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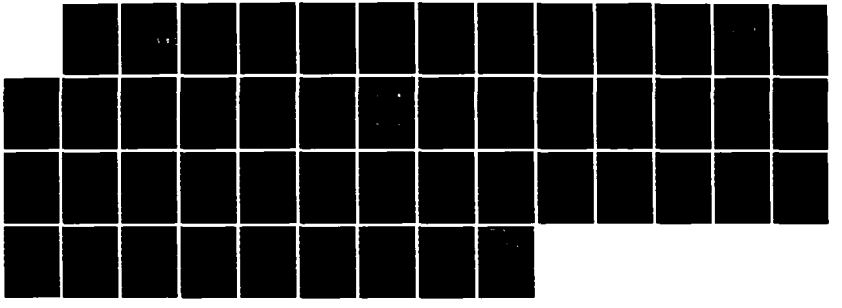

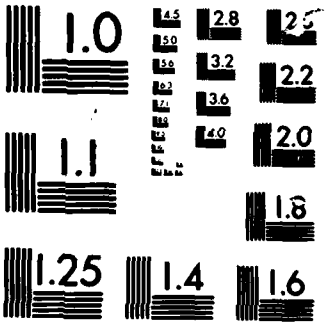

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SYNTHESIS OF ENERGETIC MATERIALS ANNUAL PROGRESS REPORT FOR THE OFFICE OF NAVAL RESEARCH

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RESEARCH AND TECHNOLOGY DEPARTMENT

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Investigation of the synthesis of polyformals from several nitro- and fluorodiols was continued. A new fluoropolyformal derived from 2,4,4,5,5,6,6-heptafluoro-2-trifluoromethyl-3-oxaheptane-1,7-diol was obtained. Formation of the homopolyformal of 4,4-dinitroheptane-1,7-diol was studied to assess effects of changing reaction parameters on molecular weight. Copolyformal formation was studied for several monomer (diol) pairs, especially DINOL/4,4-dinitroheptane-1,7-diol, and was demonstrated by GPC and ^1H NMR analysis of the polymer products. Effects of varying reaction parameters and monomer ratios were investigated qualitatively.

The synthesis of the trifluoromethyl stabilized ring system of bicyclo-HMX (2,4,5,8-tetraza-bicyclooctane) was investigated and the di-, tri-, and tetranitro derivatives were prepared and characterized. The chemistry of the 2,6-diazabicyclooctane ring system was studied toward the synthesis of tetra- and hexa-substituted nitro derivatives. Several dinitro derivatives were prepared. A new reduction of nitroamides to nitramino alcohols was discovered.

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SYNTHESIS OF ENERGETIC MATERIALS

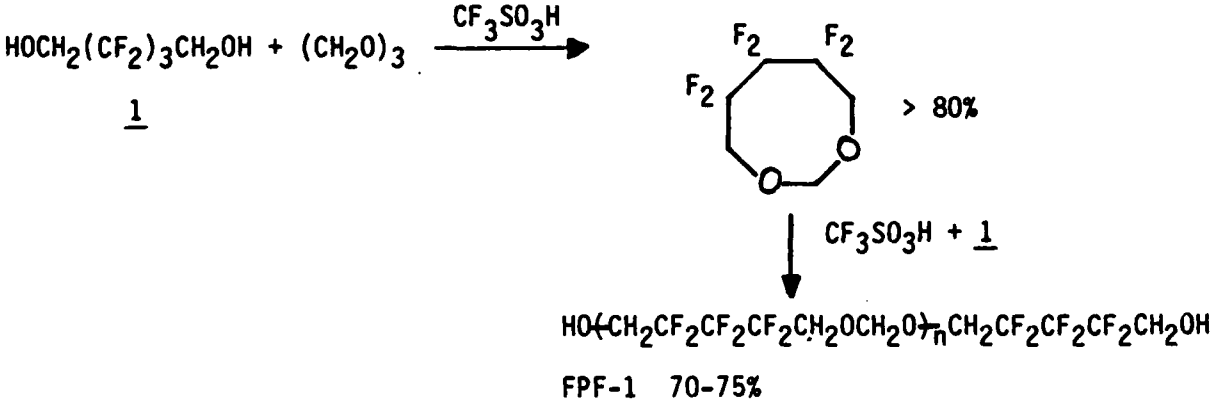
INTRODUCTION

The work described in this report was carried out during 1985 under the sponsorship of the Office of Naval Research, Code 1132P (Dr. R. S. Miller). The effort consisted of two separate tasks which will be discussed in turn: (1) synthesis of energetic monomers and polymers, and (2) synthesis of polycyclic and adamantoid nitramines. Both tasks were continuations of previous work, and pre-1985 results are reported in ref. 1. The principal objectives of the work are the synthesis of energetic (nitro and fluoro) polymers with improved energy and physical properties, specifically polyformals derived from nitro and fluoro substituted diols, and the synthesis of nitramines with high crystal density and energy-density greater than HMX.

ENERGETIC POLYMER AND MONOMER SYNTHESIS

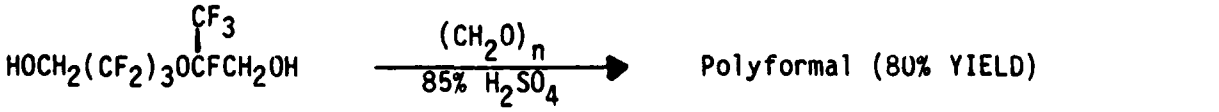
In continuation of the previous work[1] under this task, the formation of hydroxy-terminated polyformals from selected nitro- and fluorodiols was investigated further. Particular emphasis was placed on the synthesis and characterization of random copolymers containing 2 different nitrodiols or a nitro- and fluorodiol.

Last year, the preparation of 2,2,3,3,4,4-hexafluoropentane-1,5-diol polyformal (FPF-1) by the 2 step sequence shown below was reported.[1)]



Additional effort was expended this year to optimize the synthesis steps. Approximately 0.5 lb runs were made of each step using the optimized procedures. An effort was made to account for material not converted to the intended product in each step, with excellent results (see experimental section). Fig. 1 shows the GPC of a 0.5 lb batch of polymer with $\overline{M}_n$ = 2447, $\overline{M}_w$ = 4999, and OH equivalent weight (NMR method[10)]) = 1220.

An additional fluoropolyformal was prepared from the diol 2 which was obtained from Dr. A. Manzara of 3M. No attempts were made to optimize the synthesis or vary the molecular weight. Like the fluoroformals prepared



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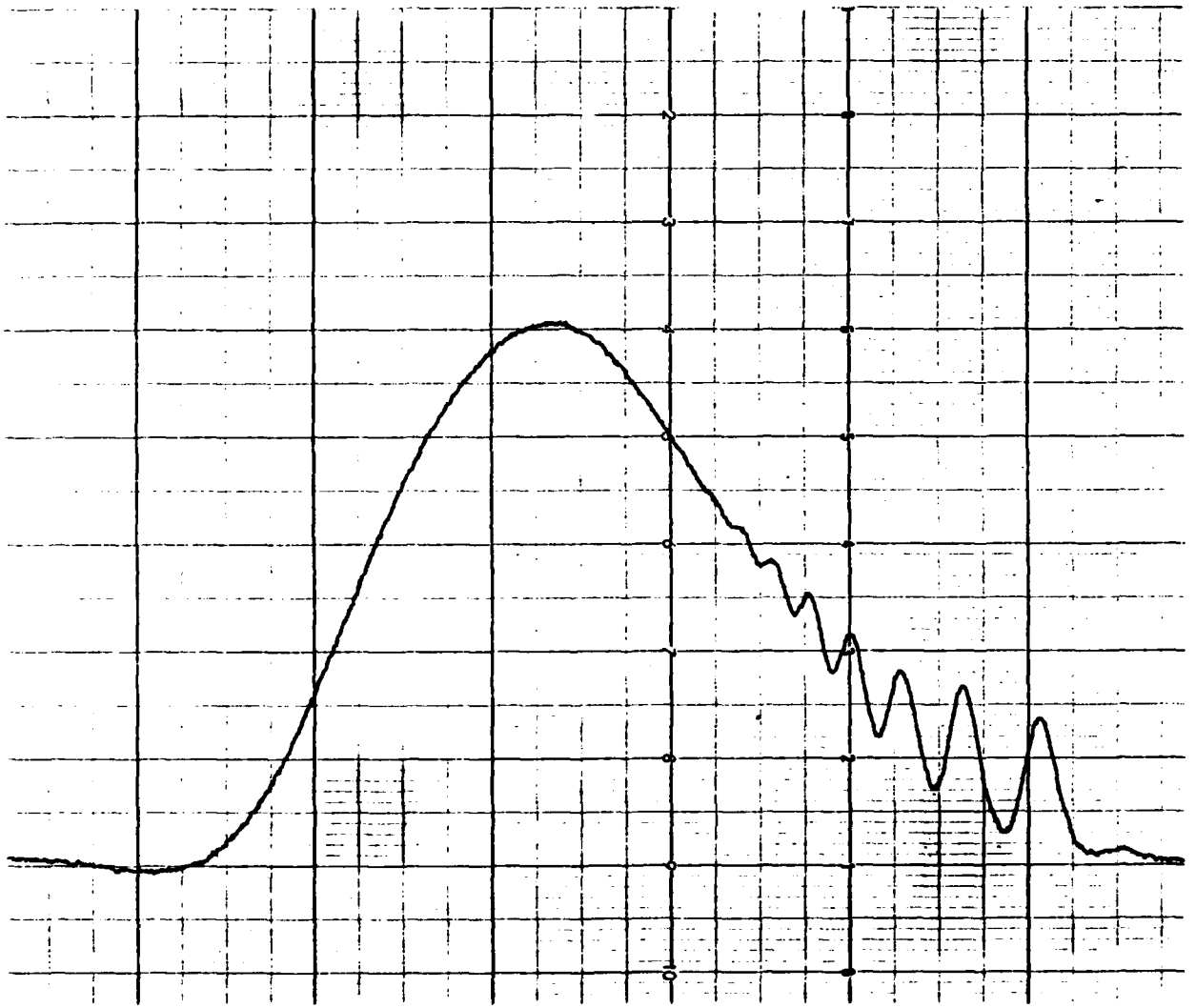


Figure 1. GP Chromatogram of Hexafluoropentanediol (1) Polyformal (0.5 lb batch)

earlier[1], this polymer is a viscous liquid. It is essentially insoluble in energetic plasticizers such as FEFO but is miscible with fluorocarbon plasticizers. A 25 g sample was sent to M. Chan at NWC for evaluation in AWAM explosive compositions. Fig. 2 shows the GPC of this polymer ($\overline{M}_n$ = 3003; $\overline{M}_w$ = 5236; OH equiv. wt. = 1552). A second, 200 g, sample was prepared and sent to R. Gill (NSWC) for evaluation in AWAM explosive compositions. This sample had the following properties: $\overline{M}_n$ = 2639; $\overline{M}_w$ = 4830; HO equiv. wt. = 1350.

The polymerization of 4,4-dinitroheptanediol (3) with formaldehyde was studied to determine the suitability of this monomer for the synthesis of random and block copolymers. The diol is prepared by BH_3 reduction of the known 4,4-dinitroheptanedioic acid. The polymerization was carried out in sulfolane using trioxone as the formaldehyde source. It was found that the

$$HOOCCH_2CH_2CH_2C(NO_2)_2CH_2CH_2CH_2COOH \xrightarrow[THF]{BH_3} HOCH_2CH_2CH_2C(NO_2)_2CH_2CH_2CH_2OH$$

3 (>90%)

molecular weight of the polymer was dependent on the nature of the Lewis acid catalyst (Table 1). Acceptable molecular weights were obtained with tin (IV) chloride. Essentially no low M. W. cyclic formals are formed under optional conditions (see Fig. 3 for a typical GPC). This polyformal is a solid. Investigation of the synthesis (molecular weight control) and characterzation of the polymer are continuing.

Table 1. Polymerization of 4,4-Dinitroheptane-1,7-diol (3) with Trioxane in Sulfolane

#	3 (mmol)	Trioxane (mmol)	Solvent (mL)	Acid (mL)		Yield (%)	$\overline{M}_n$	$\overline{M}_w$
1	4.5	5.2	1	$BF_3 \cdot O(Et)_2$	0.5	83	1600	3000
2	4.5	4.5	2	$BF_3 \cdot O(Et)_2$	0.5	95	1200	2100
3	4.5	4.5	1	BBr_3(1M)	3.5	90	OLIGOMERS	
4	4.5	4.5	1	$SnCl_4$	0.5	40	1600	3400*
5	4.5	4.5	1	$SnCl_4$	0.25	75	3200	6000

* including cyclic formals

A study of copolymer formation from mixtures of diols was begun with the objective to tailor certain properties of both nitro- and fluoropolyformals, such as T_G and plasticizer compatibility, and with the eventual objective of preparing copolymers which are suitable components of block copolymers with TPE properties. Diols which have the same reactivity in the formal reaction might be expected to form random copolymers when a mixture of them is treated with CH_2O/acid. However, because all steps in the formal reaction are reversible (see the scheme below), thermodynamically favored homopolymers

