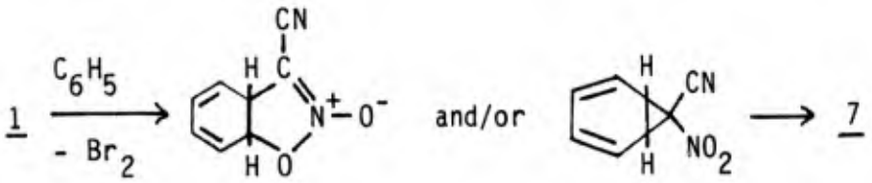
In this report we describe reactions between dibromonitroacetonitrile (a positive bromine reagent) and aromatic compounds. Although a trace of benzoyl cyanide 5 was detected in the reaction mixture, dibromonitroacetonitrile 1 did not otherwise react with benzene at 80°C for 20 hours and was recovered (80%). A more efficient formation of the cyanide 5 was brought about by the added presence of copper. The proposed intermediacy of phenylnitrocyanomethane 4 was supported by an independent quantitative conversion of compound 4 under similar conditions to the cyanide 5, eq(1).[2-7] It is believed that copper promoted debromination of the dibromide 1 and thereby afforded an interaction with benzene to produce a formal adduct with cyanonitro carbene. Since dicyanocarbene reacted with benzene by addition to an unsaturated bond and not at all by direct insertion into a CH bond, eq(2),[8] it is proposed that 3-cyanobenzisoxazol-2-in-2-oxide 2 or the isomeric norcaradiene 3 was formed initially however the formation of intermediate 4 by an isomerization of adducts 2 and/or 3 has not been differentiated from formation by direct insertion into a benzene CH bond, eq(3).



1 4 5 eq(1)

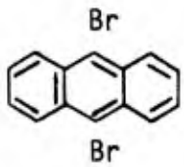


eq(2)



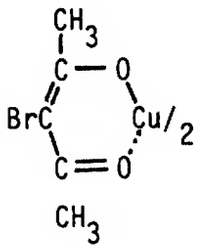
2 3 eq(3)

Anthracene and phenol underwent typical aromatic brominations to give 9,10-dibromoanthracene 6 and 4-bromophenol 7 on treatment with the dibromide 1. Formal adducts from nitrocyano carbene and these aromatic compounds were not detected. In a similar reaction the dibromide 1 converted cupric acetylacetonate to its bromo derivative 8.



6

7



8

Acknowledgment. Financial support was received from ONR.

Experimental

Instruments included Pye-Unicam SP 200 ir and Varian A-60 nmr spectrometers. Elemental analyses were obtained from Micro-Tech Laboratories,

Skokie, Il. Dibromonitroacetonitrile[9] and phenylnitroacetonitrile[10] were obtained by reported methods. Freshly precipitated copper powder[11] was used.

Benzoyl cyanide 5.: The dibromide 1 (12.2 g, 50 mmol) and copper powder (6.4 g, 100 mmol) in dry benzene (100 ml) were heated at 80°C for 15 hours. After inorganic material and the solvent were removed the residue was distilled in a Kugelrohr apparatus (130°C, 0.1 torr) to give benzoyl cyanide (1.85 g, 28%), mp 30-32°C, lit.[12] mp 32°C. Phenylnitroacetonitrile (4.05 g, 25 mmol) and copper powder (3.2 g, 50 mmol) in dry benzene (50 ml) were heated at 80°C for 10 hours to give benzoyl cyanide (3.2 g, 97%).

Brominations. Anthracene (1.78 g, 10 mmol) in methylene chloride (30 ml) was treated with the dibromo compound 1 (4.88 g, 20 mmol) in methylene chloride (20 ml) added dropwise. The mixture was stirred for 3 hours and concentrated to give 9,10-dibromoanthracene (2.20 g, 65%) as yellow needles mp 218-220°C, lit.[13] mp 220°C.

A solution of the dibromide 1 (2.44 g, 10 mmol) in methylene chloride (25 ml) was added to a solution of phenol (0.47 g, 5 mmol) in methylene chloride (25 ml) and stirred for 4 hours. The solvent was removed and the residue was placed on a neutral alumina chromatography column. Elution with ethyl acetate afforded 4-bromophenol (0.40 g, 46%), mp 63-64°C, lit.[14] mp 63°C.

To a solution of cupric acetylacetonate (2.62 g, 10 mmol) in acetone (50 ml) the dibromide 1 (4.88 g, 20 mmol) was added dropwise and the mixture was stirred for an hour to give cupric bromoacetylacetonate 12 which separated as dark green needles (1.9 g, 56%), mp 226-227°C (dec), lit.[15] mp 220°C (dec); anal. calcd. for $C_{10}H_{12}Br_2O_4Cu$: C, 28.60; H, 2.86; found: C, 28.62; H, 2.76.

References

1. J. H. Boyer and T. Manimaran, unpublished results.

2. The conversion 4 → 5 is reminiscent of the facile thermolysis of phenylbromonitroacetonitrile i to the cyanide ii.[3] It is suggested that both α-nitronitriles 4 and i underwent isomerization to a nitrite ester [4,5] and that the cyanide 5 was produced by an elimination of nitroxyl, eq(1), whereas ii was produced by an elimination of nitrosyl bromide.

$$\underset{\text{i}}{\text{o-BrC}_6\text{H}_4\text{C(NO}_2\text{)(Br)CN}} \longrightarrow \text{o-BrC}_6\text{H}_4\text{C(ONO)(Br)CN} \xrightarrow{-\ \text{NOBr}} \underset{\text{ii}}{\text{o-BrC}_6\text{H}_4\text{COCN}}$$

3. W. Wislicenus and H. Elvert, Ber., 1908, 41, 4121.

4. The isomerization of α-nitronitriles to nitrite esters has been observed.[6,7]

5. M. J. S. Dewar, J. P. Ritchie, and J. Alster, J. Org. Chem., 1985, 50, 1031. MINDO/3 calculations were reported for the thermolysis of nitro compounds via the isomeric nitrites.

6. R. Ketari and A. Foucaud, J. Org. Chem., 1981, 46, 4498.

7. W. Hochstein and U. Schollkopf, Liebig's Ann. Chem., 1978, 1823.

8. E. Ciganek, J. Amer. Chem. Soc., 1965, 87, 652.

9. W. Steinkopf and L. Boehm, Chem. Ber., 1908, 41, 1044.

10. J. T. Thurston and R. L. Shriner, J. Org. Chem., 1937, 2, 183.

11. M. Blumer, Anal. Chem., 1957, 29, 1039.

12. K. E. Koenig and W. P. Weber, Tetrahedron Lett., 1974, 2275.

13. K. Torssell, Arkiv Kemi, 1965, 23, 540.

14. R. Adams and C. S. Marvel, Org. Synth. Coll. Vol I, 128.

15. P. R. Singh, and R. Sahai, Aust. J. Chem., 1967, 20, 639.

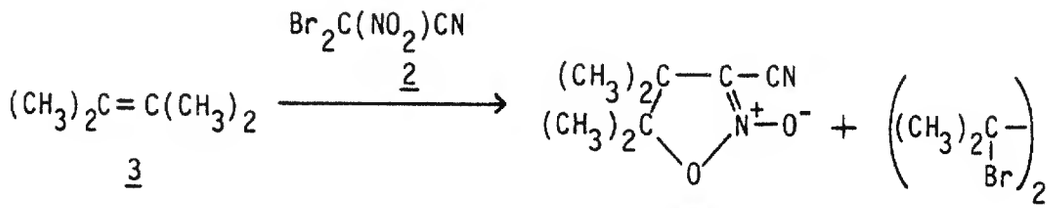
G. Formal Nitrocyanocarbene Adducts and Brominations from Nitrodibromoacetonitrile.

Joseph H. Boyer, Thanikavelu Manimaran, and T. Perumal Pillai, Department of Chemistry, University of New Orleans, New Orleans, Louisiana, 70148.

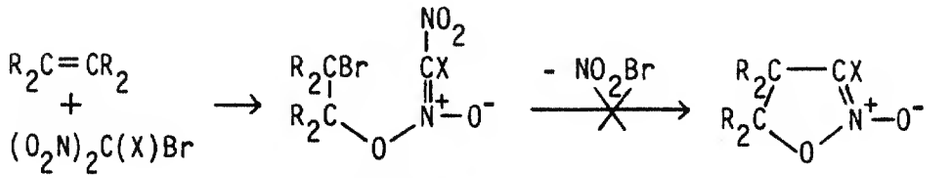
A variety of nucleophiles debrominated nitrodibromoacetonitrile 2 (NDBA) under mild conditions. This afforded typical bromination reactions and the unique formation of formal adducts derived from nitrocyanocarbene 1.

Tetramethylethylene 3 (2 moles) and NDBA[1] in an inert solvent at 25°C gave 3-cyano-4,4,5,5-tetramethylisoxazol-2-in-2-oxide 4 and 2,3-dibromo-2,3-dimethylbutane 5, eq(1). The structure of the heterocycle 4 was confirmed by an x-ray crystallographic analysis.[2] Formation of the heterocycle 4 by cyclization of the nitronate ester 7, an undetected adduct to be derived from NDBA and the olefin 3, was considered unlikely since similar cyclizations from β-bromoalkylnitronates 8, adducts from trinitrobromomethane and olefins,[3] were not observed, eq(2). That the formation of the heterocycle 4 did not proceed from a radical precursor was shown by observing no change in product formation by the added presence of either di-tert-butylnitroxide or tetracyanoethylene (radical scavengers). This observation was supported by an absence of a CIDNP signal for the reaction, eq(1). The formation of products 4 and 5 satisfied the requirements for a proposed bromonium salt intermediate 9 and its further interaction with the olefin 3, eq(3).[4] Support for the intermediate 9 was found by the complete suppression of the formation of the heterocycle 4 and no effect on the formation of the dibromide 5 by the added presence of pyridine in the reaction mixture. It was assumed that pyridine converted the salt 9 to the dibromide 5 and pyridinium nitrocyanomethylide 10, however the latter was not detected, eq(4).