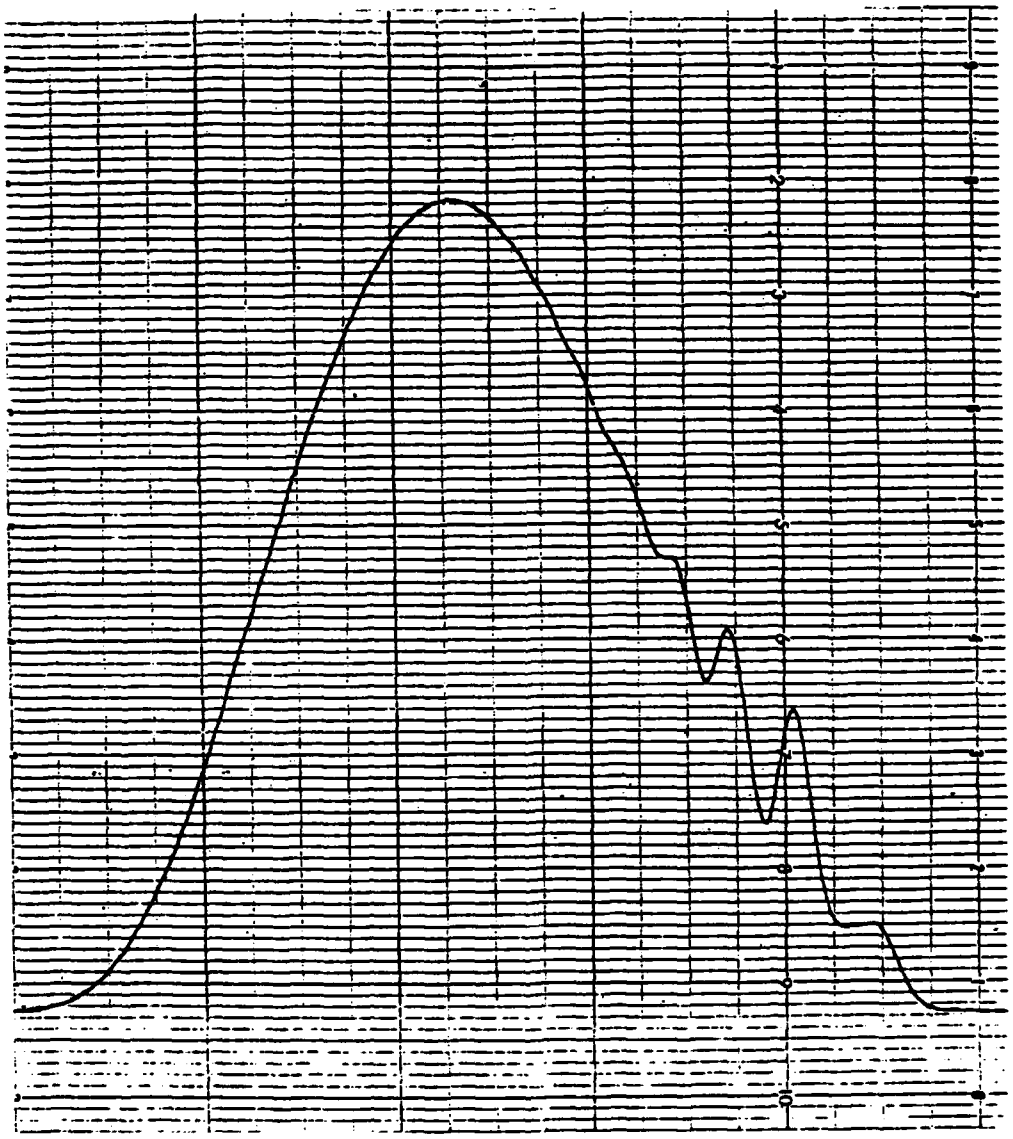


Figure 2. GP Chromatogram of Decafluorodiol (2) Polyformal

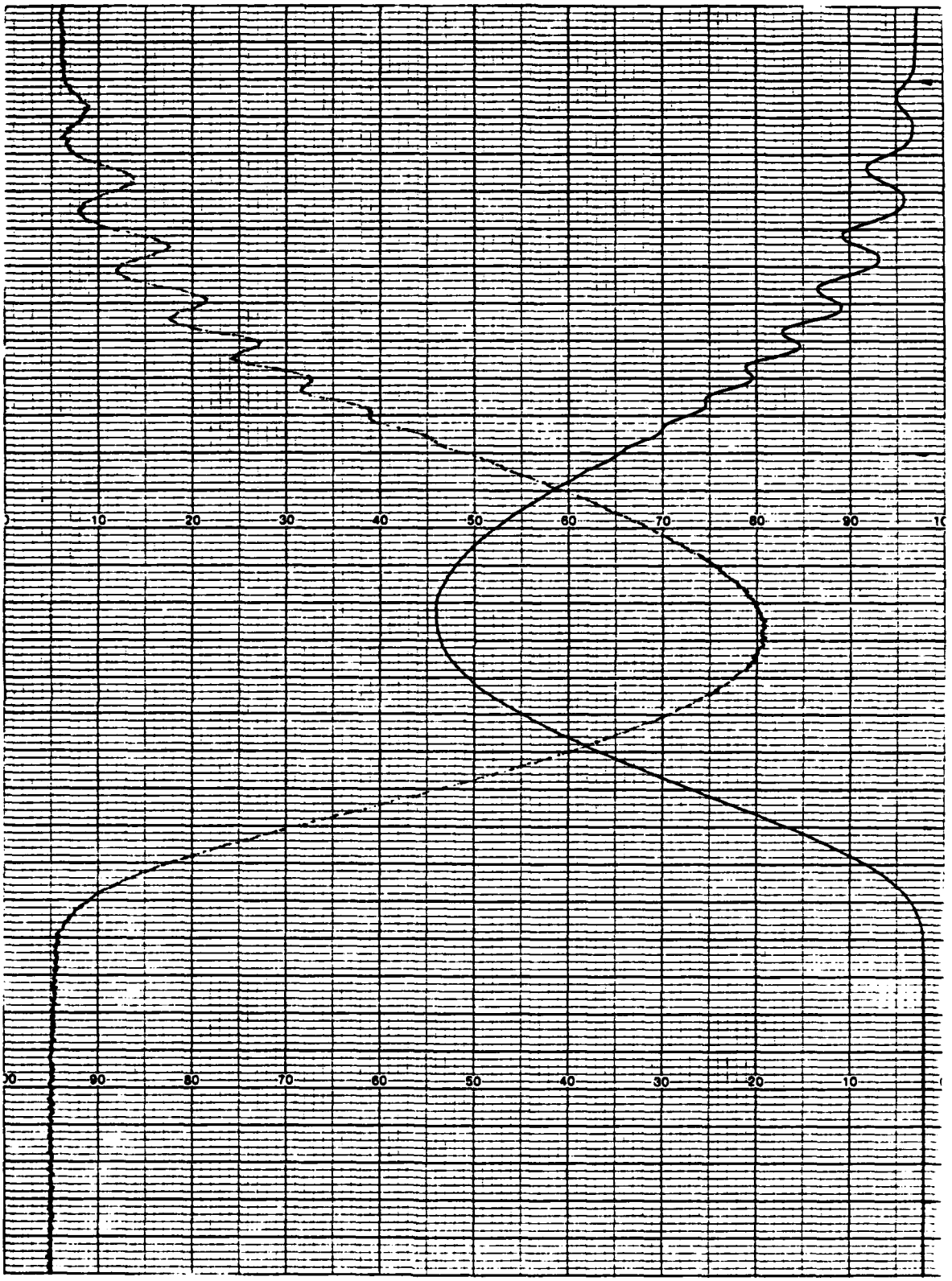
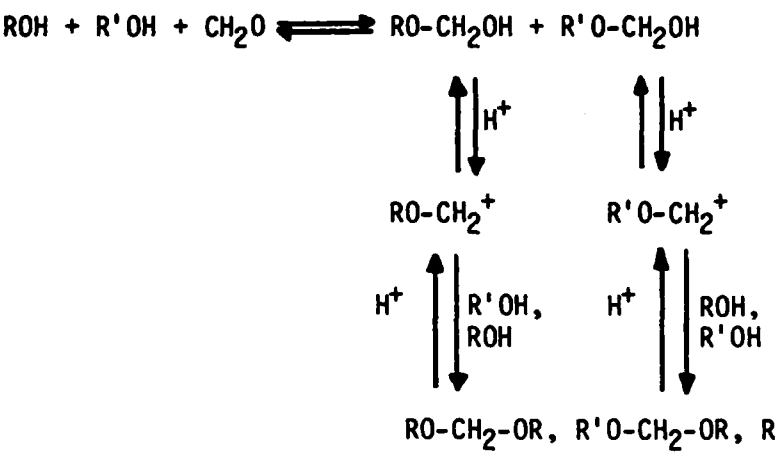


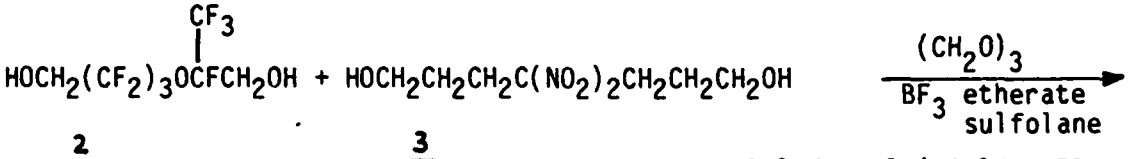
Figure 3. GP Chromatogram of 4,4-Dinitroheptanediol (3) Polyformal (Table 1, #4)

Some Equilibria Involved in Formal Reaction



could be formed too. With diols of different reactivity, it should be possible to select reaction conditions which favor copolymer formation, e.g., acidity of the reaction medium intermediate between optimum for each alcohol.

So far, we have investigated the copolymerization of several diol pairs. The incorporation of 4,4-dinitroheptanediol (3) into the polyformal of 2 was of interest as a means to tailor its miscibility with nitroplasticers. In this case, the reactivity of the diols is quite different because of the difference in acidity. BF_3 etherate is a condensing agent of intermediate acidity, not strong enough to homopolymerize 2. If used in sufficient quantity, it should form a complex with most of the 3 and thus prevent its homopolymerization. The reaction was carried out with diol (2/3) ratios from 80/20 to 95/5. The polymers obtained showed substantially increased solubility in FEFO, even at the 95:5 monomer ratio, an indication that



2 3

Polyformal (Yield: 70 - 80%)

copolymers had indeed been formed. The GPC of the product from an 80% 2/20% 3 diol mixture is shown in Fig. 4. The upper trace is from the RI detector, the lower one is from the UV detector. The UV trace indicates that a polymer containing 3 is present since the fluoropolymer is UV inactive. However, it would be difficult to distinguish between copolymer and mixture of homopolymers on the basis of the GPC alone. Fortunately the ^1H NMR spectrum (Fig. 5) at 200 MHz shows the resolved peaks for $-OCH_2O-$ flanked by 2, 2 + 3, and 3, and indicates the presence of essentially only random copolymers. Analysis of the GP chromatogram to obtain the molecular weight, and OH analysis have not yet been carried out. Qualitatively, Fig. 4 indicates that the copolymer obtained has a fairly low molecular weight.

2 was also copolymerized with 3,5,5,7-tetranitro-3,7-diaza-nonanediol[1], 4, in a ratio of 20:80. The GPC of the polymer obtained is shown in Fig. 6.

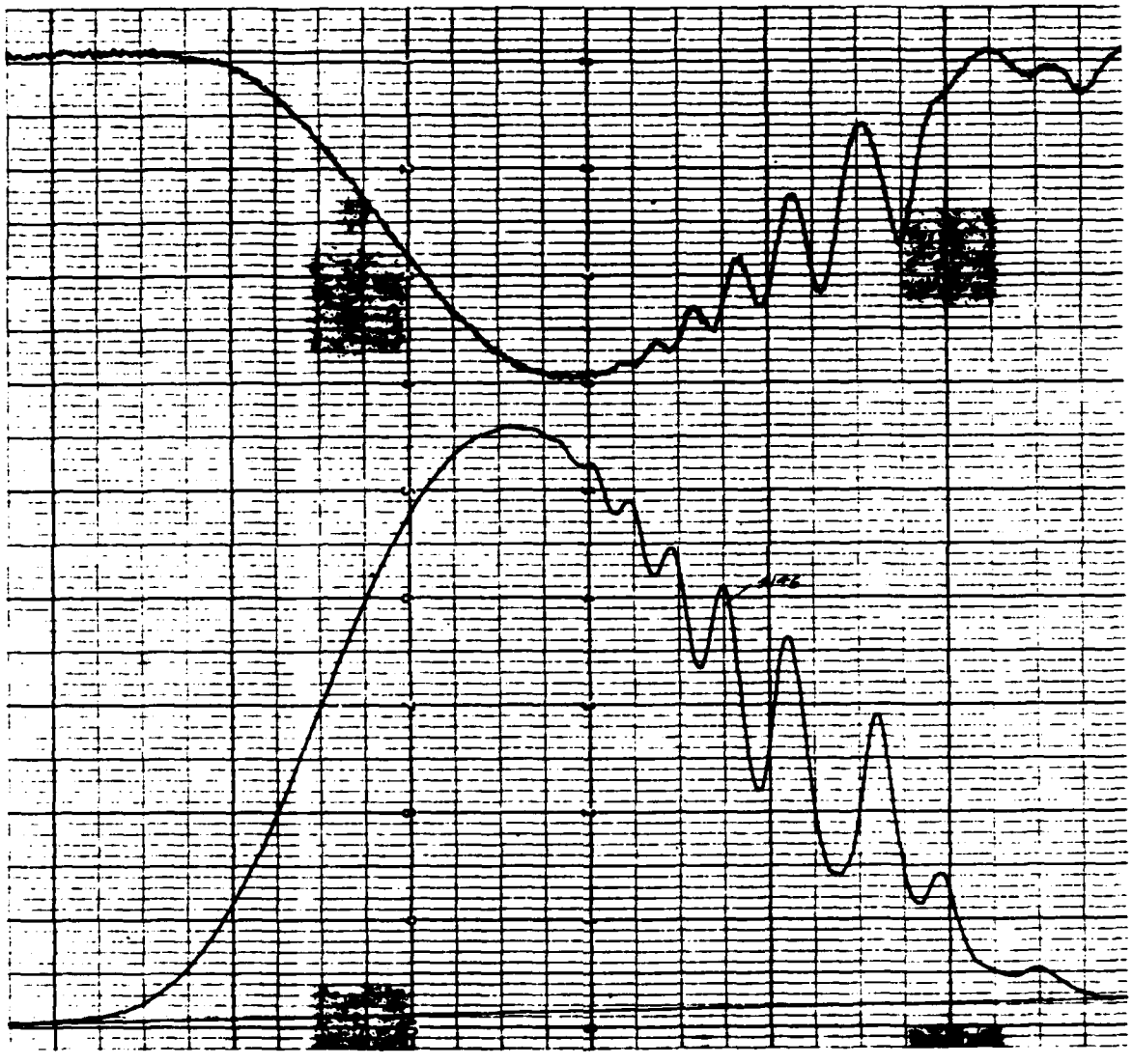


Figure 4. GP Chromatogram of Decafluorodiol (2)/Dinitroheptanediol (3) Copolymer (80/20)

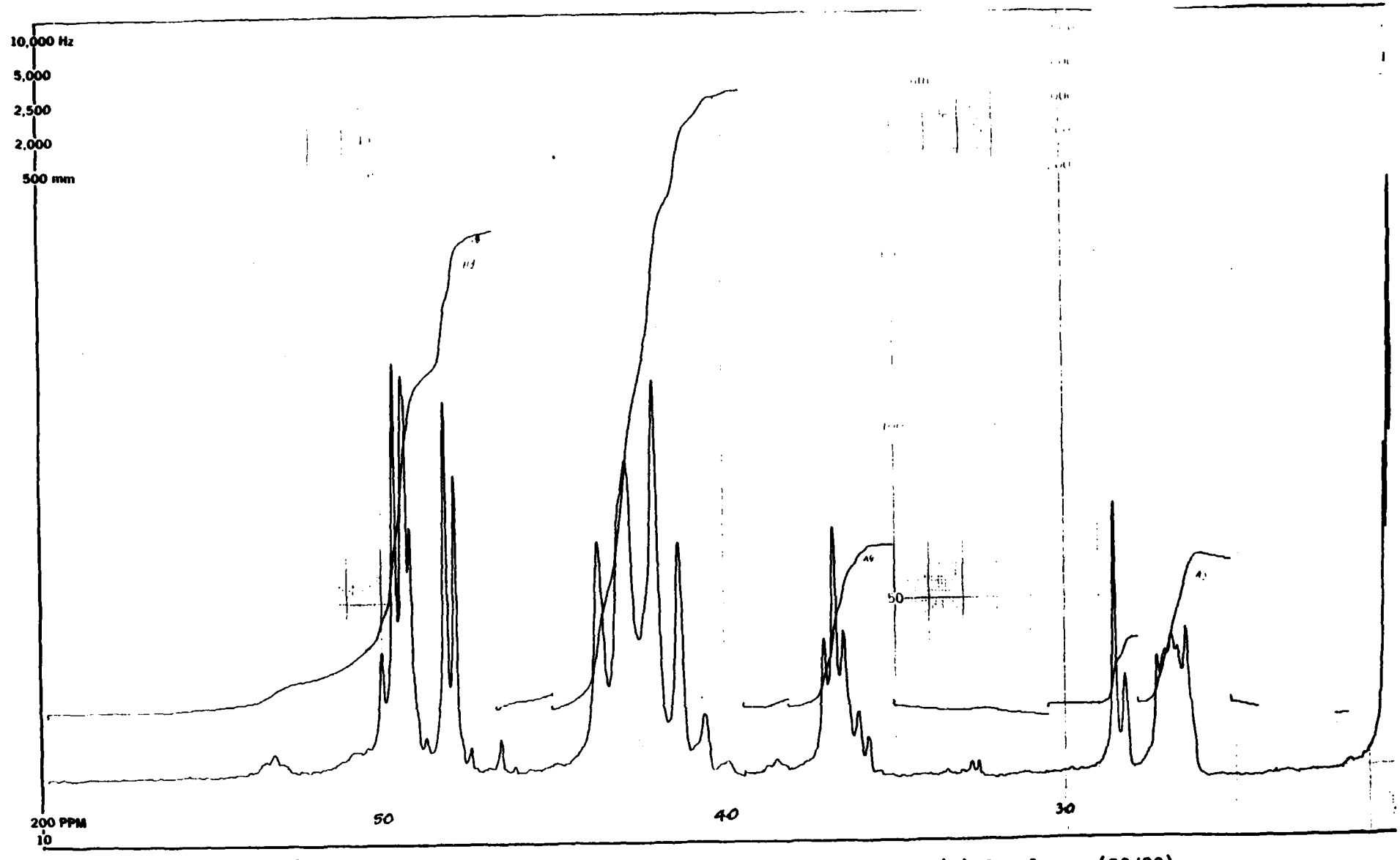


Figure 5. ^{1}H NMR Spectrum of Decafluorodiol (2)/Dinitroheptanediol (3) Copolymer (80/20)

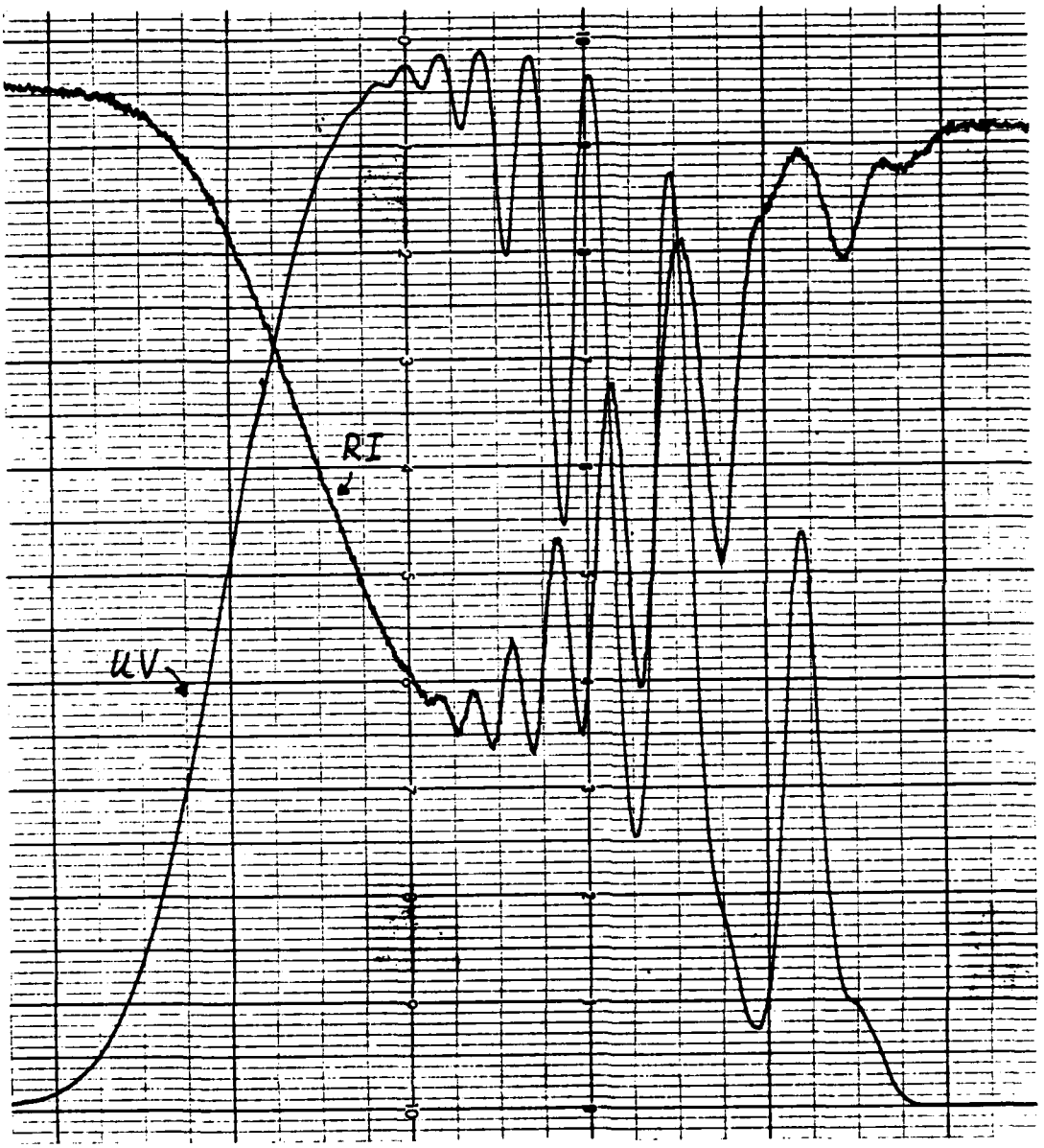


Fig. 6. GP Chromatogram of Decafluorodiol (2)/Tetranitro-3,7-diazanonanediol (4) Copolymer (20/80)

The close correspondence between RI and UV detector traces indicates that a copolymer was formed. Again, a relatively low molecular weight is indicated by the GPC (mass peak at 6 repeating units). This polymer has not yet been characterized further.

$$HOCH_2(CF_2)_3OCF(CF_3)CH_2OH + HOCH_2CH_2N(NO_2)CH_2C(NO_2)_2CH_2N(NO_2)CH_2CH_2OH$$

2 4

$$\xrightarrow[\text{sulfolane/}BF_3\cdot O(Et)_2]{\text{trioxane}} \text{POLYFORMAL (Yield: >90\%)}$$

4 was copolymerized with 3 (ratios 9:1 and 8:2) to give products of very low molecular weight (GPC, Fig. 7) which have not been characterized further.

$$HOCH_2CH_2N(NO_2)CH_2C(NO_2)_2CH_2N(NO_2)CH_2CH_2OH + HOCH_2CH_2CH_2C(NO_2)_2CH_2CH_2CH_2OH$$

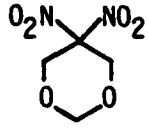
4 3

$$\xrightarrow[\text{sulfolane/}BF_3\cdot O(Et)_2]{\text{trioxane}} \text{POLYFORMAL (Yield: >90\%)}$$

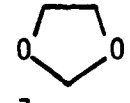
The copolymerization of DINOL, 5, with various diols was studied in some detail, because 5 is quite energetic and is easily synthesized[2]. The presence of a formal linkage in the molecule prevents it from being homopolymerized. Instead, intramolecular cyclization to form the very stable

$$HOCH_2C(NO_2)_2CH_2OCH_2OCH_2C(NO_2)_2CH_2OH \xrightarrow[H_2SO_4]{(CH_2O)_n}$$

5



dinitro-m-dioxane occurs. With BF_3 etherate instead of sulfuric acid, there is no reaction. This should permit the formation of copolymers with reactive diols using Lewis acids such as BF_3 or $SnCl_4$. Copolymer formation from 5 and ethylene glycol (6) was studied first. 1,3-Dioxolane, 7, was actually used instead of 6 because of its better miscibility with DINOL and formaldehyde

$HOCH_2CH_2OH$ 

6 7

(trioxane). DINOL and 7 reacted with additional formaldehyde and a variety of acid catalysts (BF_3 etherate, triflic acid, $SnCl_4$), in the absence of solvent. However, in all cases, incomplete reaction was obtained and only oligomers were formed. This is probably due to the relatively strong tendency of 6 to form a cyclic formal which favors polymer degradation to 7 over polymer formation. No effective method has been found as yet to shift

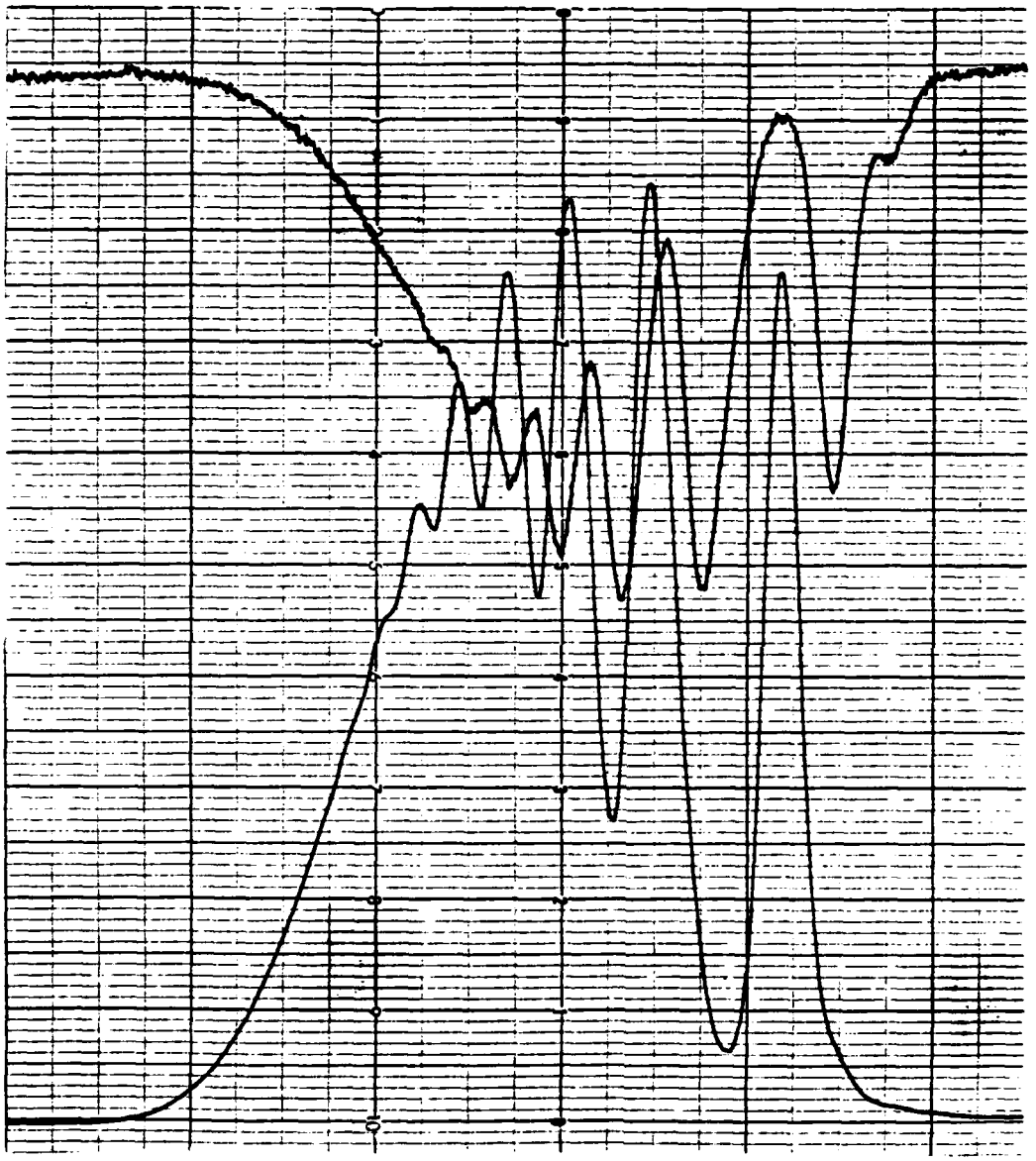
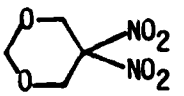


Figure 7. GP Chromatogram of Tetranitro-3,7-diazanonanediol (4)/Dinitroheptanediol Copolymer (80/20)

$$\underline{5} + \underline{7} + CH_2O \underset{\text{Acid Cat.}}{\overset{\text{Acid Cat.}}{\rightleftharpoons}} HOCH_2CH_2O\text{-}CH_2\text{-}[O\sim\sim DINOL\sim\sim O\text{-}CH_2\text{-}OCH_2CH_2O]_nH + H_2O$$

the equilibrium by removal of water from the system. Investigations are continuing but it appears that this monomer pair may not be useful for copolymer formation. Table 2 provides a list of attempted polymerizations and their results. A typical GPC of the product mixture is shown in Figure 8.

Table 2. Copolymerization of DINOL & 1,3-Dioxolane

#	DINOL (mmol)	Dioxolane (mmol)	Trioxane (mmol)	Acid, µL		Product
1	2.92	5.81	----	TA*	100	4-5 mer, DINOL, 
2	2.92	3.49	2.33	TA*	40	2 mer, much DINOL
3	2.92	3.49	2.33	$BF_3 \cdot O(Et)_2$	250	7-8 mer + lower, much DINOL
4	2.92	3.49	2.33	$BF_3 \cdot O(Et)_2$	50	5-6 mer + lower, much DINOL
5	2.92	3.49	2.33	$BF_3 \cdot O(Et)_2$	400	10-12 mer + lower, DINOL
6	2.92	3.49	2.33	$SnCl_4$	150	7-8 mer + lower, much DINOL
7	2.92	5.81	----	$SnCl_4$	250	5-6 mer + lower, much DINOL

*Triflic Acid

Copolymerization of DINOL with 4 (ratio 20/80) was studied briefly. The

$$\underline{5} + \underline{4} \xrightarrow[\text{sulfolane/}BF_3\cdot O(Et)_2]{\text{trioxane}} \text{POLYFORMAL (Yield: } \approx 90\%)$$

GPC (Fig. 9) indicates that a copolymer was formed (similarity of RI and UV traces). The molecular weight of the product, which was not further characterized, is quite low.

DINOL and 3 formed polymer quite readily when reacted with trioxane/BF_3 etherate in sulfolane. The GPC of a 2:8 product is shown in Fig. 10 . It shows that very little dinitro-m-dioxane and unreacted DINOL are present. The ^1H NMR spectrum (Fig. 11) at 200 MHz again shows a number of well resolved peaks in the $-OCH_2O-$ region. By comparison with the spectra of DINOL and the polyformal of 3, the peak for $-OCH_2O-$ in the center of 5, and the peaks for $-OCH_2O-$ flanked by one 3 and one 5, and by two 3 units, are identified as the principal absorptions in the $-OCH_2O-$ region. The ratio of the 3 peaks approximately corresponds to the 20:80 ratio of monomers used. There can therefore be little doubt that this polymer is a random copolymer, however, as in the case of 3 homopolymer, the molecular weight obtained is low. When $SnCl_4$ was used as the Lewis acid, higher molecular weights were observed, as in the case of 3 alone (see Table 3).

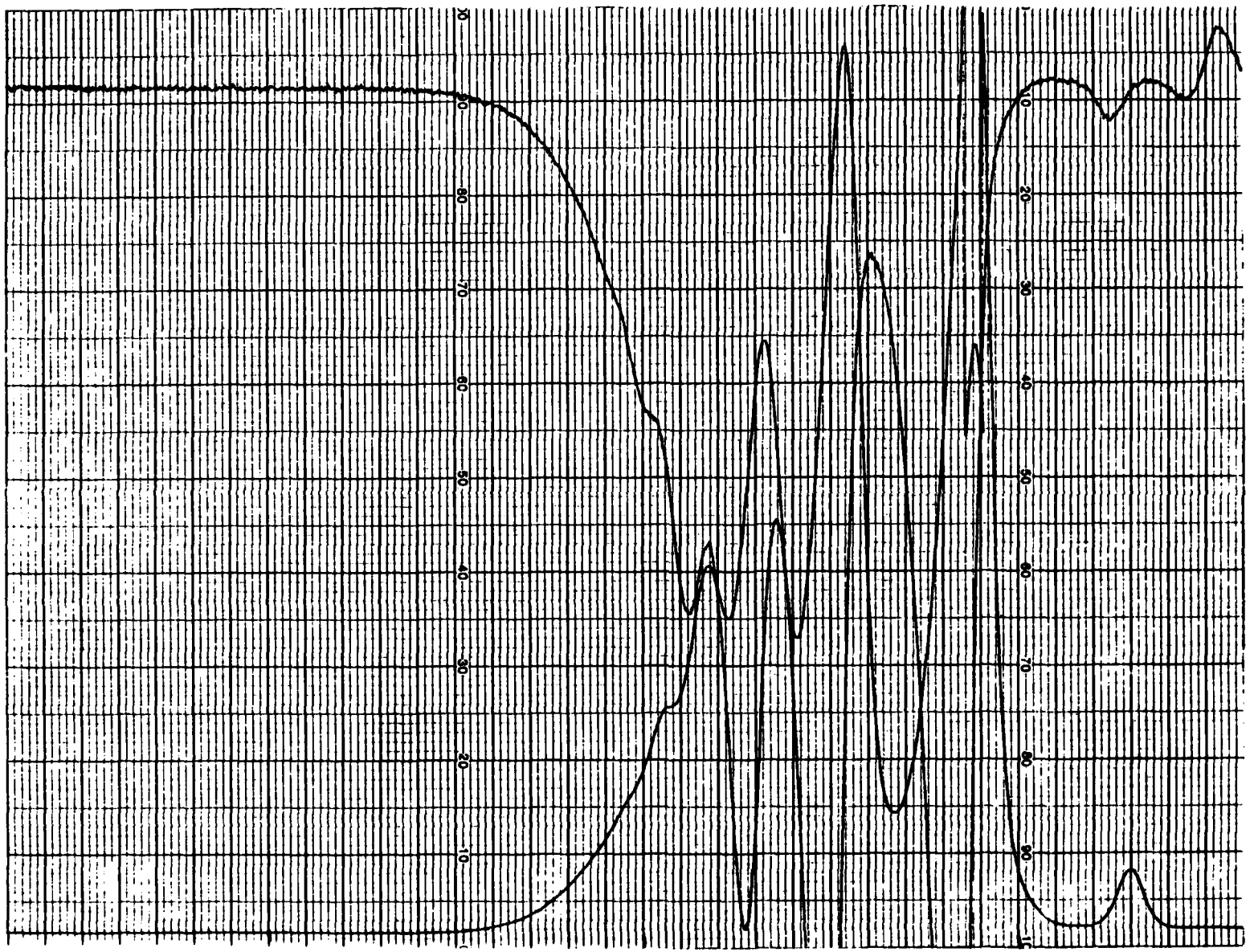


Fig. 8 GP Chromatogram of Attempted Copolymerization of Dioxolane/Dinol (Run #6, Table 2)

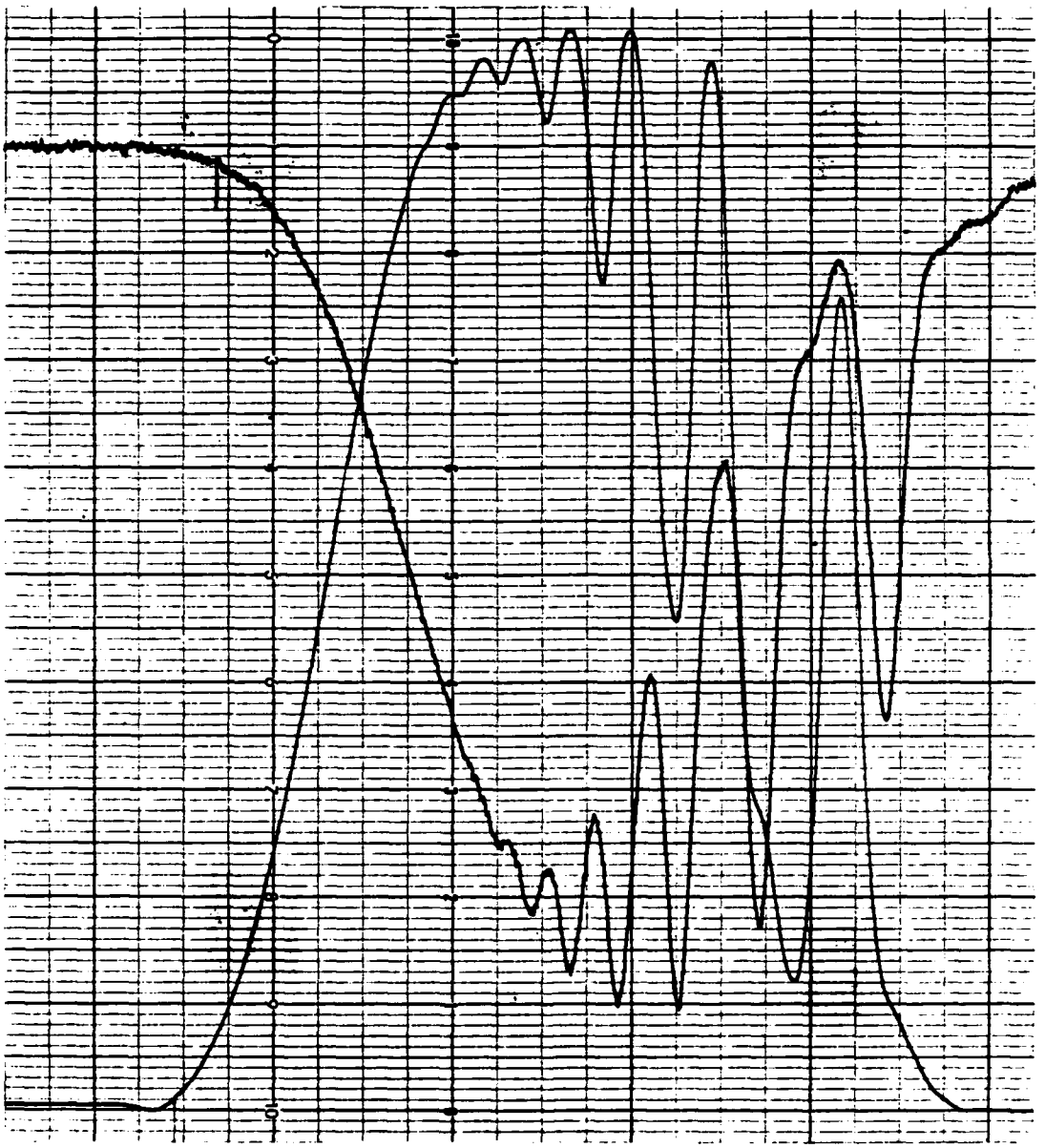


Figure 9. GP Chromatogram of DINOL (5)/Tetranitro-3,7-diazanonanediol (4) Copolymer (20/80)