1

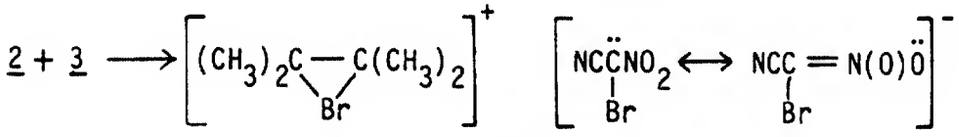


4 eq(1)



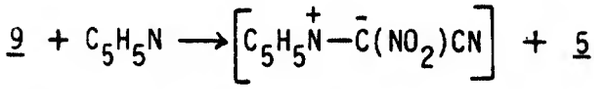
7 (not detected),
R = CH_3, X = CN

8, R = alkyl, H; X = NO_2 eq(2)

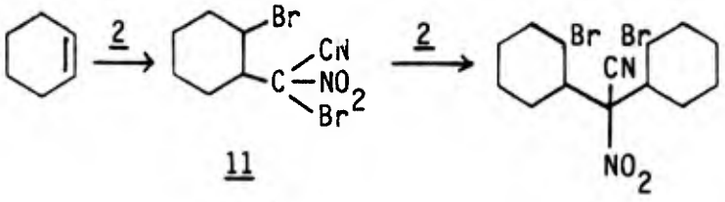


9

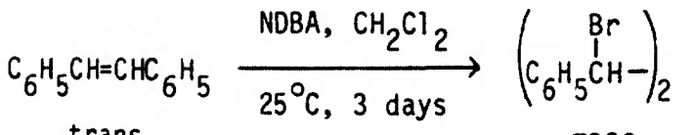
eq(3)



10 eq(4)



11 12 eq(5)



trans meso eq(6)

Additional support for the intermediacy of the salt 9 was found in a

reaction between cyclohexene and the dibromide 2 to give di-(2-bromocyclohexyl)nitroacetonitrile 12 in low yield presumably via the mono-adduct 2-bromocyclohexylbromonitroacetonitrile 11, eq(5). The structure 12 was determined by elemental analysis, molecular weight determination, ν_{as} 1550 and ν_s 1390 cm^{-1} (NO_2), δ 4.3 and 4.8 (two tertiary hydrogen atoms) and δ 1.2-2.5 (18 methylene hydrogen atoms). Formation of the intermediate 11 represented C-alkylation of the anion, see 9, of nitrobromoacetonitrile whereas formation of the nitronate ester 8 represented O-alkylation of the anion of nitroform. A bromonium ion intermediate was also proposed to explain the conversion of trans-stilbene to meso-1,2-diphenyl-1,2-dibromoethane (10%), mp 241°C (dec),[6] by treatment with NDBA, eq(6).

Dimethyl sulfide (2 equivalents) and the dibromide 2 in methylene chloride at 0°C for 30 minutes gave dimethylsulfonium nitrocyanomethylide 13 in high yield.[7,8] Tetrahydrothiophene gave tetramethylenesulfonium nitrocyanomethylide 14 by similar treatment. An excess of triethyl amine in benzene or carbon tetrachloride reacted with the dibromide 2 to give triethylammonium nitrocyanomethylide 15 in low yield and triethylammonium bromide. By analogy with eq(3) it is proposed that these reactions proceed from intermediate salts of nitrobromoacetonitrile, eq(7,8). The formation of triethylammonium bromide is known to occur in a reaction between triethylamine and bromine, eq(9).[9] Attempts to liberate nitrocyanocarbene 1, from its adduct 13 were unsuccessful.

$$R_2S \xrightarrow{2} R_2\overset{+}{S}Br\ \overset{-}{N}CC(Br)NO_2 \longrightarrow R_2\overset{+-}{S}C(CN)NO_2 + \left[Br_2\right]$$

13 R = CH_3

14 R_2 = $(CH_2)_4$ eq(7)

$$R_3N \xrightarrow{2} R_3\overset{+}{N}Br\ \overset{-}{N}CC(Br)NO_2 \longrightarrow R_3\overset{+}{N}\overset{-}{C}(CN)NO_2 + \left[Br_2\right]$$

R = C_2H_5 15 eq(8)

$$R_2NC_2H_5 \xrightarrow[-\ R_2\overset{+}{N}{=}CHCH_3\ \bar{B}r]{Br_2} HBr \xrightarrow{R_3N} R_3\overset{+}{N}H\ \bar{B}r \qquad \text{eq(9)}$$

$R = C_2H_5$

Experimental

Spectroscopic analyses were obtained from an ir Pye-Unicam SP200 and an nmr Varian A-60 spectrometers. Elemental analyses were obtained from Micro-Tech Laboratories, Skokie, Illinois.

3-Cyano-4,4,5,5-tetramethylisoxazol-2-in-2-oxide 4. To a stirred solution of NDBA 2 (4.88 g, 20 mmol) in methylene chloride (20 ml) at 25°C a solution of 2, 3-dimethylbut-2-ene 4 (3.36 g, 40 mmol) in methylene chloride (30 ml) was added dropwise. Stirring was continued for 30 minutes, solvent was removed, and the residue was chromatographed over neutral alumina. Hexane (3 X 100 ml) eluted 2,3-dibromo-2,3-dimethylbutane, 2.05 g (42%), mp 168-169°C (dec)[10] after recrystallization from hexane. The same solvent (4 X 100 ml) then eluted 3-cyano-4,4,5, 5-tetramethylisoxazol-2-in 4, 1.51 g (45%), mp 68-69°C after recrystallization from hexane; ir (KBr): 2220 (C≡N), 1605, and 1350 cm^{-1}(>C=N(O)O-) nmr ($CDCl_3$): δ 1.31 (s, CH_3) and 1.44 (s, CH_3; ^{13}Cnmr($CDCl_3$): δ 109.69 (C-3), 103.53 (CN), 90.84 (C-5), 48.79 (C-4), 21.08 (CH_3 at C-5), 20.72 (CH_3 at C-4); m/e (70 ev)(%): 168 (M^+, 36); anal. calcd. for $C_8H_{12}N_2O_2$: C, 57.14; H, 7.14; N, 16.67; found: C, 56.62; H, 7.29; N, 16.54. There was no change in the reaction when methylene chloride as solvent was replaced by benzene or cyclohexane.

Di-(2-bromocyclohexyl)nitroacetonitrile 12. A solution of NDBA 2 (12.2 g, 50 mmol) in an excess of cyclohexene (50 ml) was stirred overnight at 25°C. The mixture was concentrated to give the adduct 12 (1.9 g, 9%) as a colorless solid, mp 198-99°C (dec), ir (KBr): 1550, and 1390 cm^{-1} (NO_2); nmr ($CDCl_3$): δ 1.3-2.5 (m, 18 H) 4.3 (m, 1 H) and 4.8 (m, 1 H); m/e (70 ev): 408 (M^+); anal. calcd. for $C_{14}H_{20}N_2O_2Br_2$: C, 41.21; H, 4.90; N, 6.87; Br, 39.17; found: C, 41.00; H, 5.06; N, 6.90; Br, 39.25.

Dimethylsulfonium cyanonitromethylide 13. To a stirred solution of dimethyl sulfide (2.50 g, 40 mmol) in methylene chloride (20 ml) at 0-5°C a solution of NDBA (4.88 g, 20 mmol) in methylene chloride (50 ml) was added dropwise. Stirring at 0-5°C was continued for 30 minutes. Precipitated dimethylsulfonium cyanonitromethylide 13, 2.75 g (80%) recrystallized from hot water as a colorless solid, mp 213-214°C (dec)[8]; ir (KBr): 2200 (C≡N), 1400, and 1295 cm^{-1} (NO_2).

A similar reaction with tetrahydrothiophene gave tetramethylenesulfonium cyanonitromethylide 14 (54%), mp 166-167°C (dec) after recrystallization from hot water; ir (KBr): 2200 (C≡N), 1395, and 1300 cm^{-1} (NO_2); nmr ($CDCl_3$): δ 2.1-2.7 (m) and 3.4-3.8 (m); anal. calcd. for $C_6H_8N_2O_2S$: C, 41.86; H, 4.65; N, 16.28; S, 18.60; found: C, 41.32; H, 4.78; N, 16.34; S, 18.64.