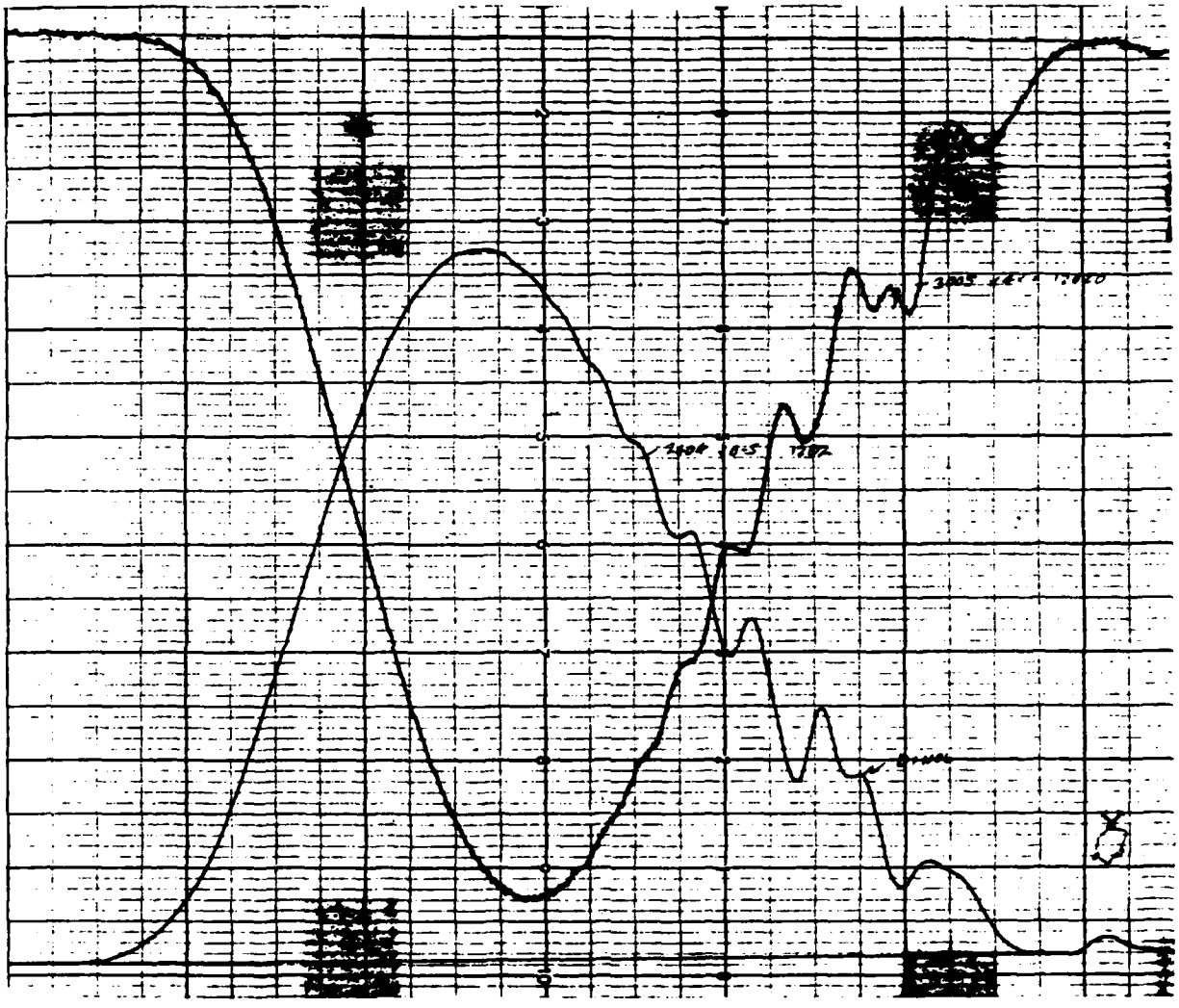


Figure 10. GP Chromatogram of Dinol (5)/Dinitroheptanediol (3) Copolymer (20/80)

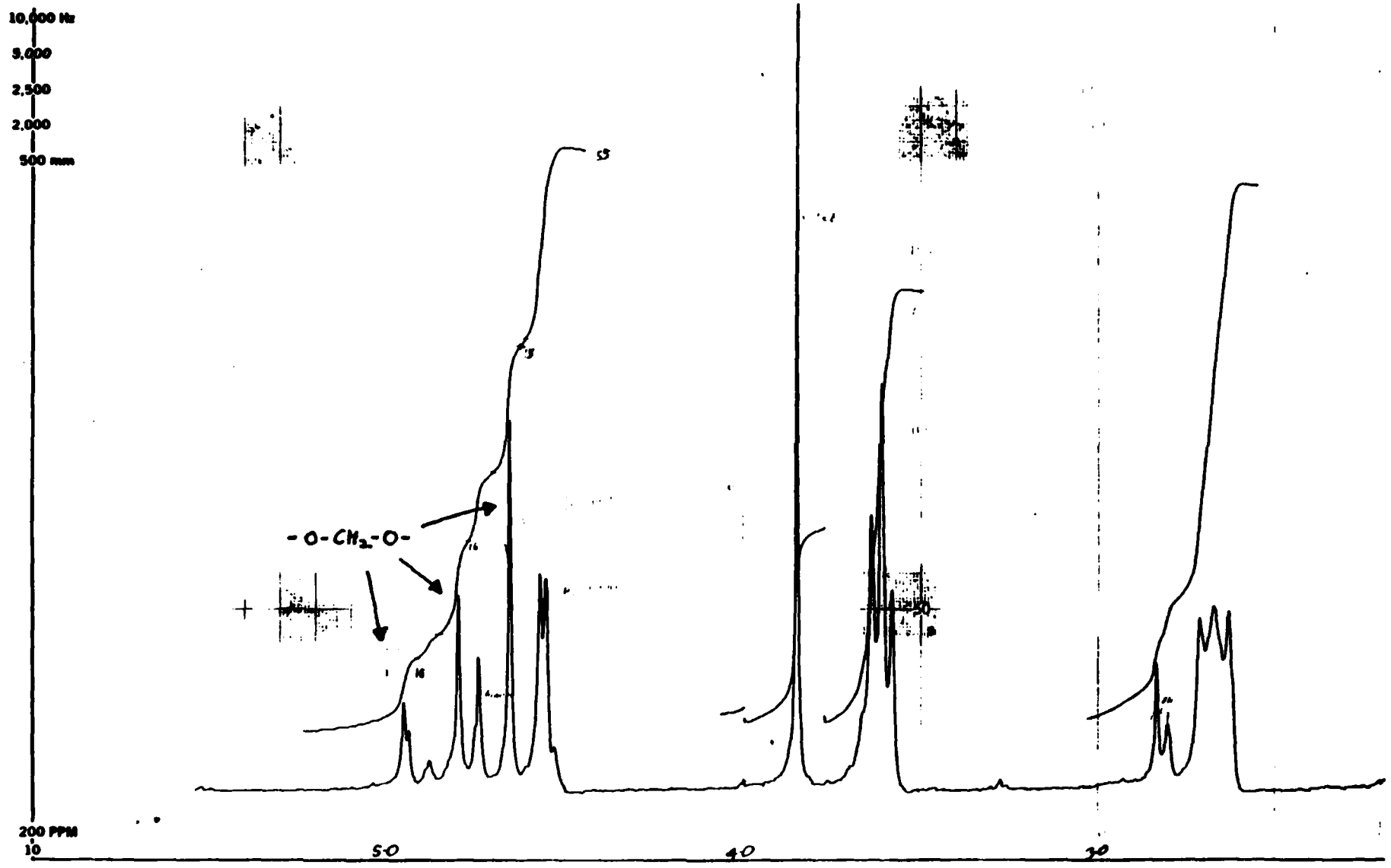


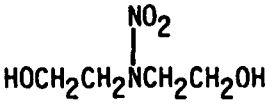
Figure 11. ^{1}H NMR Spectrum of Dinol (5)/Dinitroheptanediol (3) Copolymer (20/80)

Table 3. Copolymerization of DINOL and 3 in Sulfolane

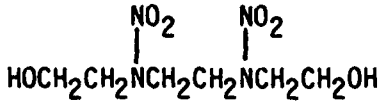
#	3 (mmol)	DINOL (mmol)	Solvent (mL)	Acid, mL		Yield (%)	$\bar{M}_n$	$\bar{M}_w$
1	3.60	0.904	1	$BF_3 \cdot O(Et)_2$	0.5	>95	1200	2500*
2	3.60	0.904	1	$SnCl_4$	0.25	75	4150	6750*
3	2.70	1.807	1	$SnCl_4$	0.25	80	2150	5250*

*based upon calibration curve of 3 homopolymer; true values will be somewhat different

GPC's and ^1H NMR spectra of polymers #2 and #3 (4:6 ratio) in Table 3 are shown in Figs. 12-15. Further characterization of these materials and reaction of DINOL with other comonomers, e.g., 8 and 9, is in progress.



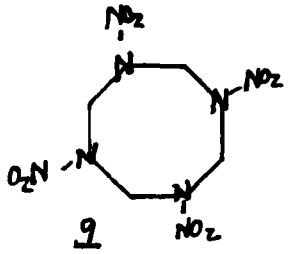
8



9

SYNTHESIS OF POTENTIALLY DENSE NITRAMINES

The calculated densities of bicyclic nitramines such as 10, 11, and 12 are significantly higher than that of HMX (9). This leads to the prediction that these molecules are potential high-energy-density compounds with estimated detonation pressures in the range of 420-430 kbar, about 10% greater than HMX. Accordingly, one of the goals of this program has been the



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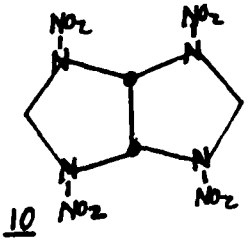

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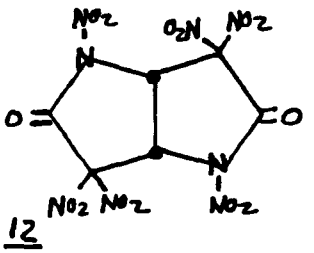


12

ρ_o (Calc'd) 1.79 1.91 1.88 2.00 g/cm^3

synthesis of bicyclo-HMX. In previous reports[1], we have described many unsuccessful attempts to prepare this compound by several synthetic approaches. Most of our efforts have involved the nitrolysis of tetraazabicyclooctane precursors in which the nitrogens were substituted with

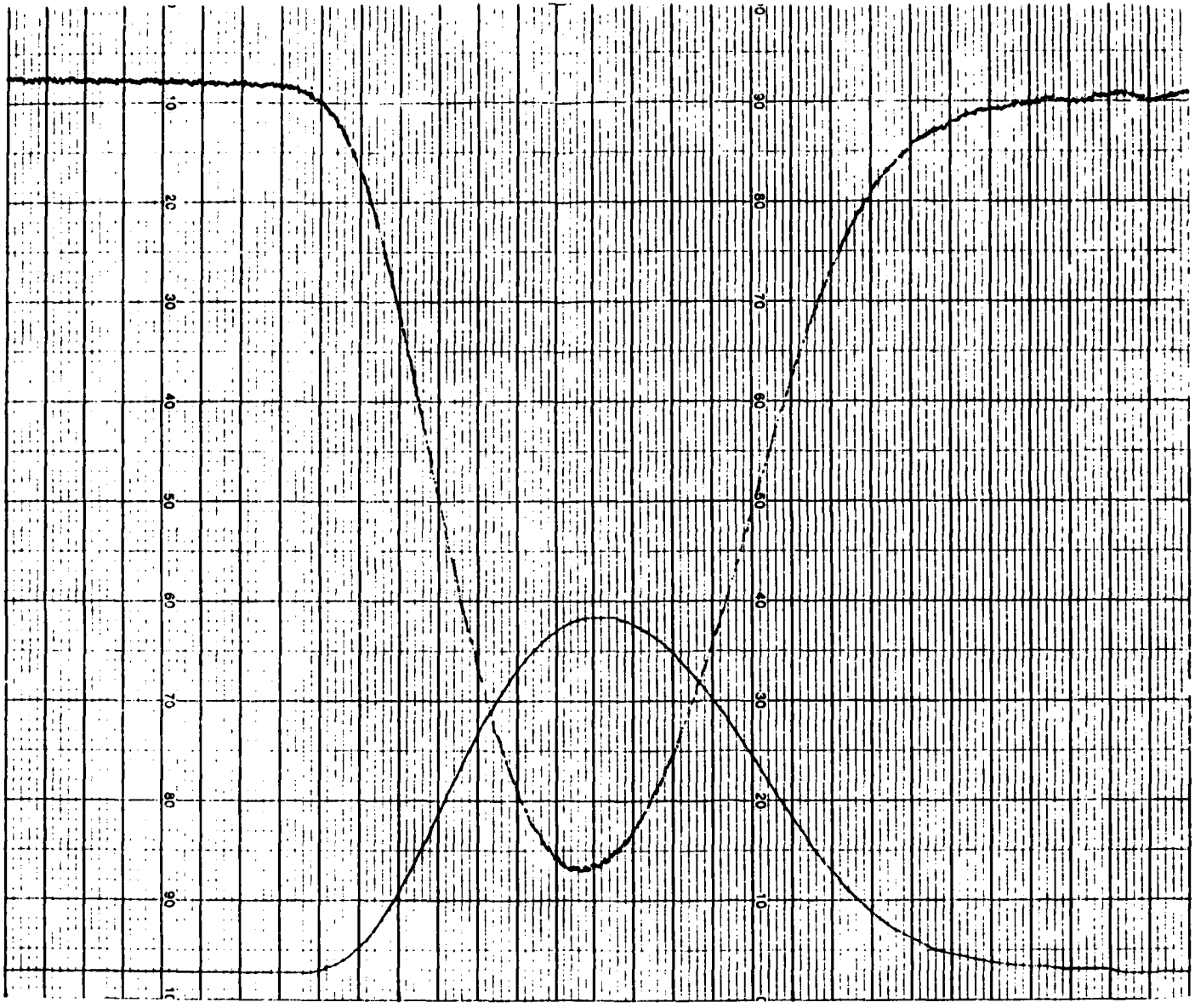


Figure 12. GP Chromatogram of DINOL (5)/Dinitroheptanediol (3) of Copolyformal (20/80, Table 3, #2)

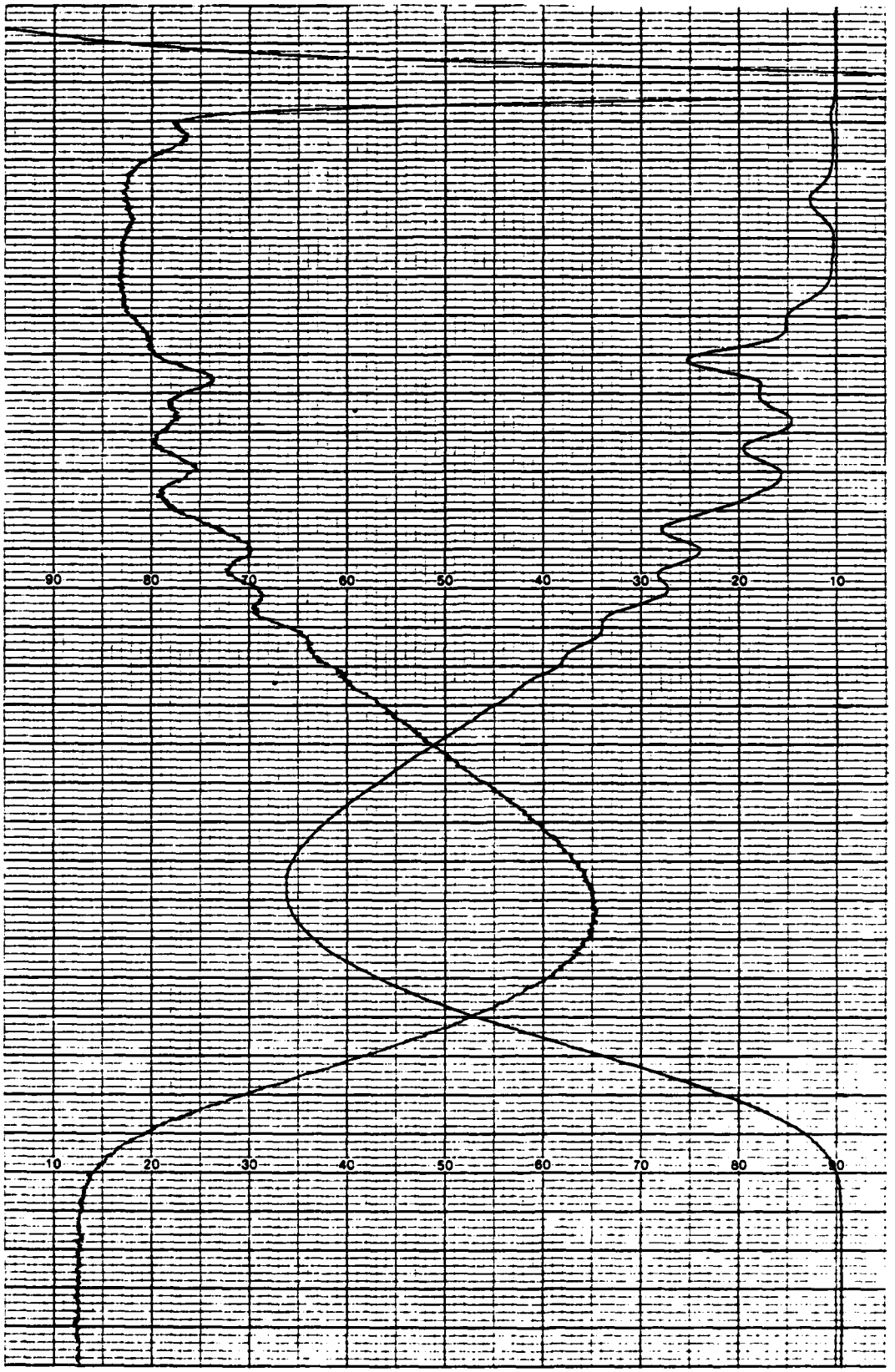


Figure 13. GP Chromatogram of DINOL (5)/Dinitroheptanediol (3) Copolyformal (40/60, Table 3, #3)

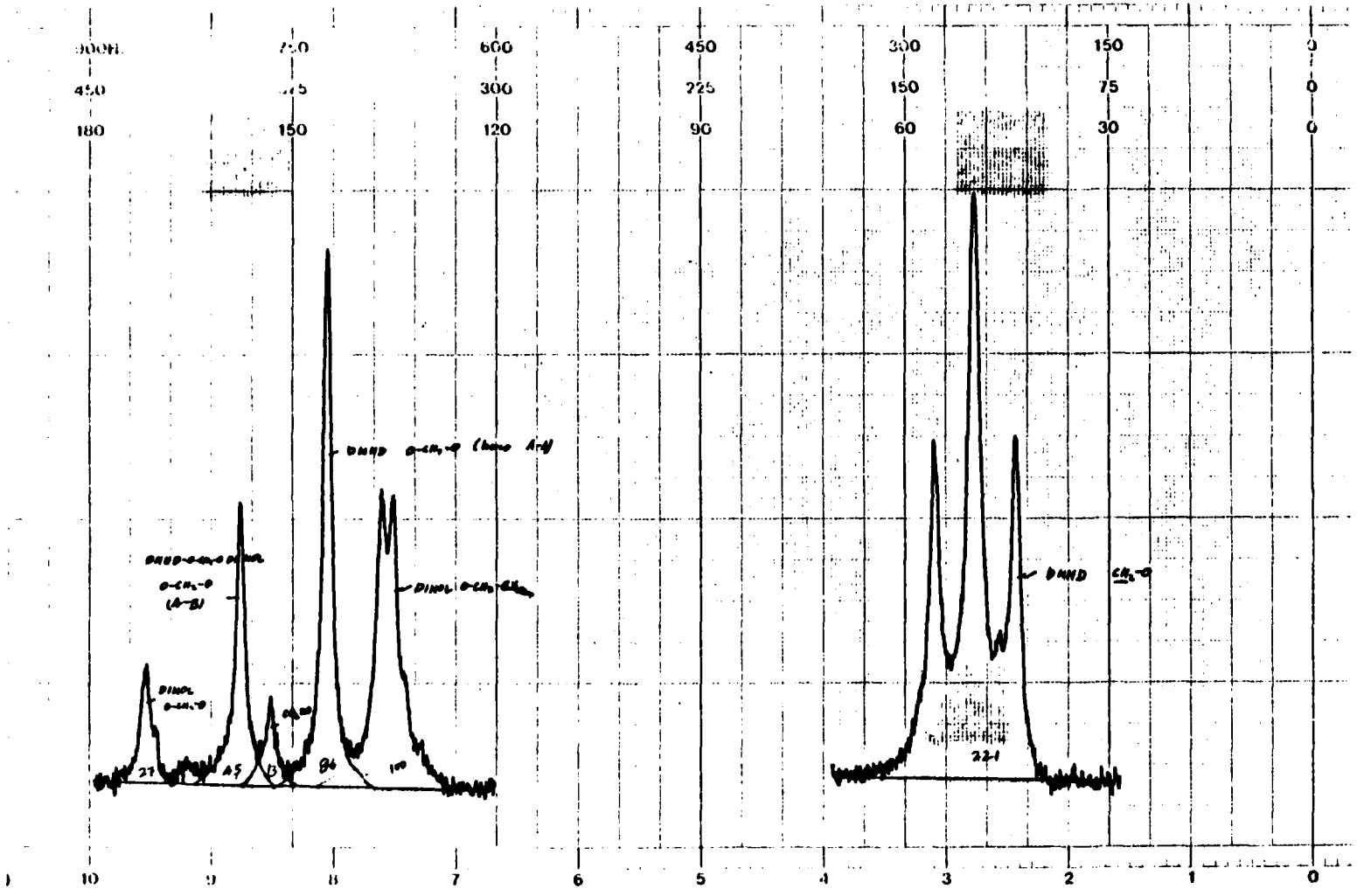


Figure 14. ^{1}H NMR Spectrum of DINOL (5)/Dinitroheptanediol (3) Copolyformal (20/80, Table 3, #2), $-OCH_2O-$ Region

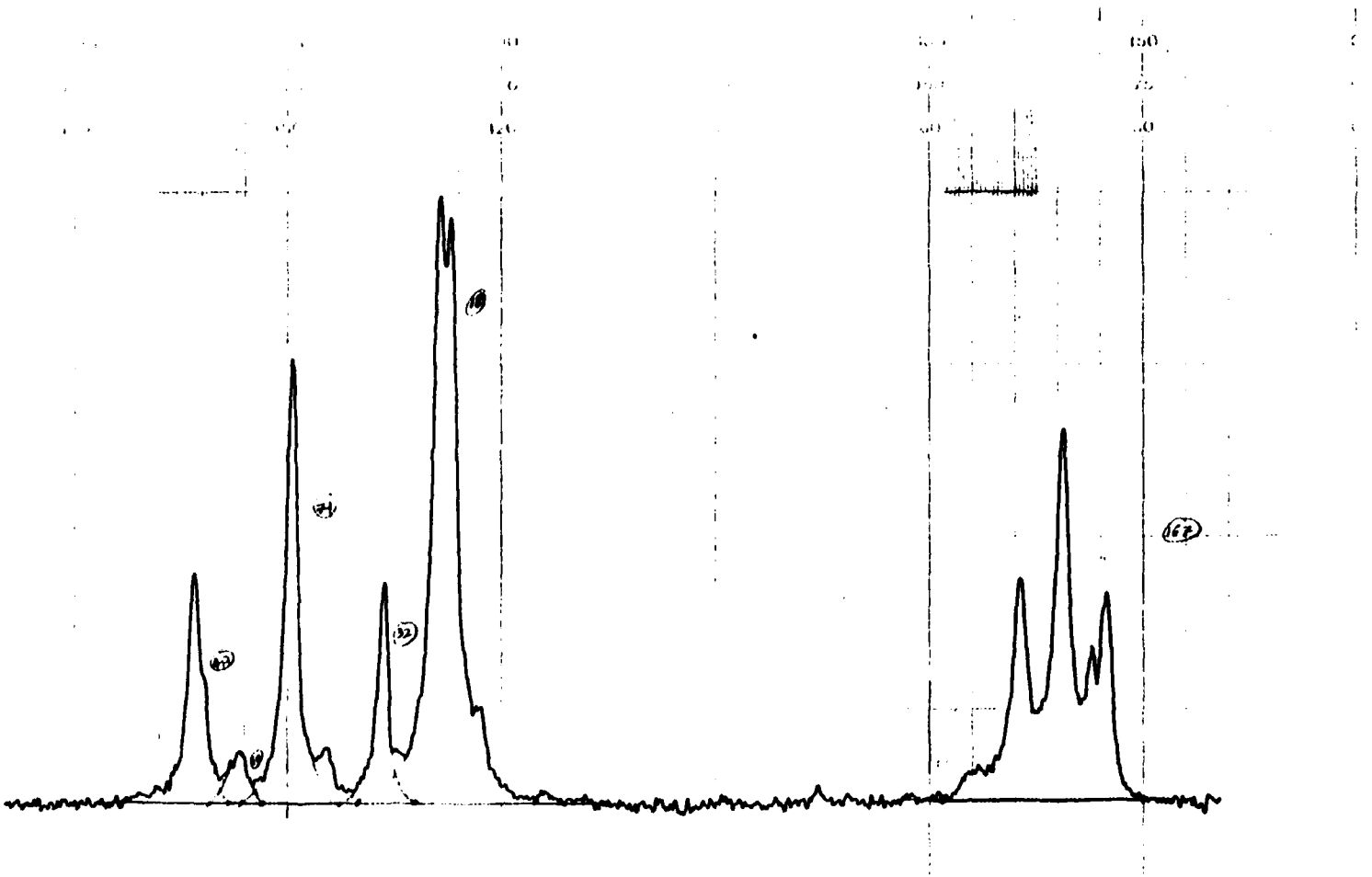
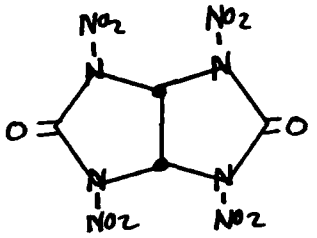


Figure 15. ^1H NMR Spectrum of DINOL (5)/Dinitroheptanediol (3) Copolyformal (40/60, Table 3, #3), $-OCH_2O-$ Region

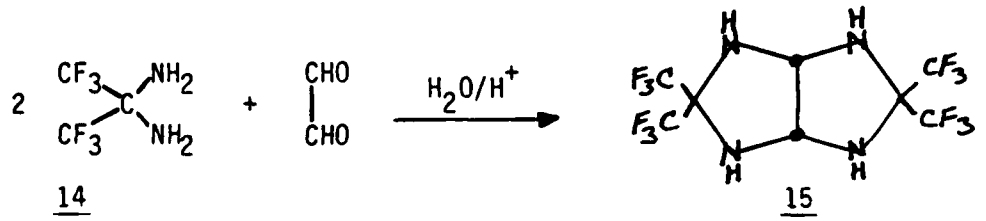
acetyl or alkyl groups. Our results indicated that the nitrolysis approach is beset with the problem of competing ring-opening reactions.

The question arose as to whether the ring system of bicyclo-HMX itself would be stable. It appeared that, since tetranitroglycoluril (TNGU, 13) was stable, bicyclo-HMX should also be stable even though there is a difference (sp^2 vs sp^3) in the hybridization of the carbon between the nitramine groups.



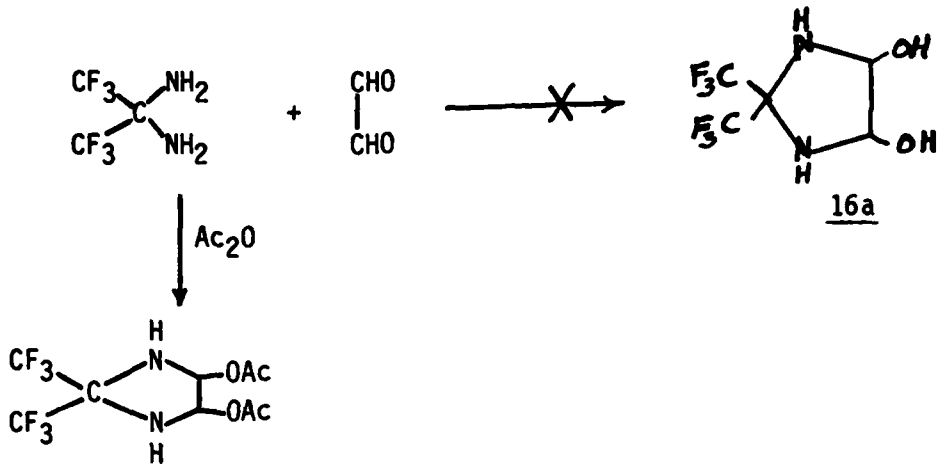
13, TNGU

In order to test the stability of the bicyclo-HMX ring system, it was decided to prepare model compounds in which the methylene groups bridging the nitrogens would contain two trifluoromethyl substituents, making use of the well-known gem-dimethyl and trifluoromethyl effects of ring-stabilization. This approach involved preparing the tetraazabicyclooctane ring system followed by successive nitrations of the amine nitrogens. The electron-withdrawing trifluoromethyl substituents should lessen ring-opening reactions through electronic as well as steric effects,[3] and information could be gained about the nitration process. Even taking into account the effect of ring-stabilization by CF_3 mentioned above, it was surprising that bis(trifluoromethyl)methylenediamine, 14, reacted readily with glyoxal to give the tetrazabicyclooctane, 15, in 85% yield. 15 is a stable solid which can be recrystallized from dichloroethane without decomposition. The crystal



14 15

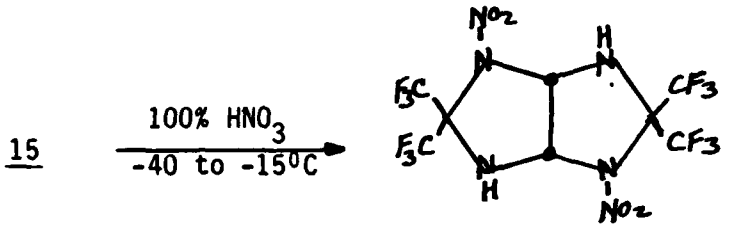
structure (determined and reported by R. Gilardi, NRL) confirms the expected cis configuration. The diaminopropane was also condensed with excess glyoxal in an effort to obtain 16a, but this could not be isolated. However, addition of acetic anhydride to the reaction mixture gave 16b in 18% yield as a mixture of cis-trans isomers.



16a

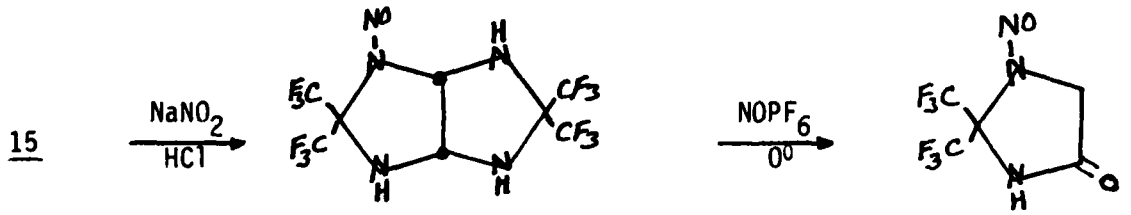
16b

Introduction of the first nitro groups into 15 required careful control of the reaction conditions and was successful only at low temperatures to give 17 in modest yield (42%). No unreacted starting material or other water-insoluble products were observed, an indication that degradation of the ring



17

system must have occurred to a substantial degree. A similar observation was made in the attempted nitrosation of 15, which gave only the mononitroso derivative 18 in 43% yield, and led to destruction of the ringsystem under



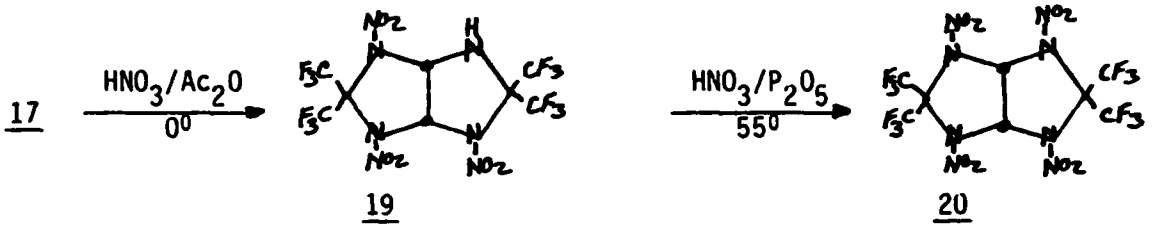
18

conditions forcing introduction of a second nitroso group. Attempted acetylation of 15 was even less successful. Only starting material was recovered after treatment with acetyl chloride/triethylamine at ambient temperature, or with acetic anhydride/pyridine at 100°C. Reaction with acetic anhydride/BF_3 etherate gave 16b in 91% yield. Thus the vulnerability of the ring systems of 15 in reactions involving electrophilic attack on nitrogen seems well established. The failure of 15 to undergo acetylation is probably

also due to steric crowding resulting from the presence of the trifluoromethyl groups.