Triethylammonium cyanonitromethylide 15. A solution of triethylamine (4.0 g, 40 mmol) in carbon tetrachloride (25 ml) was added dropwise to a stirred solution of NDBA (2.44 g, 10 mmol) in carbon tetrachloride at 25°C. The solvent was removed and the residue was triturated with acetone (20 ml), separated by filtration, and triturated with methylene chloride (25 ml) to give the methylide 15 as a colorless solid (90 mg, 5%), mp 154-155°C (dec); ir (KBr): 2200 (C≡N), 1420 (NO_2), 1330 cm^{-1} (NO_2); nmr: δ 1.50 (t, 9, CH_3), 3.17 (q, 6, CH_2); anal. calcd. for $C_8H_{15}N_3O_2$: C, 51.88; H, 8.16; N, 22.69; found: C, 51.20; H, 8.10; N,22.96. The combined filtrates were concentrated to give triethylammonium bromide as a colorless solid (1.65 g, 45%), mp 248-249°C (dec).[11] Similar results were obtained when benzene replaced carbon tetrachloride as solvent.

Acknowledgment: Financial support was received from ONR.

References

1. W. Steinkopf and L. Boehm, Ber., 1908, 41, 1044.
2. R. Gilardi and C. George, Naval Research Laboratory, Washington, D.C. The analysis will be published elsewhere.
3. K. Torssell, Arkiv Kemi, 1965, 24, 537, 543.

4. An intermediate bromonium ion for the addition of trinitrobromomethane and an olefin to form a nitronate ester 8 was proposed.[3,5]

5. V. I. Gulevskaya, E. I. Gorbachevich, T. I. Cherkasova, and L. V. Okhlobystina, Izv. Akad. Nauk SSSR, Ser. Khim., 1980, 1093; Eng p 800.

6. R. E. Buckles, J. M. Baden and R. J. Thurmaier, J. Org. Chem., 1962, 27, 4523.

7. The ylide 13 was previously obtained from nitroacetonitrile and dimethylsulfoxide.[8]

8. O. P. Shitov, V. V. Kondrat'ev, A. P. Seleznev, and V. A. Tartakovskii, Izv. Akad. Nauk SSSR, Ser. Khim., 1977, 240; Eng. p 214.

9. N. S. Isaacs, M. Hodgson and S. O. Tumi, Tetrahedron Lett., 1981, 22, 4139.

10. A. V. Grosse and V. N. Ipatieff, J. Org. Chem., 1943, 8, 438.

11. L. Wagner, Z. Kryst. Min., 1907, 43, 177.

H. Conversion of α-Aminoacids to α-Amino Derivatives of Nitros- and Nitramines

Joseph H. Boyer and Govindarajulu Kumar
Chemistry Department, University of New Orleans, New Orleans, Louisiana 70148

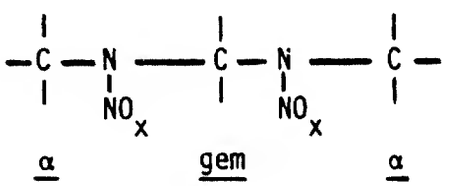
Abstract. N-Nitropipecolic acid 5 was converted to N-nitropipecolyl azide 8 (75%) via the acid chloride (not isolated). Thermolysis of the azide 8 in benzene gave 1-nitro-2-isocyanatopiperidine 9 (100%). Methanol converted the isocyanate to methyl N-(1-nitropiperidin-2-)carbamate 10 (65%, 49% overall). In one step diphenylphosphoryl azide in methanol converted the acid 5 to the carbamate 10 (50%). Thermolysis of the azide 8 in benzene containing tert-butanol gave tert-butyl N-(1-nitropiperidin-2-)carbamate 11 (50%). Attempts to liberate 1-nitro-2-aminopiperidine 12 from its carbamate 10 by treatment with trimethylsilyl iodide and methanol gave instead 1-nitro-Δ^2-tetrahydropyridine 12. The azide 8 was also obtained by the treatment of N-nitropipecolic acid hydrazide 7 with nitrous acid. Methyl N-nitrosopipecolate and hydrazine gave the expected hyrazide 16 (60%). The latter with sodium nitrite in hydrochloric acid gave the azide 17 (50%). A Curtius conversion of the azide gave 1-nitroso-2-isocyanatopiperidine 18 (70%) an unstable liquid; thermolysis of the azide in the presence of methanol gave methyl 1-nitrosopiperidin-2 carbamate 19 (55%). Attempts to convert N-nitrosopipecolic acid 14 to the acid chloride by treatment with ethyl chloroformate in the presence of triethylamine gave instead tetramethylene sydnone 20 (100%)

Diethyl 1,3-dinitrosoimidazolidin-4,5-dicarboxylate 38 was obtained in 80% yield from diethyl erythro-diaminosuccinate 26 by a condensation with formalin followed by nitrosation. Nitric acid (100%) converted the dinitrosamine 38 to diethyl 1,3-dinitroimidazolidin-4,5-dicarboxylate 39 (78%) and a similar conversion afforded the dimethyl esters 34 and 35. Ester hydrolysis by concentrated hydrochloric acid gave 1,3-dinitroimidazolidin-4,5-dicarboxylic acid

31 (65%) but similar treatment with dilute hydrochloric acid brought about decomposition of dimethyl 1,3-dinitrosoimidazolidin-4,5-dicarboxylate 34 with the evolution of brown fumes of nitrogen dioxide and a trace of an unidentified colorless solid. Attempted saponification of the diester 34 with dilute sodium hydroxide gave intractable mixtures. Although trimethylsilyl iodide was unreactive toward the dinitramine diester 39 it combined with the dinitrosamine diester 34 to give an intractable black tar. Attempts to convert diethyl imidazolidin-4,5-dicarboxylate 36 to the dinitrosamine 38 by nitrosation with sodium nitrite in sulfuric acid and to the dinitramine 39 by nitration with nitronium tetrafluoroborate in acetonitrile were unsuccessful. Diphenylphosphoryl azide with triethylamine in an alcohol converted the dinitramino acid 31 to an intractable mixture and had no effect on either the disodium or disilver salts of the acid 31. Attempts to convert the dinitraminoacid 31 to the corresponding dicarboxylic acid chloride by treatment with methyl chloroformate in the presence of triethylamine, phosphorous pentachloride, or thionyl chloride were unsuccessful. Thionyl chloride in the presence of pyridine gave the anhydride 40. Although tri-n-butyltin azide converted phthalic anhydride to isatoic anhydride (33%), it converted the dinitramine anhydride 40 to the tri-n-butyltin salt 42 of 1,3-dinitro-4-azidocarbonylimidazolidin-5-carboxylic acid and, when an alcohol was present, to the bistri-n-butyltin salt 41 of the dinitramino acid 31. Methanol converted the anhydride 40 to the monomethyl ester 44 of 1,3-dinitroimidazolidin-4,5-dicarboxylic acid. Treatment with diphenylphosphoryl azide converted the half-ester 44 to the monomethyl ester 45 of imidazole-4,5-dicarboxylic acid with the evolution of nitrogen dioxide (brown fumes). An equivalent of hydrazine converted the dinitraminoester 35 to dimethyl imidazole-4,5-dicarboxylate 46 and, when an excess of hydrazine was present, the dihydrazide 47 of imidazole-4,5-dicarboxylic acid. In contrast hydrazine converted the dinitrosaminoester 38 to the dihydrazide 48 of 1,3-dinitrosoimidazolidin-4,5-dicarboxylic acid that gave the expected

bis-condensation derivative of acetone. Nitrous acid converted the dihydrazide 48 to the diazide 49 of 1,3-dinitrosoimidazolidin-4,5-dicarboxylic acid. Thermolysis of the diazide 49 in benzene proceeded with the disappearance of azido and carbonyl functions but without a detectable formation of an isocyanate. A similar thermolysis in an alcohol also gave an intractable mixture that did not afford a carbamate ester.

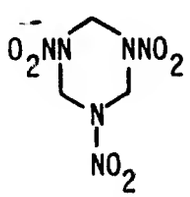
Introduction. Geminal bisnitrosamino and bisnitramino units 1 and 2 have rarely been derived from either a monoamine or a gem-diamine. The preparation of RDX from ammonium nitrate and formaldehyde in acetic anhydride offered a derivative of the bisnitramino unit 2.[1] In similar reactions formalin and sodium nitrite in sulfuric acid converted ethylenediamine to 1,3-dinitrosamidazolidine 3 and trimethylenediamine to 1,3-dinitroso hexahydro-pyrimidine 4.[2]



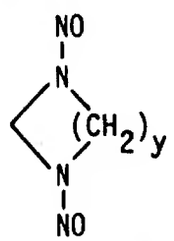
α gem α

1 x = 1

2 x = 2



RDX

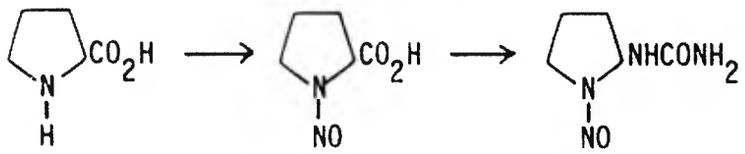


3 y = 2

4 y = 3

Functional group interchange offers, in principle, alternative routes to geminal bisnitrosamines and bisnitramines. Known α-functions in nitramines include hydroxyl (unstable),[3] secondary amino (unstable),[4] tertiary amino,[5] alkoxy,[6] cyano,[7] chloro,[8] fluoro,[9] azido,[10], and certain heterocyclic groups.[11] A primary α-aminonitramine is unknown and is presumably unstable. Known α-functions in nitrosamines include In two examples α-nitrosaminocarboxylic acids have been converted to α-aminonitrosamines isolated as ureido derivatives, eq(1,2).[xx]

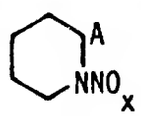
$$CH_3NHCH_2CO_2H \longrightarrow CH_3\underset{NO}{N}CH_2CO_2H \longrightarrow CH_3\underset{NO}{N}CH_2NHCONH_2 \qquad \text{eq(1)}$$



eq(2)

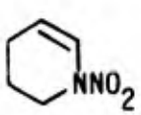
This investigation was undertaken to examine (a) the previously unknown conversion of an α-aminoacid to a stable derivative of an α-aminonitramine and (b) conversions available to α,α'-dicarboxy derivatives of a geminal bisnitramino unit 2 and bisnitrosamino unit 1.