17 is stable to storage as a solid, and can be recrystallized from dichloroethane without decomposition.

Further nitration of 17 was more straight forward - HNO_3/Ac_2O gave the trinitro compound 19 in ≈ 90% yield, and this was nitrated with HNO_3/P_2O_5 to the tetranitro compound 20 in 65% yield. Evidently, the two nitro groups in 17 provide protection against the heterolytic ring-opening discussed above,



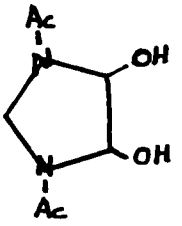
counteracting the introduction of considerable steric strain with the advent of the third and fourth nitro groups. 19 is stable as a solid but decomposes in dichloromethane solution at room temperature in a matter of hours. 20 is more stable but also decomposes gradually in dichloromethane solution (20% in 3 days at room temperature). It represents the first example of a bicyclo-HMX derivative with the bonding character of the parent compound. R. Gilardi and associates determined the crystal structures of compounds 17, 19, and 20; they were in accord with the proposed structures. The crystal densities of 15, 19, and 20 are appreciably above the calculated value. This can be attributed to very high molecular densities (Table 4)[4].

Table 4. Crystal Properties of Tetrazabicyclooctanes Calculated from the Crystal Structure

Compound	ρ_0(calc'd)[5]	ρ_0(X-ray)	ρ(mol)	Pack. Coeff.
15	1.91	2.029	2.783	0.728
17	1.97	1.978	2.882	0.684
19	2.02	2.110	2.876	0.731
20	2.04	2.184	2.904	0.751

The ^1H NMR spectra of the tetrazabicyclooctanes show no unusual features. With the introduction of nitro groups, the CH signal is shifted progressively from δ 5.26 in 15 to δ 7.40 ppm in 20. The IR spectra, however, exhibit unusual features for the assym. NO_2 stretch absorption. The normally unresolved band near 1600 cm^{-1} (1570 cm^{-1} in RDX) is split into 2 bands at 1595 and 1650 cm^{-1} in 19, and into four bands between 1610 and 1660 cm^{-1} in 20. The blue shift is similar in magnitude to that observed for 2,4,6-tris (trifluoromethyl)-1,3,5-trinitrohexahydrotriazine[6]. Presumably, it results from the electron-withdrawing effect of the trifluoromethyl groups which appears to outweigh the effect of the slight N-N bond lengthening in the series 17, 19, and 20[7].

The ease with which 14 condensed with glyoxal to form the fused five-membered ring system of 15 gave rise to the expectation that it would react to form a fused five-membered ring onto substrates such as 21 and 22. This would provide a precursor for 23, a bicyclo-HMX analog with fewer trifluoromethyl



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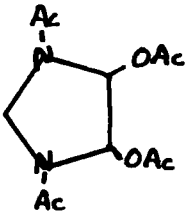

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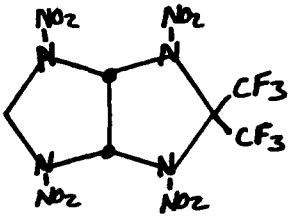
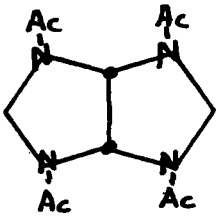


23

groups than 15. However, 14 and 21 failed to react in dil. sulfuric acid under the conditions which produced 15. Attempted condensations in ether and acetonitrile were also unsuccessful. 22 also failed to react with 14 under the conditions (CH_3CN, reflux, TsOH cat.) where methylene bisacetamide reacts with 22 to give 24. No reaction occurred in acetic acid at 20° with H_2SO_4 as



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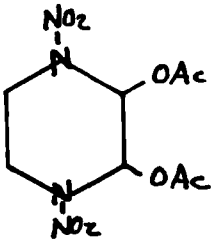


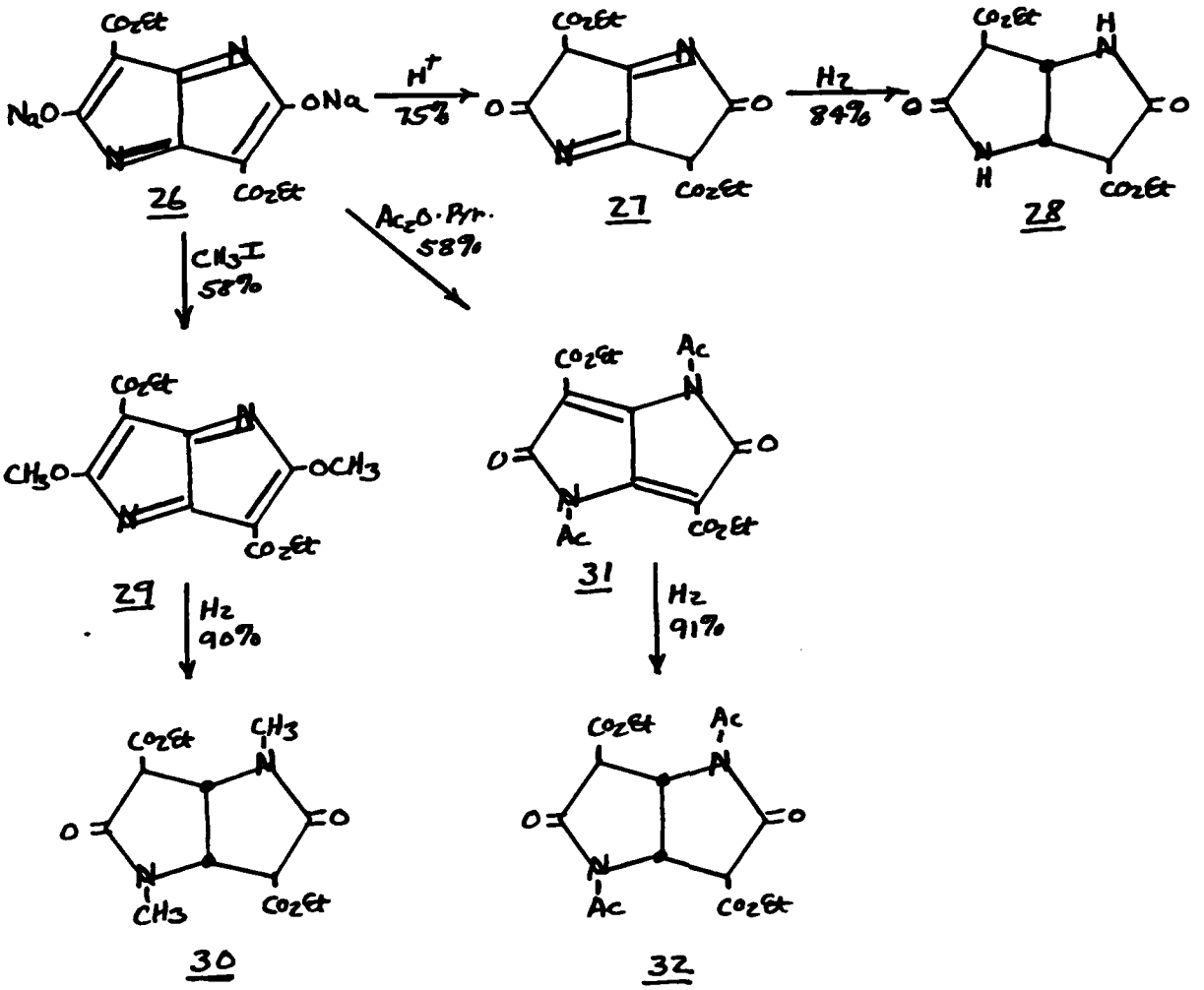
25

catalyst. Prolonged heating at 100° in acetic acid with no catalyst produced decomposition products which were water soluble. Finally, fusion of a mixture of 22 and $(CF_3)_2\ C(NH_2)_2 \cdot H_2SO_4$ (a stable salt) also resulted in water-soluble products. The six-membered ring substrate 25 also failed to react with the gem-diamine 14 after heating in acetonitrile with H_2SO_4 as catalyst, 25 being recovered in good yield. The solvent/catalyst system $CF_3COOH/BF_3 \cdot O(Et)_2$ which effects self-condensation of 25, also did not bring about a reaction between 25 and 14. These results were unexpected since in carbocyclic systems the bicyclo [3.4.0]nonane is less strained and more readily formed than the bicyclo[3.3.0]octane.

A second major effort during the past year was concerned with the synthesis of the diazabicyclooctanes 11 and 12. The starting materials in this work were obtained by the reaction of cyanogen with sodio diethylmalonate[8] to give a condensation product 26 which was converted into the unsaturated double lactam 27. The chemistry of these materials were explored in detail in an effort to find routes which would lead to 11 and 12.

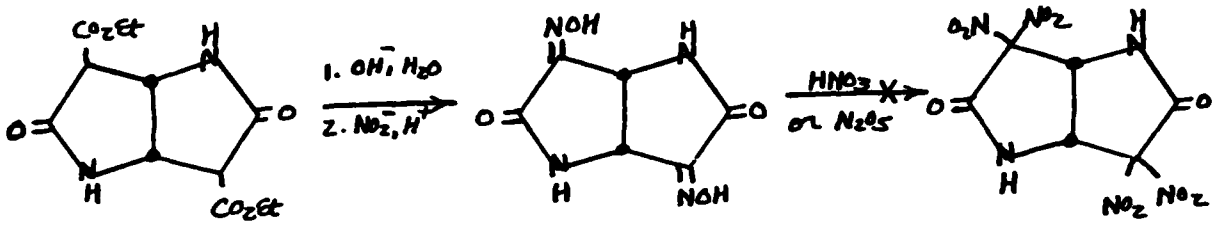
Catalytic hydrogenation of 27 gave the double lactam 28. The sodio derivative 26 was methylated to give the known[8] enol ether 29. Upon

hydrogenation, during which methyl migration from oxygen to nitrogen occurred, 29 gave the double lactam 30. Acetylation of either 26 or 27 yielded the N-



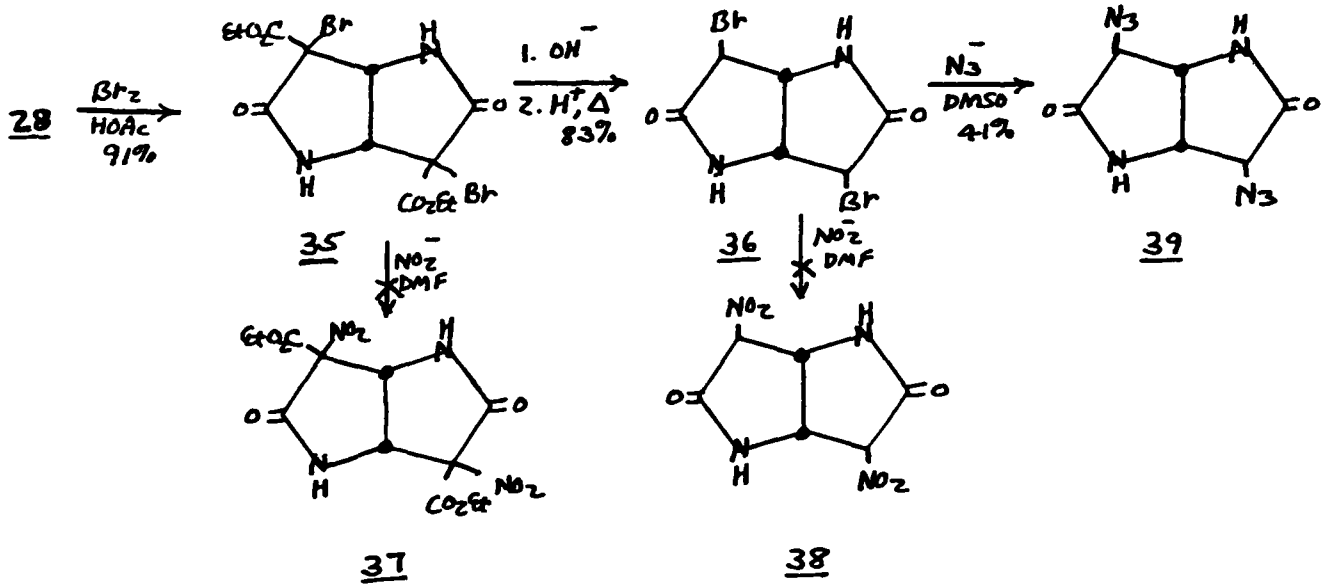
acetyl derivative 31, rather than an enol acetate corresponding to structure 29. Hydrogenation of 31 gave the N-acetyl double lactam 32.

The first approach toward the synthesis of the nitrated diazabicyclo-octanes 11 and 12 started with the substituted double lactam 28. Attempts to introduce a nitro group adjacent to the carbethoxy substituent with acetone cyanohydrin nitrate or tetranitromethane under basic conditions failed to yield any product containing a nitro group. Treatment of 28 with aqueous alkali, followed by sodium nitrate and acid, gave an excellent yield of a high-melting product which was thought to contain the double oxime 33. Attempts to convert this product into the gem-dinitro compound 34 under various conditions of oxidative nitration were unsuccessful.



28 33 34

Compound 28 was successfully brominated in acetic acid to give the α-bromoester 35, which underwent facile hydrolysis and decarboxylation to the dibromide 36. Although α-bromoesters usually react with nitrite ion in polar solvents to give α-nitroesters in high yield (Kornblum reaction), compound 35 reacted to give a complex mixture of water-soluble products of no synthetic utility. Conversely, the dibromide 36 was almost completely inert under Kornblum reaction conditions, over a period of several days. The product consisted mostly of starting material and contained no nitro groups. The bromine substituents in 36 are probably exo to the fold of the ring system and therefore not readily displaced for steric reasons. However, 36 did undergo

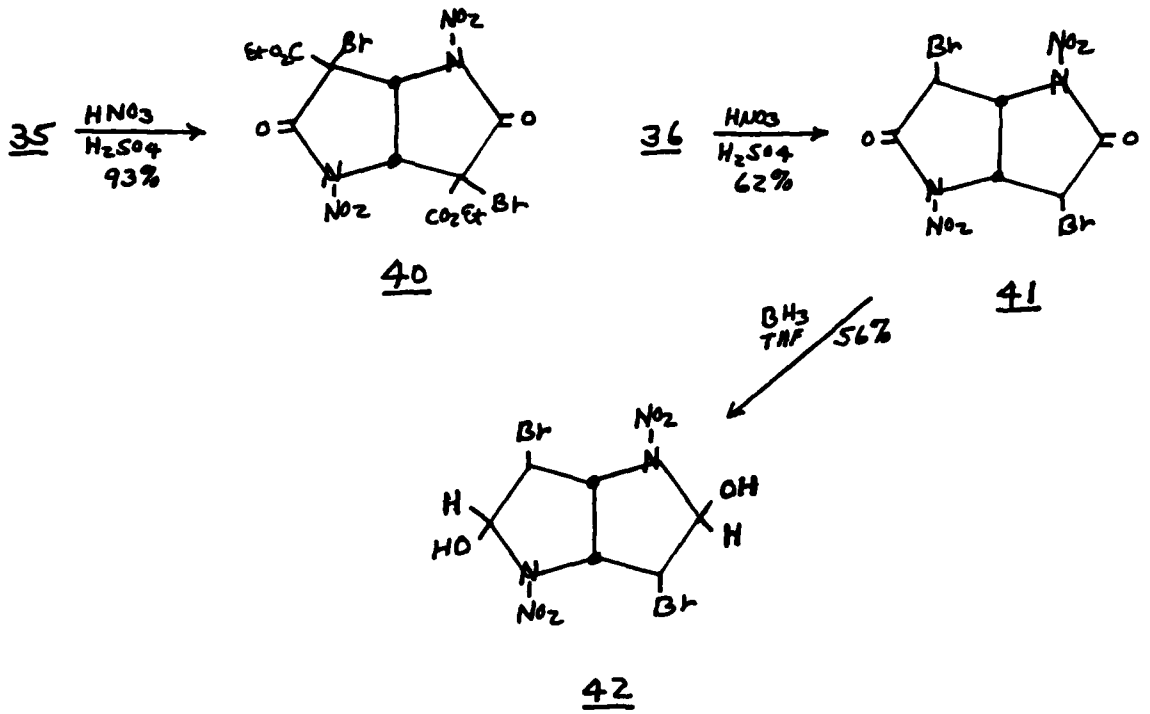


35 36 39

37 38

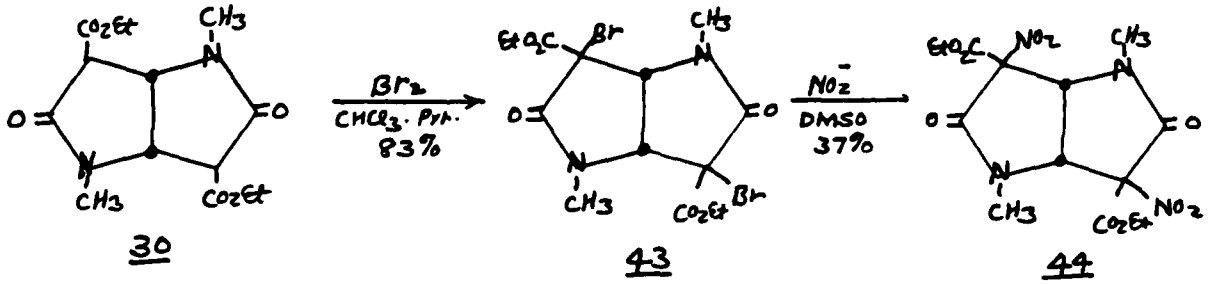
a displacement reaction with azide in DMSO to give a low yield of the diazide 39.

The double lactams 35 and 36 were readily converted into the nitramides 40 and 41 with mixed acid. These compounds reacted readily with nitrite ion in polar solvents, and, although no C-nitro products have been isolated and



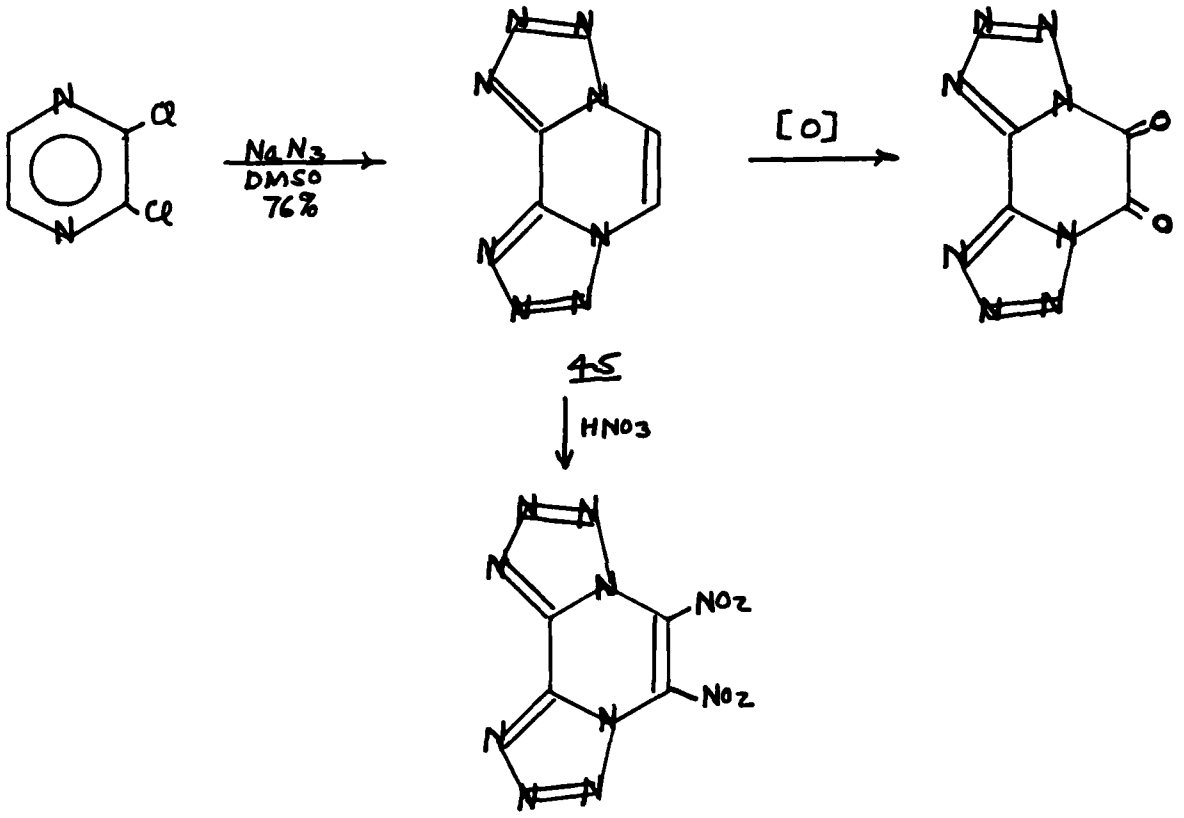
identified, work is continuing to study the reaction in less polar solvents. In an attempt to reduce the carbonyl group of 41 to a methylene group with diborane (as occurs with amides), the unexpected diol 42 was produced. This appears to be a new reaction of nitramides and it will be further explored in other systems.

In another approach to the target diazabicyclooctanes 11 and 12, the N-methyl substituted double lactam 30 was brominated to give the α-bromoester 43, which reacted with sodium nitrite in DMF to give the α-nitroester 44.



Thus, it appears that, when the amide nitrogen is substituted, the Kornblum reaction proceeds to the desired C-nitro product. A successful synthetic approach to the target compounds may have to utilize intermediates in which amide nitrogen is substituted with a nitro group or perhaps an easily nitrolyzable group such as acetyl.

In confirmation of earlier work in another area, the interesting ditetrazolopyrazine 45, whose synthesis we reported previously[1], was synthesized by a direct route from 2,3-dichloro-pyrazine.[9] Sufficient quantity is now available for nitration or other derivatization at the six-membered ring.



EXPERIMENTAL SECTION

Melting points are uncorrected. Temperatures are in °C. Microanalyses are by Galbraith Laboratories, Knoxville, Tennessee. NMR spectra were obtained in part on a Varian EM-390 spectrometer, in part on a Varian XL-200 NMR spectrometer. Chemical shifts are in ppm relative to TMS internal standard.

5,5,6,6,7,7-Hexafluoro-1,3-dioxocane. - 318.13 g of 2,2,3,3,4,4-hexafluoropentanediol (1.50 mol) and 48.29 g of paraformaldehyde (1.61 mol) were placed in a 3L 3-neck flask fitted with a thermometer and mechanical stirrer. 1200 mL of dichloromethane were added, and the slurry was stirred vigorously. The internal temperature was 20°C. 127.4 mL (216.1 g, 1.44 mol) of triflic acid was added rapidly; the temperature dropped to 18°C, then rose to 23°C, then slowly dropped again. After 2 h stirring 800 mL of ice-water were added, the mixture was stirred 30 min., and the layers were separated. The aqueous layer was washed with 200 mL of dichloromethane, and the combined dichloromethane layers were washed with 2 x 500 mL of 5% KOH solution. After drying ($MgSO_4$) and filtering, the dichloromethane was distilled off at atmospheric pressure to a bath temperature of 150°C, using a Vigreux column to facilitate separation from the product. The crude product was transferred to a smaller round bottom flask and was vacuum distilled through a Vigreux column into an ice-cooled receiver; b.p. 65°C at ≈ 12 Torr. A forerun of about 50 g was collected which contained about 2% of trioxane by NMR. The main fraction weighed 239.5 g. About 5 g of material was distilled from the forerun through a Vigreux column in vacuo; this contained most of the trioxane. The pot residue was combined with the main fraction to give 284.5 g (84.6%) of pure product; m.p. 24-25°C; density = 1.584 g/cm^3.

The original aqueous phase was extracted with ether; the KOH solution was acidified and also extracted with ether. Work-up gave 16.5 g of recovered diol. The pot residue from the vacuum distillation (polymeric material) weighed 10.7 g; 0.7 g was recovered from a dry-ice trap which was used in the distillation. The total amount of recovered material, including the trioxane-rich fraction, was 32.9 g, corresponding to about 10% of the diol used.

2,2,3,3,4,4-Hexafluoropentanediol Polyformal. - In a 1L round bottom 3-neck flask were placed, under a nitrogen blanket, 300.0 g of 5,5,6,6,7,7-hexafluoro-1,3-dioxocane (dried over 4A Molecular Sieves) and 22.46 g of 2,2,3,3,4,4-hexafluoropentane-1,5-diol (dried in vacuo over KOH). The mixture was stirred with a mechanical stirrer at 60°C until homogeneous. 2.86 mL of triflic acid (A = 0.8789) were added in 0.3 - 0.5 mL increments over a period of about 1 h. The internal temperature rose to 66°C over a 90 minute period, then slowly fell to 60°C. After 16-20 h total stirring, the viscous mixture was allowed to cool and was diluted with dichloromethane and transferred to a 3L erlenmeyer flask (total dichloromethane used was 1L). The solution was immediately quenched with a mixture of 100 mL of 30% aqueous H_2O_2, 400 mL of 10% aqueous KOH, and 500 mL of saturated NaCl solution and was stirred efficiently for 1 h. The phases were separated, the aqueous phase was washed with 200 mL of dichloromethane and the combined dichloromethane solutions were washed with 1L of brine. The dichloromethane solution was dried ($MgSO_4$) and filtered through a Whatman 1PS filter. The solvent and a portion of the unreacted monomer were distilled off (collect and recover monomer). The crude polymer was heated with internal stirring (magnetic bar) at 130°C for 24 h

with the flask being totally immersed in the oil bath. Volatiles were collected in a dry-ice trap. The yield of polymer was 235.8 g (73.1%); 80.9 g monomer was recovered (98% material balance). M_n = 2447; hydroxyl equivalent weight (NMR method) = 1220.

The molecular weight ($\bar{M}_n$) obtained by the above procedure is determined by the "activity" A of the triflic acid:

$$A = \frac{n(\text{mol monomer})224 + n(\text{mol diol})212 - \bar{M}_n(\text{observed})n(\text{mol diol})}{\bar{M}_n(\text{observed})n(\text{mol triflic acid})} \quad (1)$$

A is determined by a small scale run using the procedure above; $\bar{M}_n$ is calculated using equation (2) and A is obtained from equation (1). A second small scale run using an amount of diol calculated from (2) with the revised

$$\bar{M}_n = \frac{n(\text{mol monomer})}{n(\text{mol triflic acid})A + n(\text{mol diol})} \times 224 + \frac{n(\text{mol diol})}{n(\text{mol triflic acid})A + n(\text{mol diol})} \times 212 \quad (2)$$

A will indicate whether the new A is adequate or needs to be adjusted again by repeating the above process.

2,4,4,5,5,6,6-Heptafluoro-2-trifluoromethyl-3-oxaheptane-1,7-diol Polyformal. - In a 1L 3-neck flask 146.1 g of diol and 90.0 mL of 80% (w/w) H_2SO_4 were mixed under a N_2 blanket until homogeneous. The mixture was cooled in an ice-bath and 117 mL of dry dichloromethane were added. To the vigorously stirred mixture, a solution of 10.8 g of paraformaldehyde in 63 mL of 90% sulfuric acid (w/w) was added with continued cooling, and then the mixture was stirred for 20 h at room temperature. The reaction mixture was poured over ice. 900 mL of ether and 90 mL of 30% H_2O_2 was added, and the mixture was stirred vigorously for 1 h. The organic layer was washed thoroughly with 675 mL of 5% aqueous KOH + 45 mL of 30% H_2O_2, then with 675 mL of brine. After drying ($CaSO_4$), the solution was filtered through a medium porosity sinterglass funnel and freed of solvents in vacuo. The resulting polymer was heated overnight at 120°C, collecting volatiles in a trap immersed in an acetone-dry-ice bath. The yield of polymer was 113 g (74.6%). $\bar{M}_n$ = 2770; $\bar{M}_w$ = 5147; $\bar{M}_w/\bar{M}_n$ = 1.86. The dry-ice trap contained 35.7 g of mostly unreacted diol; based on reacted diol, the polymer yield was ≈ 98%.

4,4-Dinitroheptane-1,7-diol Polyformal (#1, Table 1). - 1.0 g (4.5 mmol) of diol and 0.155 g (5.17 mmol) of trioxane were dissolved in 1.0 mL of sulfolane. 0.5 mL of BF_3 etherate were added with stirring and cooling (ice-bath), and stirring was continued overnight at room temperature. The reaction solution was diluted with dichloroethane and poured onto ice. Saturated bicarbonate soution was added with stirring until bubbling ceased (5% H_2O_2 was added also to decompose any excess formaldehyde). The phases were separated. The dichloroethane layer was washed once with acidic (HCl) brine, 3 times with brine, was then dried, filtered, and evaporated. Obtained was 0.83 g (≈ 83%) of a solid polymer. $\bar{M}_n$ = 1611; $\bar{M}_w$ = 3043.

4,4-Dinitroheptane-1,7-diol Polyformal (#5, Table 1). - 1.0 g (4.5 mmol) of diol and 0.135 g (4.5 mmol) of trioxane were dissolved in 1 mL of sulfolane. 0.125 mL of $SnCl_4$ were added at room temperature with stirring. After 16 h, the gel was dissolved with 3:1 dichloromethane/methanol. This solution was added to brine and the mixture was stirred vigorously for about 0.5 h. The layers were then evaporated. The organic layer was washed once with acidic brine (HCl), 3 times with brine and was then dried, filtered, and evaporated. The resulting resin was triturated with methanol. The methanol was decanted and replaced in 0.5 h intervals until the polymer solidified. The final methanol increment was decanted and the polymer was dried. The yield was 0.75 g (≈ 75%). $\overline{M}_n$ = 3200; $\overline{M}_w$ = 6000.

Copolymerization of 2,4,4,5,5,6,6-Heptafluoro-2-trifluoromethyl-3-oxaheptane-1,7-diol and 4,4-Dinitroheptanediol (80/20). - 4.0 g of Decafluorodiol, 0.675 g of dinitroheptanediol, and 0.503 g of trioxane were dissolved in 5 mL of sulfolane. With ice-cooling and stirring, 2.5 mL of $BF_3 \cdot O(Et)_2$ were added, and the mixture was stirred at room temperature overnight. The mixture was poured on ice, ether was added and the mixture was stirred for 1 h. The ether layer was washed with 1:1 5% NaOH solution/brine containing some 30% H_2O_2. and 3 times with brine. Drying and removal of the ether gave a resin which was triturated twice with water and then heated in vacuo at 120°C for 4 h. Obtained was 3.39 g (68%); GPC and ^1H NMR, see Figs. 4 and 5.

Copolymerization of DINOL and 4,4-Dinitroheptanediol (20/80) with Trioxane/BF_3 etherate. - 0.8 g (3.6 mmol) of dinitroheptanediol, 0.31 g (0.9 mmol) of DINOL, and 0.15 g (5.0 mmol) of trioxane were dissolved in 1 mL of sulfolane. 0.5 mL of BF_3 etherate were added with ice-cooling, and the mixture was stirred at room temperature overnight. Saturated $NaHCO_3$ solution was added to the reaction flask with stirring until the gas evolution subsided. The aqueous layer was decanted, and the residue was triturated 3 times with water for 1 h, after which time each portion of water was decanted. The resin was taken up in ether and the solution was dried, filtered, and evaporated. Obtained was 1.2 g of polymer. Figs. 10 and 11 show the GPC and the ^1H NMR spectrum of this material.

Copolymerization of DINOL and 4,4-Dinitroheptanediol (20/80) with Trioxane/$SnCl_4$ (runs # 2 and 3, Table 3). - The quantities of reagents shown in Table 3 were reacted using the procedure given above for the dinitroheptanediol homopolyformal (#5, Table 1), except that trituration of the polymer was done with water instead of methanol. The polymers obtained were resins. Yields and molecular weight data are given in Table 3; the GPCs and NMR spectra are shown in Figs. 12-15.

3,3,7,7-Tetra(trifluoromethyl)-2,4,6,8-tetraazabicyclo[3.3.0]octane (15). - A solution of 7.20 g (0.040 mol) of hexafluoro-2,2-diaminopropane[11] and 2.80 g of 40% aqueous glyoxal solution (0.019 mol) in 20 mL of water was chilled in an ice bath while a solution of 2.00 g of conc. H_2SO_4 in 20 mL of water was added dropwise. After an overnight period of stirring at 20°C a white, crystalline precipitate was collected by filtration, washed with water, and dried over $CaSO_4$ to give 6.63 g (87%) of pure 15; mp 92-93.5°C (from 1,2-dichloroethane); ^1H NMR ($CDCl_3$) δ 5.26 (br s, 2), 2.89 (br s, 4); mass spectrum (CI, CH_4), m/z (rel. intensity): 387 (6, M+1) 367(15), 347(2), 317(7), 222(39), 57(100). Anal. Calc'd. for $C_8H_6F_{12}N_4$: C, 24.88; H, 1.57; F, 59.04; N, 14.51. Found: C, 24.78; H, 1.69; F, 58.86; N, 14.50.