Results and Discussion. Routine conversions from N-nitropipecolic acid 5 [xx] gave the first examples of nitramines with α-carboxyl, α-alkoxycarbonyl, α-hydrazinocarbonyl, α-azidocarbonyl, α-isocyanato, and α-carbamoyl functions 5 - 11. Attempted liberation of 1-nitro-2-aminopiperidine 12 from the carbamate 10 under anhydrous conditions by treatment with trimethylsilyl iodide followed by methanol[xx] gave instead 1-nitro-1,2,3,4-tetrahydropyridine 13 presumably by a spontaneous loss of ammonia from the primary amine 12.

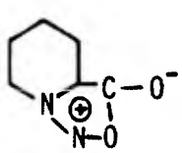


x = 2: 5 A = CO_2H, 6 A = CO_2CH_3, 7 A = CON_2H_3, 8 A = CON_3, 9 A = NCO,
10 A = $NHCO_2CH_3$, 11 A = $NHCO_2C(CH_3)_3$, 12 A = NH_2

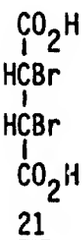
x = 1: 14 A = CO_2H, 15 A = CO_2CH_3, 16 A = CON_2H_3, 17 A = CON_3, 18 A = NCO,
19 A = $NHCO_2CH_3$, 20 A = NH_2



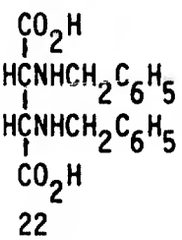
13



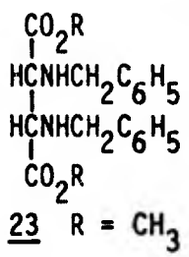
20



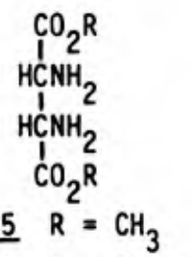
21



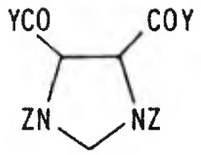
22



23 R = CH_3
24 R = C_2H_5



25 R = CH_3
26 R = C_2H_5



No.	28	29	30	31	32	33	34	35
Y	OH	OH	OH	OH	OCH_3	OCH_3	OCH_3	OCH_3
Z	H	$C_6H_5CH_2$	NO	NO_2	H	$C_6H_5CH_2$	NO	NO_2

NO.	36	37	38	39	41	48	49
Y	$O_{C2}H_5$	OC_2H_5	OC_2H_5	OC_2H_5	$OSn(C_4H_9)_3$	N_2H_3	N_3
Z	H	$C_6H_5CH_2$	NO	NO_2	NO_2	NO	NO

In a less efficient one-step operation the acid 5 was converted to the methyl carbamate 10 by treatment with diphenylphosphoryl azide, triethylamine, and methanol in benzene.[xx] An intractable product mixture was obtained when N-nitrosopipecolic acid 14 was subjected to similar treatment.

For conversion to the carbamate derivative 19 of 1-nitroso-2-aminopiperidine, N-nitrosopipecolic acid hydrazide 16 was prepared by treating the methyl ester 15 with hydrazine. Attempts to obtain the acid chloride from the acid 14 by treatment with ethyl chloroformate and triethylaminie were unsuccessful and gave instead tetramethylene sydnone 20 by dehydration.[xx] Routine treatment converted the hydrazide 16 to the carbamate 19 via the acid azide 17 and the isocyanate 18. No attempt was made to liberate the amine 20 from its carbamate derivative.

To investigate their conversions to isocyanates 50 and 51 and carbamates 52 and 53, preparations of the 1,3-dinitroso- 30 and the 1,3-dinitro- 31 derivatives of imidazolidine-4,5-dicarboxylic acid 28 were developed. Ethyl meso-diaminosuccinate 27 was obtained from meso-dibromosuccinic acid 21 by

treatment first with benzyl amine.[xx] This was followed by esterification of the dicarboxylic acid 22 to esters 23 and 24 and hydrogenolytic removal of benzyl groups from the dibenzyl diamine 24 to obtain the amines 25 and 26. Ring closure by treatment of the diamine 26 with formaldehyde gave the diethyl ester 36 of imidazolidin-4,5-dicarboxylic acid 28.[xx] Although ring closure by treatment with formaldehyde converted the meso-dibenzylamines 23 and 24 to the dimethyl ester 33 and the diethyl ester 37 of 1,3-dibenzylimidazolidin-4,5-dicarboxylic acid 29, subsequent hydrogenolytic removal of the benzyl groups and nitrosation of the unstable gem-diamine 36 (not isolated) gave an intractable mixture. A routine nitrosation converted the diamine 36 to the dinitrosamine 38 and treatment of the latter with nitric acid (100%) gave the corresponding diester dinitramine 39.[xx] Attempted oxidation of the dinitrosamine 38 to the dinitramine 39 by treatment with hydrogen peroxide (90%) and trifluoroacetic acid anhydride in methylene chloride gave an intractable mixture instead.[xx]

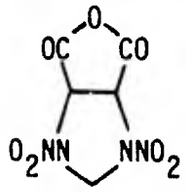
Aqueous hydrochloric acid hydrolysed each of the diesters 35 and 39 to the dicarboxylic acid 31. The free acid 31, its disodium salt, and its disilver salt were each treated with diphenylphosphoryl azide in unsuccessful attempts to convert carboxyl groups to amino groups (or derivatives);[xx] instead intractable mixtures were obtained. Attempts to convert the diacid 31 to the diacid chloride were also unsuccessful and intractable mixtures were obtained following treatment with either ethyl chloroformate and triethyl amine, or phosphorous pentachloride, or thionyl chloride. Thionyl chloride and pyridine (trace) converted the diacid to the anhydride 40.[xx] Moisture quickly converted the anhydride to the diacid 31.

Following a procedure for the conversion of an acid anhydride to an aminoacid the anhydride 40 was treated with tri-n-butyltin azide.[xx] The product isolated and identified was the bistributyltin salt 41 of 1,3-dinitroimid-

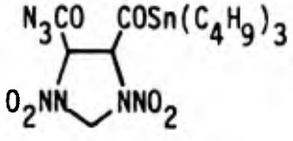
azolidin-4,5-dicarboxylic acid 31. Warm alcohol (methyl, ethyl, or tert-butyl) disproportionated the intermediate momo-azide 42 (detected by ir) to the ditin salt 41 without a trace of the Curtius conversion of the azidocarbonyl group to an isocyanate group (or its carbamate derivative). In contrast phthalic anhydride and tri-n-butyltin azide under comparable conditions gave isatoic anhydride 43 presumably via a Curtius conversion of an intermediate azidocarbonyl substituent.

To investigate the stepwise conversion of the two vicinal carboxyl groups the anhydride 40 was converted to the mono ester 44 by treatment with methanol. Diphenylphosphoryl azide failed to convert the acid 44 to an acid azide and/or an isocyanate; instead aromatization by the elimination of the elements of nitrous acid gave the half ester 45 of imidazole-4,5-dicarboxylic acid as the only product identified.[xx] A similar aromatization occurred when hydrazine hydrate and the diester 39 gave the diester 46 of imidazole-4,5-dicarboxylic acid and by further reaction the corresponding dihydrazide 47.

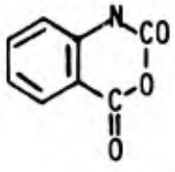
In contrast the dinitrosamino diester 38 and hydrazine hydrate gave the dihydrazide 48 of 1,3-dinitrosoimidazolidine-4,5-dicarboxylic acid. Apparently aromatization by the elimination of nitrous acid from compound 39 occurred more readily than it did by the elimination of nitroxyl from compound 38. Nitrous acid converted the dihydrazide 48 to the expected diazide 49. Thermolysis of the latter in either benzene or in t-butanol gave an intractable mixture of products and no trace of an isocyanate 50 or its carbamate derivative 52 was detected.



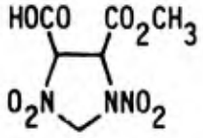
40



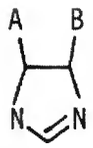
42



43



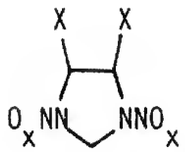
44



45 A = CO_2CH_3, B = CO_2H

46 A = B = CO_2CH_3

47 A = B = N_2H_3



50 X = NCO, x = 1

51 X = NCO, x = 2

52 X = $NHCO_2R$, x = 1

53 X = $NHCO_2R$. x = 2

Footnotes and References.

1. George F. Wright, "Methods of Formation of the Nitramino Group, its Properties and Reactions," in H. Feuer, ed., "The Chemistry of the Nitro and Nitroso Groups," in S. Patai, ser. ed., "The Chemistry of Functional Groups," John Wiley and Sons, New York, 1969, pp 614-684.

2. J. H. Boyer and G. Kumar, Heterocycles, 1984, 22, 2351.

I. Formal Dinitrocarbene and Nitrosyl Bromide Adducts from Dinitrodibromomethane

Joseph H. Boyer and Robert T. Patterson

Chemistry Department, University of New Orleans, New Orleans, Louisiana 70148

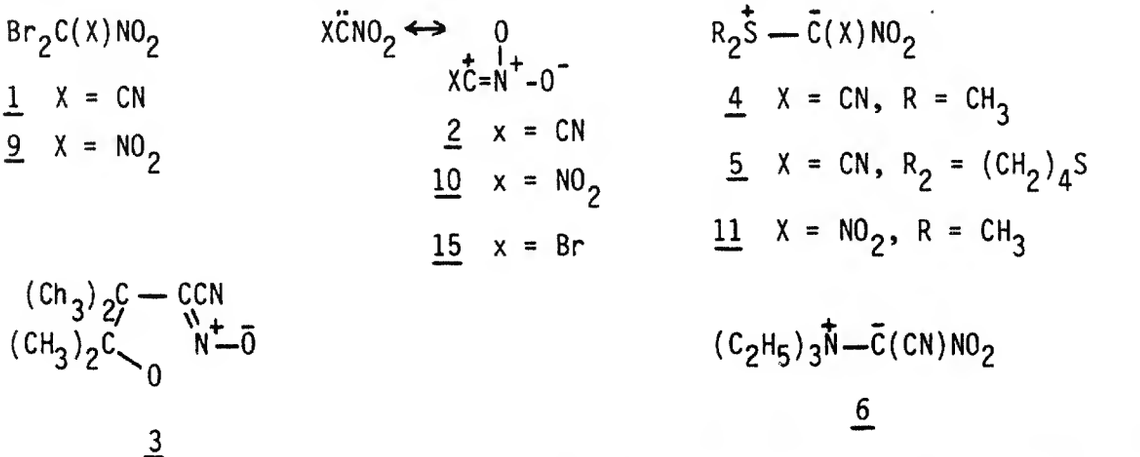
It was previously shown that nitrodibromoacetonitrile 1 afforded the adducts 3 - 6 formally derived from nitrocyanocarbene 2 and tetramethylethylene, dialkyl sulfides, and triethylamine. Coproducts were a dibromide 7 from the olefin and an ammonium bromide 8 from the amine.[1]

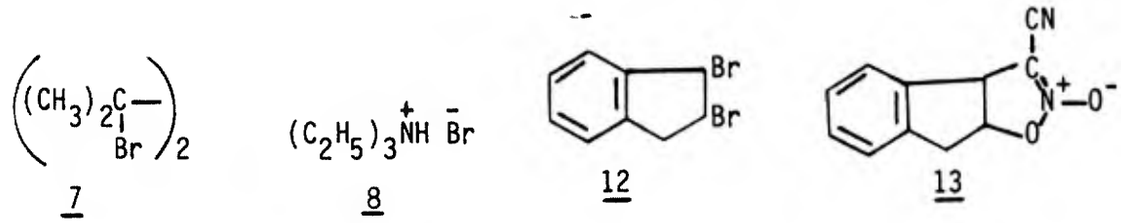
Similar reactions for dibromodinitromethane 9 (DDM) have been investigated. Dimethylsulfoniumdinitromethylide 11 (54%), previously obtained from dinitromethane and dimethyl sulfoxide,[2,3] was obtained from DDM 9 and dimethyl sulfide in methylene chloride and represented an adduct formally derived from dinitrocarbene 10. In contrast with nitrodibromoacetonitrile 1 DDM 9 was unreactive toward tetramethylethylene, acrylonitrile, and ethyl acrylate; and both 1,1,4,4,-tetramethylbutadiene and ethylvinyl ether with DDM gave intractable product mixtures. Indene and DDM in acetonitrile gave 2,3-dibromoindan 12 but failed to give the expected adduct 13 formally derived from dinitrocarbene 9.

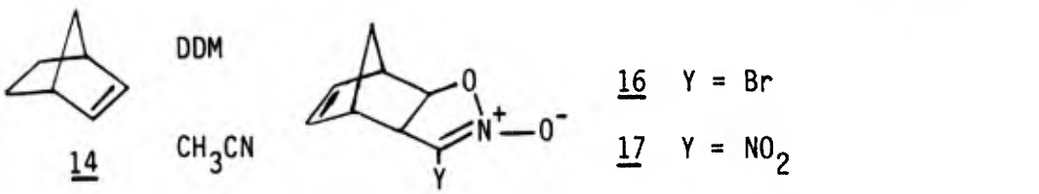
An unexpected dissociation of DDM 9 occurred in the presence of norbornene 14 in acetonitrile to bring about the formation of 3-bromo-3a,4,5,-6,7,7a-hexahydro-4,7-methano-1,2-benzisoxazole-2-oxide 16 (25%), an adduct formally derived from the olefin and nitrobromocarbene 15. The adduct 17 formally derived from dinitrocarbene 10 was not detected. When the solvent acetonitrile was replaced with methylene chloride the adduct 16 was not obtained and the only product detected was the dimer 19 (25%) of 2-bromo-3-nitrosobicyclo[2.2.1]heptane 18, a known adduct from norbornene and nitrosyl bromide 21. Formation *in situ* of the latter by a previously unknown

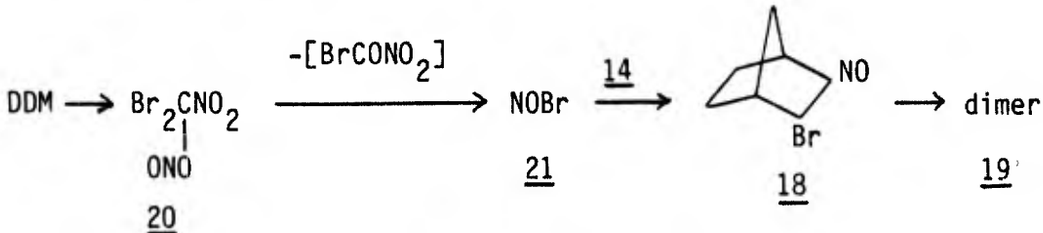
dissociation of DDM was accounted for by an initial isomerization to nitrodibromomethyl nitrite 20 followed by a 1,2-elimination.

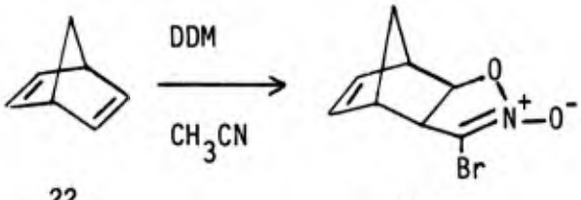
In acetonitrile bicyclo[2.2.1]hepta-2,5-dione 22 and DDM 9 afforded 3-bromo-3a,4,7,7a-tetrahydro-4,7-methano-1,2-benzisoxazole-7-oxide 23 (29%) an adduct formally derived from the olefin and bromonitrocarbene 15.











Acknowledgment: Financial support was received from ONR.

Experimental. Spectroscopic analyses were obtained from an ir Pye-Unicam SP200, an nmr Varian A-60 spectrometers and an Hitachi Perkin-Elmer RMU-6E mass spectrometer. Elemental analyses were obtained from Micro-Tech Laboratories, Skokie, Illinois.

Dimethylsulfoniumdinitromethylide 11. A solution of dimethylsulfide (1.0 g, 16.1 mmol) in methylene chloride (15 ml) was cooled to 4°C and a solution of methylene chloride (5 ml) containing dibromodinitromethane (2.0 g, 7.6 mmol) was added over 5 minutes. After stirring for 0.5 hr at 4°C, it was stored (0°C) overnight. The precipitate was filtered and washed with chloroform and with distilled water (5 ml) and air dried for 2 hr. to give a yellow solid (0.68 g, 54%) mp 215-218°C (dec.) (lit.[1,2] mp 224-226°C (dec.)); IR(KBr): 3070, 3040, 2920, 1595, 1405, 1355, 1260, 1050, 990, 940, 835, 735 cm^{-1}; ^{13}C NMR(DMSO-d_6): δ 26.75, 121.83 (lit.[2] δ 26.83, 124.7); M/e (70 ev): 166 (M^+, 90), 151 (30), 104 (61), 62 (100), 47 (80).

3-Bromo-3a,4,5,6,7,7a-hexahydro-4,7-methano-1,2-benzisoxazole-2-oxide 16. A solution of acetonitrile (5 ml) containing bicyclo[2.2.1]hept-2-ene (1.5 g, 16.0 mmol) was cooled to 10-15°C and dibromodinitromethane (1.0 g, 3.8 mmol) was added over 2 minutes followed by more acetonitrile (5 ml). After 2.75 h at 10-15°C the solvent was stripped under reduced pressure and the oil chromatographed on silica gel (30 g) using benzene (150 ml) and 30% ethyl acetate/benzene (200 ml) to give a colorless solid (0.22 g, 25%); mp 140-141°C; IR (KBr): 2975, 2880, 1630, 1310, 1250, 945, 890, 872, 845, 810, 795, 760 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.2 - 1.7 (m, 6H); 2.5 - 2.70 (m, 2H); 3.3 (m, 1H); 4.70 (m, 2H); ^{13}C NMR ($CDCl_3$): δ 26.8, 27.9, 32.5, 39.7, 42.2, 55.9, 81.6; M/e

(70ev): 233(M^+ + 2,8), 231(M^+,9), 91(30), 67(100); anal. calcd for $C_8H_{10}NO_2Br$: C, 41.40; H, 4.35; N, 6.04; Br, 34.43; found: C, 41.40; H, 4.37; N, 5.97; Br, 34.86.

2-Bromo-3-nitrosobicyclo[2.2.1]heptane dimer 19. To a solution of methylene chloride (7 ml) and bicyclo[2.2.1]hept-2-ene (1.5 g, 16.0 mmol) at 10°C was added dibromodinitromethane (1.0 g, 3.8 mmol) followed by methylene chloride (3 ml). After 22 hr at room temperature, the solvent was stripped under reduced pressure and solid (0.39 g) was precipitated with benzene. Recrystallization from a mixture of 40% methylene chloride and ethanol gave the bis-2-bromo-3-nitroso-bicyclo[2.2.1]heptane (0.19 g, 25%); mp 143-144°C; (lit.[1] mp 138-139°C); IR(KBr): 2980, 2880, 1395, 1320, 1310, 1275, 1265, 1245, 1230, 955, 935, 855, 835 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.18-2.2 (m,6H), 2.5 (bs,1H), 2.76 (bs,1H), 4.4 (m,1H), 4,87 (m,1H); ^{13}C NMR ($CDCl_3$): δ 26.5, 27.1, 35.8, 39.7, 46.1, 54.0, 73.6; M/e (70 ev): 206 (M^+,4), 204 (M^+,4), 175 (53), 173 (55), 124 (23), 121 (8), 119 (9), 93 (99), 79 (39), 77 (6), 67 (54), 66 (100), 65 (41); anal. calcd for $C_{14}H_{20}N_2O_2Br_2$: C, 41.19; H, 4.95; N, 6.87; Br, 39.15; found: C, 41.12; H, 4.95; N, 6.79; Br, 40.26.

3-Bromo-3a,4,7,7a-tetrahydro-4,7-methano-1,2-benzisoxazole-7-oxide 23. A solution of bicyclo[2.2.1]hepta-2,5-diene. (2.0 g, 21.7 mmol) in dry acetonitrile (10 ml) was cooled to 10°C and dibromodinitromethane (1.0 g, 3.8 mmol) diluted in dry acetonitrile (5 ml) was added over 3 minutes. After 1.25 h solvent was removed under reduced pressure to give an oily residue (1.94 g). Flash chromotography on silica gel (30 g) with benzene/ethyl acetate (70/30) gave a yellow oil (0.78 g). A second flash chromotography on silica gel (30 g) with benzene/diethyl ether 95/5 gave a solid (0.53 g, mp 65-67°C). Lyophilization at 100 torr from methylene chloride/heptane 50/50 gave a solid

(0.25 g, 29%), mp 75-76°C; IR (KBr): 3030, 2960, 2875, 1635, 1260, 1150, 1060, 1000, 900, 845, 805 cm^{-1}; H'NMR ($CDCl_3$): δ 6.1 (m, 2H), 4.6 (m, 1H), 3.2 (m, 3H), 1.7 (m 2H); ^{13}C NMR ($CDCl_3$): δ 42.5, 45.3, 48.5, 53.2, 79.7, 98.2, 133.9, 139.2; M/e (70 ev): 231 $(M + 2)^+$(3); 229 (M^+)(3); 214 (4); 212 (4); 202 (8); 200 (8); 133 (5); 123 (7); 121 (5); 105 (15); 104 (17); 91 (24); 79 (21); 77 (19); 66 (100); anal. calcd. for $C_8H_8NO_2Br$: C, 41.76; H, 3.51; N, 6.09; Br, 34.73; found: C, 41.72; H, 3.62; N, 6.07; Br, 34.90.

1. J. H. Boyer, T. Manimaran and T. P. Pillai, J. Chem. Res., submitted.
2. O. P. Shitov, V. N. Kondratév, A. P. Seleznev and V. A. Tartakovskii; Isv. Akad. Nauk SSSR, Ser. Khim., 1976, 479; Eng. P 468.
3. S. A. Shevelev, V. V. Semenov and A. A. Fainzilberg, Izv. Akad, Nauk SSSR, Ser. Khim., 1976, 2032; Eng. P 1906.

J. Ligand Transfer From Iodobenzene Ditrifluoroacetate To An α-Iodoketone

Joseph H. Boyer and Anbazhagan Natesh

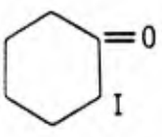
Chemistry Department, University of New Orleans, New Orleans, LA 70148

Phenacyl alcohol 6 (74%) and 1,4-diiodobenzene 8 (51%) were obtained from phenacyl iodide by treatment with iodobenzene ditrifluoroacetate followed by hydrolysis. Similar treatment converted 2-oxo-3-iodonorbornane 3 to the diiodide 8 (30%) but the formation of 2-oxo-3-hydroxynorbornane was not detected. An intractable mixture was obtained from 2-iodocyclohexanone 2 when treated with iodobenzene ditrifluoroacetate.

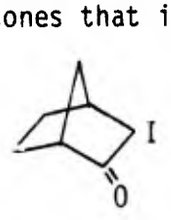
A search for mild facile conversions of base sensitive enolizable ketones to their α-hydroxy derivatives led to an investigation of the preparation and dissociation of α-ditrifluoroacetoxyiodoketones.[1,2] Phenacyl iodide 1,[3] 2-iodocyclohexanone 2,[3] and 2-oxo-3-iodonorbornane 3 [4] were examined. The latter was prepared from the trimethylsilyl ether of 2-oxonorbornane and N-iodosuccinimide according to a method previously reported[3] for the preparation of α-iodoketones that included compounds 1 and 2.

$C_6H_5COCH_2I$

1



2



3

Treatment with iodobenzene ditrifluoroacetate converted phenacyl iodide 1 to phenacyl trifluoroacetate 5 detected by nmr in a mixture with iodobenzene, 1,4-diiodobenzene 8, and phenacyl alcohol 6. Chromatographic separation of the mixture from a column of silica gel by a mixture of methanol and methylene chloride completed the conversion of the ester 5 to the alcohol 6 and afforded the isolation of the diiodide 8.[5] In conformity with similar reactions from other alkyl iodides[5,6] it is proposed that the overall exchange of an iodo with a trifluoroacetoxy group occurred via a ligand transfer from iodobenzene ditrifluoroacetate to give iodobenzene and α-iodoacetophenone ditrifluoroacetate 4 [5-8] and that dissociation of

the latter gave phenacyl trifluoracetate 5 and trifluoroacetoxy iodide 7, a positive iodine reagent undetected except for its probable role in the conversion of iodobenzene (released from its ditrifluoroacetate derivative) to 1,4-diiodobenzene 8.

$$\underline{1} + C_6H_5I(OCOCF_3)_2 \longrightarrow C_6H_5I + \underset{\underline{4}}{C_6H_5COCH_2I(OCOCF_3)_2}$$

$$\underline{4} \longrightarrow \underset{\underline{5}}{C_6H_5COCH_2OCOCF_3} \xrightarrow{H_2O} \underset{\underline{6}}{C_6H_5COCH_2OH} + \underset{\underline{7}}{CF_3CO_2I}$$

$$CF_3CO_2I + C_6H_5I \longrightarrow \underset{\underline{8}}{\underline{p}\text{-}IC_6H_4I} + CF_3CO_2H$$

EXPERIMENTAL

Instruments included Varian EM-360 (60 MHz), JEOL FX-90 (90 MHz), and JEOL FA-90 nuclear magnetic resonance spectrometers, a Pye Unicam (Sargent-Welch) 3-200 infrared spectrometer, and a Hitachi Perkin-Elmer RMU-6E mass spectrometer.

Trimethylsilyl trifluoromethanesulfonate (99%) and N-iodosuccinimide (95%) were purchased from the Aldrich Chemical Co. Iodobenzene ditrifluoroacetate was prepared from iodobenzene diacetate and trifluoroacetic anhydride.[6] Phenacyl iodide 1 and α-iodocyclohexanone 2 were prepared from the appropriate enol silyl ether[10] and N-iodosuccinimide.[3] The iodide 2 was stored successfully in the refrigerator but decomposed on storage at 25°C.

Trimethyl silyl ether of the enol of 2-oxonorbornane 3. A solution of 2-oxonorbornane (3.5 g, 31.8 mmol) and triethylamine (freshly distilled)

(4.7 g, 46.2 mmol) in dry benzene (45 ml) was cooled to 0-5°C under nitrogen. Trimethylsilyl trifluoromethanesulfonate (10.3 g, 46.2 mmol) was added dropwise with stirring. After continued stirring (80°C, 3 h) the mixture was cooled to room temperature and transferred to a separatory funnel. The benzene layer was separated and the solvent was removed. The crude product was distilled to give the enol silyl ether as a colorless liquid (4.5 g, 77.8 %), b.p. 60 - 62°C 14 torr (lit.[4] 58 - 63°C/14 torr).

3-Iodo-2-oxonorbornane 3. A solution of the enol trimethylsilyl ether of 2-oxonorbornane (3.8 g, 20.6 mmol) in dry tetrahydrofuran (40 ml) was cooled to 0 - 5°C with the exclusion of moisture. N-Iodosuccinimide (5.6 g, 24.8 mmol) was added and the mixture was stirred (< 5°C, 3.5 h). An ether extraction of the reaction mixture was washed with aqueous sodium thiosulfate (10%, 75 ml), saturated aqueous sodium bicarbonate (2 X 75 ml) and brine, before it was dried ($MgSO_4$). Evaporation left an oily residue. Flash chromatography [silica gel, Merck grade 60, methylenechloride/hexane(1:1) as the eluent] of the residue gave the iodide 3 as a light brown oil, 4.4 g, 90.5%; ir (film) 1750 cm^{-1} (CO);[4] nmr 'H (CCl_4): δ 1.5 - 2.5 (6 H, m), 2.5 - 2.9 (2 H, m), 4.1 (1 H, d, J 3.4 H_Z);[4] nmr^{13}C($CDCl_3$): δ 22.5, 26.6, 28.2, 36.0, 45.1, 49.3, 211.7 (>C=O).

Reaction of phenacyl iodide 1 with iodobenzene ditrifluoroacetate. To a solu-tion of phenacyl iodide 1 (0.3 g, 1.2 mmol) in dry methylene chloride (5 ml) iodobenzene ditrifluoroacetate[5] (0.6 g, 1.4 mmol) was added and the resulting mixture was stirred at room temperature for 6 h. The reaction mixture was diluted with ether (15 ml) and washed successively with 10% aqueous sodium bisulfite (2 X 10 ml), saturated aqueous sodium bicarbonate (10 ml) and brine solution. The ether extract was dried (Na_2SO_4), and the solvent was removed under reduced pressure. The 'H nmr of the crude pro-

duct showed a mixture of phenacyl trifluoroacetate (5), iodobenzene, 1,4-diiodobenzene (8) and some phenacyl alcohol (6). Iodobenzene was removed by evaporation at 25°C (1.0 torr). Flash column chromatography [silica gel, Merck grade 60, methylene chloride/methanol (40:1) eluent] of the residue gave 1,4-diiodobenzene 8 m.p. 126 - 128°C[10] (0.20 g, 50.5%): ir (KBr): 1460, 1370, 1065, 990 and 795 cm^{-1}; nmr $^1H(CDCl_3)$: δ 7.4(s); nmr $^{13}C(CDCl_3)$: δ 93.3, 139.2; m/z (70 ev): 330(M^+), 203(M^+ - I), 76(M^+ - 2 I); and phenacylalcohol 6 m.p. 83 - 85°C[12] (0.12 g, 74%): ir (nujol): 3350 and 1680 cm^{-1}; nmr ^1H ($CDCl_3$): δ 3.5 (1H, br,s), 4.8 (2H, s), 7.4 - 7.7 (3H, m), 7.8 - 8.1 (2H, m); nmr $^{13}C(CDCl_3)$: δ 65.4, 127.7, 128.9, 133.4, 134.2, 198.41; m/z (70 ev): 136 (M^+), 105(M^+ - CH_2OH).

REFERENCES

1. No reaction occurred in an attempted oxidative replacement of hypervalent iodine to give an α-hydroxyester by the treatment of erythro-3-azido-2-iodo-3-phenylpropanoate with m-chloroperbenzoic acid in a mixture of t- butanol and water.[2]
2. R. C. Cambie, D. Chambers, B. G. Lindsay, P. S. Rutledge, and P. D. Woodgate, J. Chem. Soc. Perkin Trans. 1, 822 (1980).
3. Y. D. Vankar and G. Kumaravel, Tetrahedron Lett., 25, 233 (1984).
4. X. Creary and A. J. Rollin, J. Org. Chem., 42, 4226 (1977); 44, 1798 (1978).
5. J. Gallos and Anastasios Varvoglis, J. Chem. Soc., Perkin Trans. 1, 1999, (1983). p-Diiodobenzene was detected (nmr) in reactions between alkyl halides and phenyliodine (111) dicarboxylates.
6. T. L. Macdonald and N. Narasimhan, J. Org. Chem., 50, 5000 (1985).
7. Comparable hypervalent iodine intermediates were previously proposed.[6,7]

8. Iodosobenzene with boron trifluoride etherate in water converted the trimethylsilyl enol ether from acetophenone to phenacyl alcohol 6 (57%). R. M. Moriarty, O. Prakash, and M. P. Duncan (Synthesis, 943, 1985) proposed the intermediacy of $C_6H_5COCH_2I(OBF_2)C_6H_5$.

9. Iodosobenzene (or iodophenyl diacetate) in methanolic sodium hydroxide converted acetophenone 1 to phenacyl alcohol 6 (60%). R. M. Moriarty, H. Hu, and S.C. Gupta (Tetrahedron Lett., 22, 1283, 1981) proposed the intermediacy of $C_6H_5COCH_2I(OH)C_6H_5$.

10. G. Simchen and W. Kober, Synthesis, 259 (1976).

11. E. B. Merkushev, N. D. Simakhina and G. M. Koveshnikova, Synthesis, 486 (1980).

12. G. M. Rubottom, M. A. Vazquez, and D. R. Pelgrina, Tetrahedron Lett., 4319 (1974).

DISTRIBUTION LIST

Dr. R.S. Miller
Office of Naval Research
Code 432P
Arlington, VA 22217
(10 copies)

Dr. A.L. Slafkosky
Scientific Advisor
Commandant of the Marine Corps
Code RD-1
Washington, DC 20380

JHU Applied Physics Laboratory
ATTN: CPIA (Mr. T.W. Christian)
Johns Hopkins Rd.
Laurel, MD 20707

Dr. Kenneth D. Hartman
Hercules Aerospace Division
Hercules Incorporated
Alleghany Ballistic Lab
P.O. Box 210
Washington, DC 21502

Mr. Otto K. Heiney
AFATL-DLJG
Elgin AFB, FL 32542

Dr. Merrill K. King
Atlantic Research Corp.
5390 Cherokee Avenue
Alexandria, VA 22312

Dr. R.L. Lou
Aerojet Strategic Propulsion Co.
Bldg. 05025 - Dept 5400 - MS 167
P.O. Box 15699C
Sacramenta, CA 95813

Dr. R. Olsen
Aerojet Strategic Propulsion Co.
Bldg. 05025 - Dept 5400 - MS 167
P.O. Box 15699C
Sacramento, CA 95813

Dr. J. Pastine
Naval Sea Systems Command
Code 06R
Washington, DC 20362

Dr. Henry P. Marshall
Dept. 93-50, Bldg 204
Lockheed Missile & Space Co.
3251 Hanover St.
Palo Alto, CA 94304

Dr. Ingo W. May
Army Ballistic Research Lab.
ARRADCOM
Code DRXBR - 1BD
Aberdeen Proving Ground, MD 21005

Dr. R. McGuire
Lawrence Livermore Laboratory
University of California
Code L-324
Livermore, CA 94550

P.A. Miller
736 Leavenworth Street, #6
San Francisco, CA 94109

Dr. W. Moniz
Naval Research Lab.
Code 6120
Washington, DC 20375

Dr. K.F. Mueller
Naval Surface Weapons Center
Code R11
White Oak
Silver Spring, MD 20910

Prof. M. Nicol
Dept. of Chemistry & Biochemistry
University of California
Los Angeles, CA 90024

DISTRIBUTION LIST

Dr. Randy Peters
Aerojet Strategic Propulsion Co.
Bldg. 05025 - Dept 5400 - MS 167
P.O. Box 15699C
Sacramento, CA 95813

Dr. D. Mann
U.S. Army Research Office
Engineering Division
Box 12211
Research Triangle Park, NC 27709-2211

Mr. R. Geisler
ATTN: DY/MS-24
AFRPL
Edwards AFB, CA 93523

Naval Air Systems Command
ATTN: Mr. Bertram P. Sobers
NAVAIR-320G
Jefferson Plaza 1, RM 472
Washington, DC 20361

R.B. Steele
Aerojet Strategic Propulsion Co.
P.O. Box 15699C
Sacramento, CA 95813

Mr. M. Stosz
Naval Surface Weapons Center
Code R10B
White Oak
Silver Spring, MD 20910

Mr. E.S. Sutton
Thiokol Corporation
Elkton Division
P.O. Box 241
Elkton, MD 21921

Dr. Grant Thompson
Morton Thiokol, Inc.
Wasatch Division
MS 240 P.O. Box 524
Brigham City, UT 84302

Mr. L. Roslund
Naval Surface Weapons Center
Code R10C
White Oak, Silver Spring, MD 20910

Dr. David C. Sayles
Ballistic Missile Defense
Advanced Technology Center
P.O. Box 1500
Huntsville, AL 35807

Director
US Army Ballistic Research Lab.
ATTN: DRXBR-IBD
Aberdeen Proving Ground, MD 21005

Commander
US Army Missile Command
ATTN: DRSMI-RKL
Walter W. Wharton
Redstone Arsenal, AL 35898

T. Yee
Naval Weapons Center
Code 3265
China Lake, CA 93555

Dr. E. Zimet
Office of Naval Technology
Code 071
Arlington, VA 22217

Dr. Ronald L. Derr
Naval Weapons Center
Code 389
China Lake, CA 93555

T. Boggs
Naval Weapons Center
Code 389
China Lake, CA 93555

Lee C. Estabrook, P.E.
Morton Thiokol, Inc.
P.O. Box 30058
Shreveport, LA 71130

DISTRIBUTION LIST

Dr. R.F. Walker
Chief, Energetic Materials Division
DRSMC-LCE (D), B-3022
USA ARDC
Dover, NJ 07801

Dr. Janet Wall
Code 012
Director, Research Administration
Naval Postgraduate School
Monterey, CA 93943

R.E. Shenton
Atlantic Research Corp.
7511 Wellington Road
Gainesville, VA 22065

Mike Barnes
Atlantic Research Corp.
7511 Wellington Road
Gainesville, VA 22065

Dr. Lionel Dickinson
Naval Explosive Ordinance
Disposal Tech. Center
Code D
Indian Head, MD 20340

Prof. J.T. Dickinson
Washington State University
Dept. of Physics 4
Pullman, WA 99164-2814

M.H. Miles
Dept. of Physics
Washington State University
Pullman, WA 99164-2814

Dr. T.F. Davidson
Vice President, Technical
Morton Thiokol, Inc.
Aerospace Group
110 North Wacker Drive
Chicago, IL 60606

Dr. D.D. Dillehay
Morton Thiokol, Inc.
Longhorn Division
Marshall, TX 75670

G.T. Bowman
Atlantic Research Corp.
7511 Wellington Road
Gainesville, VA 22065

Brian Wheatley
Atlantic Research Corp.
7511 Wellington Road
Gainesville, VA 22065

Mr. G. Edwards
Naval Sea Systems Command
Code 62R32
Washington, DC 20362

C. Dickinson
Naval Surface Weapons Center
White Oak, Code R-13
Silver Spring, MD 20910

Prof. John Deutch
MIT
Department of Chemistry
Cambridge, MA 02139

Dr. E.H. deButts
Hercules Aerospace Co.
P.O. Box 27408
Salt Lake City, UT 84127

David A. Flanigan
Director, Advanced Technology
Morton Thiokol, Inc.
Aerospace Group
110 North Wacker Drive
Chicago, IL 60606

DISTRIBUTION LIST

Mr. J. Consaga
Naval Surface Weapons Center
Code R-16
Indian Head, MD 20640

Naval Sea Systems Command
ATTN: Mr. Charles M. Christensen
NAVSEA62R2
Crystal Plaza, Bldg. 6, Rm 806
Washington, DC 20362

Mr. R. Beauregard
Naval Sea Systems Command
SEA 64E
Washington, DC 20362

Dr. Anthony J. Matuszko
Air Force Office of Scientific Research
Directorate of Chemical & Atmospheric Sciences
Bolling Air Force Base
Washington, DC 20332

Dr. Michael Chaykovsky
Naval Surface Weapons Center
Code R11
White Oak
Silver Spring, MD 20910

J.J. Rocchio
USA Ballistic Research Lab.
Aberdeen Proving Ground, MD 21005-5066

G.A. Zimmerman
Aerojet Tactical Systems
P.O. Box 13400
Sacramento, CA 95813

B. Swanson
INC-4 MS C-346
Los Alamos National Laboratory
Los Alamos, NM 87545

Dr. L.H. Caveny
Air Force Office of Scientific Research
Directorate of Aerospace Sciences
Bolling Air Force Base
Washington, DC 20332

W.G. Roger
Code 5253
Naval Ordance Station
Indian Head, MD 20640

Dr. Donald L. Bell
Air Force Office of Scientific Research
Directorate of Chemical & Atmospheric Sciences
Bolling Air Force Base
Washington, DC 20332

Dr. H.G. Adolph
Naval Surface Weapons Center
Code R11
White Oak
Silver Spring, MD 20910

U.S. Army Research Office
Chemical & Biological Sciences Division
P.O. Box 12211
Research Triangle Park, NC 27709

G. Butcher
Hercules, Inc.
MS X2H
P.O. Box 98
Magna, Utah 84044

W. Waesche
Atlantic Research Corp.
7511 Wellington Road
Gainesville, VA 22065

DISTRIBUTION LIST

Dr. James T. Bryant
Naval Weapons Center
Code 3205B
China Lake, CA 93555

Dr. L. Rothstein
Assistant Director
Naval Explosives Dev. Engineering Dept.
Naval Weapons Station
Yorktown, VA 23691

Dr. M.J. Kamlet
Naval Surface Weapons Center
Code R11
White Oak, Silver Spring, MD 20910

Dr. Henry Webster, III
Manager, Chemical Sciences Branch
ATTN: Code 5063
Crane, IN 47522

Dr. R.S. Valentini
United Technologies Chemical Systems
P.O. Box 50015
San Jose, CA 95150-0015

Administrative Contracting
Officer (see contract for
address)
(1 copy)

Defense Technical Information Center
Bldg. 5, Cameron Station
Alexandria, VA 22314
(12 copies)

Arpad Junasz
Code DRDAR-IBD
Ballistic Research Lab
Aberdeen, MD 21005

Mr. C. Gotzmer
Naval Surface Weapons Center
Code R-11
White Oak
Silver Spring, MD 20910

Dr. John S. Wilkes, Jr.
FJSRL/NC
USAF Academy, CO 80840

Dr. H. Rosenwasser
Naval Air Systems Command
AIR-320R
Washington, DC 20361

Dr. A. Nielsen
Naval Weapons Center
Code 385
China Lake, CA 93555

Dr. Joyce J. Kaufman
The Johns Hopkins University
Department of Chemistry
Baltimore, MD 21218

Dr. J.R. West
Morton Thiokol, Inc.
P.O. Box 30058
Shreveport, LA 71130

Director
Naval Research Laboratory
Attn: Code 2627
Washington, DC 20375
(6 copies)

Dr. Robert J. Schmitt
SRI International
333 Ravenswood Avenue
Menlo Park, CA 94025

Dr. Michael D. Coburn
Los Alamos National Lab
M-1, Explosives Technology
Mail Stop, C920
Los Alamos, NM 87545

DISTRIBUTION LIST

Dr. G. Neece
Office of Naval Research
Code 413
Arlington, VA 22217

Mr. C.M. Havlik
0/83-10, B/157-3W
Lockheed Missiles & Space Co., Inc.
P.O. Box 504
Sunnvale, CA 94086

Dr. Philip Howe
Ballistic Research Labatory
Code DRXBR-TBD
Aberdeen Proving Ground, MD 21005

Prof. C. Sue Kim
Department of Chemistry
California State University, Sacramento
Sacramento, California 95819

Mr. J. Moniz
Naval Ordnance Station
Code 5253L
Indian Head, MD 20640

Dr. R. Reed Jr.
Naval Weapons Center
Code 38904
China Lake, CA 93555

L.H. Sperling
Materials Research Center #32
Lehigh University
Bethlehem, PA 18015

Dr. Kurt Baum
Fluorochem, Inc.
680 South Ayon Ave.
Azusa, CA 91702

Dr. Andrew C. Victor
Naval Weapons Center
Code 3208
China Lake, CA 93555

Dr. J.C. Hinshaw
Morton Thiokol Inc.
P.O. Box 524
Mail Stop 240
Brigham City, Utah 84302

Dr. V.J. Keenan
Anal-Syn Lab. Inc.
P.O. Box 547
Paoli, PA 19301

G.E Manser
Morton Thiokol
Wasatch Division
P.O. Box 524
Brigham City, Utah 84302

P. Politzer
Chemistry Department
University of New Orleans
New Orleans, Louisiana 70148

Mr. David Siegel
Office of Naval Research
Code 253
Arlington, VA 22217

Dr. Rodney L. Willer
Morton Thiokol, Inc.
P.O. Box 241
Elkton, MD 21921

Dr. R. Atkins
Naval Weapons Center
Code 3852
China Lake, CA 93555

DISTRIBUTION LIST

Prof. J.H. Boyer
University of Illinois
Department of Chemistry
Box 4348
Chicago, Illinois 60680

Prof. J.C. Chien
University of Massachusetts
Department of Chemistry
Amherst, MA 03003

Dr. B. David Halpern
Polysciences, Inc.
Paul Valley Industrial Park
Warrington, PA 18976

Dr. M. B. Frankel
Rockwell International
Rocketdyne Division
6633 Canoga Avenue
Canoga Park, CA 91304

Dr. R. A. Earl
Hercules, Inc.
Magna, Utah 84109

Dr. C. Bedford
SRI International
333 Ravenswood Avenue
Menlo Park, CA 94025

Dr. Robert R. Ryan
INC-4, Ms C346
Los Alamos National Laboratory
Los Alamos, New Mexico 87545

Dr. Robert D. Champman
AFRPL/LKLR
Edwards AFB, CA 93525

Dr. L. Erwin
MIT
Room 35-008
Cambridge, MA 02139

Dr. M. Farber
Space Sciences, Inc.
135 W. Maple Avenue
Monrovia, CA 91016

Dr. W.H. Graham
Morton Thiokol, Inc.
Huntsville Division
Huntsville, AL 35807-7501

Dr. C. Coon
Lawrence Livermore Lab.
University of California
P.O. Box 808
Livermore, CA 94550

Dr. R. Gilardi
Naval Research Laboratory
Code 6030
Washington, DC 20375

Dr. Alan Marchand
Dept. of Chemistry
North Texas State University
NTSU Station, Box 5068
Denton, Texas 76203

T.B. Brill
Department of Chemistry
University of Delaware
Newark, Delaware 19716

Dr. A.A. Defusco
Code 3858
Naval Weapons Center
China Lake, CA 93555

Dr. Richard A. Hollins
Naval Weapons Center
Code 3853
China Lake, CA 93555

Dr. R. Armstrong
MIT
Room 66-505
Cambridge, MA 02139

Professor Philip E. Eaton
Department of Chemistry
University of Chicago
5735 South Ellis Avenue
Chicago, IL 60637