2,2-Bis(trifluoromethyl)-4,5-diacetylimidazolidine (16b). - A. By condensation of 2,2-diaminohexafluoropropane with glyoxal: A solution of 0.36 g (2.0 mmol) of diaminohexafluoropropane, 0.42 g of 40% aqueous glyoxal solution (3.0 mmol), and 2.0 g of acetic acid containing one drop of sulfuric acid was heated in a 90°C bath for 0.5 h. The solution was cooled to room temperature, and 4.0 g of acetic anhydride was added. After 16 h at 20°C, the solution was warmed to 50°C under vacuum. Trituration of the yellow liquid residue with ethyl ether gave 0.15 g (18%) of the title compound with mp 144-146°C. Its NMR spectrum was identical to that of a recrystallized (ethyl ether) sample with mp 169-170°C; ^{1}H NMR ($CDCl_3$) δ 6.51 (s, 2), 2.28 (s, 6); 2.20 (s, 6). Anal. Calc'd. for $C_{13}H_{14}F_6N_2O_6$: C, 38.24; H, 3.46; F, 27.92; N, 6.86. Found: C, 38.25; H, 3.30; F, 27.90; N, 6.77.
B. by acetylation of 15: A mixture of 0.39 g (1.0 mmol) of 15, 4 mL of acetic anhydride, and 0.13 g of boron trifluoride etherate was let stand for 60 h at 20°C. The solution was stirred with water until the acetic anhydride layer disappeared, and the solid was extracted with dichloromethane. The dried ($MgSO_4$) extract yielded 0.37 g (91%) of the title compound with mp 142-152°C.

This and the material from method A are probably mixtures of cis-trans isomers; samples melting as high as 174-6°C were obtained by recrystallization of the crude products from chloroform/hexane. The highest melting samples were found to have the trans configuration (crystal structure). The ^{1}H NMR spectra of the differently melting samples were identical.

3,3,7,7-Tetra(trifluoromethyl)-2,6-dinitro-2,4,6,8-tetraazabicyclo[3.3.0] octane (17). - The amine 15 (2.0 g) was added in portions to 13 mL of HNO_3 (100%), while the solution temperature was kept at -35° to -40°C. Following the 20 min addition period, the temperature was allowed to rise to -30°C (10 min). The flask was raised to allow the solution to reach -15°C (15 min) and then the contents were poured on 45 g of ice. The isolated solid was washed with water and dried over $CaCl_2$ (20°C/1mm) to give 1.04 g (42%) of 17; mp 167-8°C; IR (KBr) 1585 (NO_2); ^{1}H NMR ($CDCl_3$) δ 6.13 (s, 2), 4.17 (br s, 2); mass spectrum (CI, CH_4) m/z (rel. intensity): 477 (0.2, M+1), 415 (0.3), 220 (0.8), 57 (30), 48 (82), 46 (43), 44 (100).

2-Nitroso-3,3,7,7-tetra(trifluoromethyl)-2,4,6,8-tetraazabicyclo[3.3.0]octane (18). - A solution of 0.19 g (0.050 mmol) of 15 in 4 mL of ethyl ether was added to a solution of 0.28 g (4.0 mmol) of sodium nitrite in 2 mL of water. This mixture was cooled in an ice bath while 5 mL of 1 M HCl was added dropwise. After 2 h at 20°C, the solution was poured into a dish and the ether was allowed to evaporate. A crystalline solid precipitated and was extracted into dichloromethane. Following a wash with $NaHCO_3$ solution, the solution was dried ($MgSO_4$) and evaporated to give 0.09 g (43%) of the title compound containing minor impurities by TLC and NMR analysis. Recrystallized ($CHCl_3/CCl_4$) material had mp 52-4°: ^{1}H NMR ($CDCl_3$) δ 5.77, 5.49 (m, m, 1, C_1-H), 5.28 (br s, 1, C_5-H), 3.63, 3.38 (br s, br s, 1, N_2-H), 2.90 (br s, 2, $N_{4,6}$- H); mass spectrum, m/z (rel. intensity) 416 (M+1, 16), 387 (78), 367 (43), 317 (37), 222 (75), 205 (29), 58 (100).

1-Nitroso-2,2-di(trifluoromethyl)imidazolidine-4-one. - A stirred suspension of 2 g (5 mmol) of 18 in 15 mL of nitromethane was cooled to 0°C while a solution of 4 g (22 mmol) of $NOPF_6$ in 15 mL of nitromethane was added dropwise. After 1 h at 0°C, the reaction mixture was allowed to warm to 20°

and was then poured onto ice. A dichloromethane extract was dried ($MgSO_4$) and concentrated to a mixture of solid and liquid residue. This was dissolved into hot dichloroethane and on cooling 0.11 g (9%) of the title compound was obtained with mp (sealed capillary) 179-180°C (dec.): ^1H NMR (acetone-d_6) δ 4.48 (s, 2); mass spectrum, m/z (rel. intensity) 292 (M+41, 11), 280 (M+29, 18), 252 (M+1, 100), 222 (19). The structure was confirmed by X-ray diffraction (R. Gilardi, NRL).

3,3,7,7-Tetra(trifluoromethyl)-2,4,6-trinitro-2,4,6,8-tetraazabicyclo[3.3.0]octane (19). - A nitric acid-acetic anhydride nitration solution was prepared at -15°C by a dropwise addition of 4 mL of Ac_2O to 8 mL of HNO_3 (100%). The solution was allowed to warm to 0°C (0.5 h), then cooled to -10°C during the addition of 1.00 g of 17, in portions. After 0.5 h at -10°C and 4 h at 0°C, the solution was poured onto 50 g of ice. The precipitated solid was washed with water and dried over $CaCl_2$ (20°C, 1 mm) to give 0.96 g (88%) of 19: mp 109-110°C (dec.); IR (Fluorolube) 1650 and 1595 (NO_2) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 7.35 (d, 1, J = 6Hz), 6.30 (m, 1) 4.58 (br s, 1).

3,3,7,7-Tetra(trifluoromethyl)-2,4,6,8-tetranitro-2,4,6,8-tetranitro-2,4,6,8-tetraazabicyclo[3.3.0]octane (20). - Under a N_2-atmosphere, 7.5 g (2 mL) of 100% HNO_3 was slowly added to 2.5 g of P_2O_5. After the exothermic reaction had subsided, 0.25 g (0.48 mmol) of 19 was added and heat was applied to raise the solution temperature from 25°C to 55°C in 0.25 h. The temperature was maintained at 55° to 60°C for 0.3 h and then the mixture was poured on ice. The collected precipitate was dried ($CaCl_2$, 1 mm) to give 0.18 g (67%) of 20: mp 110-111°C; IR (KBr) 1655, 1625, and 1610 cm^{-1}; ^1H NMR (CD_2Cl_2) δ 7.40 (s).

Disodium salt of diethyl-3,7-dioxo-2,6-diazabicyclo[3.3.0]octa-1,5-diene-4,8-dicarboxylate (26). - A solution of sodium ethoxide was prepared by dissolving sodium metal (23 g, 1.0 mol) in ethanol (700 mL). To this was added diethyl malonate (160 g, 1.0 mol). Cyanogen gas (31.2 g, 0.6 mol or 33 mL of previously condensed liquid) was then bubbled into the stirred solution, with slight external cooling, over several hours. After stirring overnight, the deep red precipitate was filtered, washed thoroughly with acetone, and dried under a vacuum. The yield of crude impure product was 138 g (85%).

Diethyl-3,7-dioxo-2,6-diazabicyclo[3.3.0]octa-1,5-diene-4,8-dicarboxylate (27). - Acetic acid (100 mL) was added to a stirred suspension of the crude disodium salt (26, 97.3 g, 0.30 mol) in ethanol (500 mL), followed by the addition of water (100 mL). After 15 min the precipitated green-yellow solid was filtered, washed with water, and dried to yield 63.2 g (75%) of the diester (27): mp > 350°C (dec). ^1H NMR (Me_2SO-d_6) δ 1.30(t, 6H, CH_3), 4.25(q, 4H, CH_2)ppm.

Diethyl-3,7-dioxo-2,6-diazabicyclo[3.3.0]octane-4,8-dicarboxylate (28). - A suspension of the diester (27, 5.6 g, 20 mmol) and 10% palladium on carbon catalyst (0.6 g) in DMF (250 mL) was hydrogenated in a Parr apparatus at 40 psig until hydrogen uptake ceased (1.5 h). The mixture was filtered to remove the catalyst and the filtrate was evaporated under reduced pressure to leave an almost colorless oil. The oil was dissolved in a mixture of 1:1 ethanol-ether (40 mL), the solution was refrigerated overnight, and filtered to give 4.8 g (84.4%) of 28 as a white solid: mp 173-180°C. Recrystallization from ethanol gave colorless prisms: mp 179-187°C. ^1H NMR (Me_2CO-d_6) δ 1.38(t, 6H,

CH_3), 3.41(s, 2H, CHCO), 4.25(q, 4H, CH_2), 4.74(s, 2H, CHN), 7.53(br s, 2H, NH)ppm; mass spectrum (CI, CH_4) m/z 43(100), 47(39), 55(30), 56(15), 57(20), 285(M+1, 18), 313(M+29, 3), 325(M+41, 2). Anal. Calcd for $C_{12}H_{16}N_2O_6$: C, 50.70; H, 5.67; N, 9.86. Found: C, 50.75; H, 5.46; N, 9.90.

Diethyl-3,7-methoxy-2,6-diazabicyclo[3.3.0]octa-1,3,5,7-tetraene-4,8-dicarboxylate (29). - A mixture of the crude disodium salt (26, 32.4 g, 0.1 mol) and methyl iodide (42.58 g, 0.3 mol) in ethanol (300 mL) was refluxed for 2 h, then cooled in ice and filtered to yield 18 g (58.4%) of 29 as a cottony orange solid: mp 153-154°C. Recrystallization from ethanol gave deep yellow needles of the same mp. ^1H NMR ($CDCl_3$) δ 1.40(t, 6H, CH_3), 3.55(s, 6H, CH_3O), 4.44(q, 4H, CH_2)ppm.

Diethyl-2,6-dimethyl-3,7-dioxo-2,6-diazabicyclo[3.3.0]octane-4,8-dicarboxylate (30). - A suspension of the diester (29, 30.8 g, 0.1 mol) and 10% palladium on carbon catalyst (1.5 g) in DMF (250 mL) was hydrogenated in a Parr apparatus at 40 psig until hydrogen uptake ceased (3.5 h). The mixture was filtered to remove the catalyst and the filtrate was evaporated under reduced pressure to leave a pale yellow oil. The oil was triturated with ether (200 mL), cooled and filtered to yield 28.15 g (90.1%) of white solid: mp 107-109°C. Recrystallization from benzene-isopropyl ether gave colorless prisms: mp 108-110°C. ^1H NMR ($CDCl_3$) δ 1.37(t, 6H, CH_3), 2.95(s, 6H, CH_3N), 3.49(br s, 2H, CHCO), 4.38(q, 4H, CH_2), 4.62(m, 2H, CHN)ppm; mass spectrum (CI, CH_4) m/z 313(M+1, 100), 341(M+29, 20), 353(M+41, 10). Anal. Calcd for $C_{14}H_{20}N_2O_6$: C, 53.84; H, 6.45; N, 8.97. Found: C, 53.81; H, 6.01; N, 9.00.

Diethyl-2,6-diacetyl-3,7-dioxo-2,6-diazabicyclo[3.3.0]octa-1(8),4-diene-4,8-dicarboxylate (30). - (A) from 26. A mixture of the crude disodium salt (26, 3.24 g, 10 mmol), acetic anhydride (30 mL) and pyridine (5 mL) was refluxed for 1 h, then cooled to room temperature and filtered to yield a yellow solid. The solid was stirred with water (20 mL), filtered and dried to give 2.11 g (58%) of almost white needles: mp 260-262°C (dec). Recrystallization from CH_3CN gave colorless needles: mp 265-266°C (dec). ^1H NMR(CF_3CO_2H) δ 1.50(t, 6H, CH_3), 2.83(s, 6H, CH_3CO), 4.68(q, 4H, CH)ppm; mass spectrum (CI, CH_4) m/z 43(100), 45(30), 47(52), 365(M+1, 2), 367(3), 393(M+29, 1.5), 395(1), 405(M+41, 1), 407(0.5). Anal. Calcd. for $C_{16}H_{16}N_2O_8$: C, 52.75; H, 4.43; N, 7.69. Found: C, 52.95, H, 4.63; N, 7.72.

(B) from 27. A mixture of 27 (7.0 g, 25 mmol), acetic anhydride (125 mL) and pyridine (10 mL) was refluxed for 30 min, then cooled to room temperature and filtered to yield 8.95 g (98.3%) of 31: mp 264-266°C (dec).

Diethyl-2,6-diacetyl-3,7-dioxo-2,6-diazabicyclo[3.3.0]octane-4,8-dicarboxylate (32). - A mixture of 31 (7.29 g, 20 mmol) and 10% palladium on carbon catalyst (0.6 g) in DMF (250 mL) was hydrogenated in a Parr apparatus at 40 psig until hydrogen uptake ceased (1.5 h). The mixture was filtered to remove the catalyst and the filtrate was evaporated under reduced pressure to leave a colorless oil. The oil was triturated with a 1:1 mixture of ether-isopropyl ether (40 mL), the mixture was refrigerated overnight and filtered to yield 6.71 g (91%) of white solid: mp 168-175°C. Recrystallization from benzene-isopropyl ether gave colorless prisms: mp 175-177°C. ^1H NMR ($CDCl_3$) δ 1.39(t, 6H, CH_3), 2.57(s, 6H, CH_3CO), 3.77(m, 2H, CHCO), 4.40(q, 4H, CH_2), 5.23(m, 2H, CHN)ppm; mass spectrum (CI, CH_4) m/z 43(100), 45(27), 47(25), 60(11), 323(24), 327(12), 369(M+1, 35), 397(M+29, 10), 409(M+41, 5). Anal.

Calcd. for $C_{16}H_{20}N_2O_8$: C, 52.17; H, 5.47; N, 7.61. Found: C, 51.91; H, 5.22; N, 7.56.

Diethyl-4,8-dibromo-3,7-dioxo-2,6-diazabicyclo[3.3.0]octane-4,8-dicarboxylate (35). - A solution of bromine (9.91 g, 62 mmol) in acetic acid (30 mL) was added to a stirred solution of 28 (8.53 g, 30 mmol) in acetic acid (70 mL). After 1 h the reaction mixture was evaporated to dryness under vacuum and the residue was triturated with a 1:1 mixture of ether and isopropyl ether (60 mL). Filtration gave 12.13 g (91.5%) of white solid: mp 163-170°C. Recrystallization from ethanol gave colorless prisms: mp 173-176°C. ^{1}H NMR (Me_2CO-d_6) δ 1.33(m, 6H, CH_3), 4.40(m, 4H, CH_2), 5.03(m, 2H, CH), 8.13(br d, 2H, NH) ppm; mass spectrum (CI, CH_4) m/z 47(100), 285(76), 441, 39), 443(68), 444(12), 445(M+1, 27, Br = 81), 473(M+29, 3, Br = 81), 485(M+41, 3, Br=81). Anal. Calcd. for $C_{12}H_{14}Br_2N_2O_6$: C, 32.60; H, 3.19; N, 634; Br, 36.15. Found: C, 33.27; H, 3.33; N, 6.47; Br, 35.94.

4,8-Dibromo-3,7-dioxo-2,6-diazabicyclo[3.3.0]octane (36). - Aqueous sodium hydroxide (4 mL of 10N) was added to a stirred suspension of 35 (8.84 g, 20 mmol) in water (75 mL). After 30 min the solution was acidified with conc HCl to pH 1.5, then refluxed for 40 min followed by cooling overnight in a refrigerator. Filtration of the precipitate gave 4.94 g (82.9%) of almost white solid: mp 252-254°C (dec). Recrystallization from CH_3NO_2 gave colorless needles: mp 250-252°C (dec). ^{1}H NMR (CF_3CO_2H) δ 5.13(m, 4H, CHBr and CHN), 8.42(br s, 2H, NH)ppm; mass spectrum (CI, CH_4) m/z 141(100), 219(39), 221(34), 297(27), 299(54), 301(M+1, 27, Br = 81), 329(M+29, 1.5, Br = 81), 341(M+41, 1.8, Br = 81). Anal. Calcd. for $C_6H_6Br_2N_2O_2$: C, 24.18; H, 2.03; N, 9.40; Br, 53.64. Found: C, 24.39; H, 2.18; N, 9.41; Br, 53.73.

4,8-Diazido-3,7-dioxo-2,6-diazabicyclo[3.3.0]octane (39). - A solution of 36 (149 mg, 0.5 mmol) and lithium azide (294 mg, 6 mmol) in DMSO (2 mL) was stirred at room temperature for 18 h, then poured into a mixture of ice and water (15 mL) and filtered to yield 45 mg (41%) of white solid: mp 220-225°C (dec); IR (KBr), 2240 (sh) and 2120 cm^{-1} (N_3); ^{1}H NMR (CF_3CO_2H) δ 4.63(d, 4H, CHN_3 and CHN), 8.33(br s, NH)ppm.

Diethyl-4,8-dibromo-2,6-dinitro-3,7-dioxo-2,6-diazabicyclo[3.3.0]octane-4,8-dicarboxylate (40). - A 1:1 (V:V) mixture of nitric acid (98%) and conc sulfuric acid (8 g) was cooled in an ice bath during the addition, with stirring, of 35 (884 mg, 2.0 mmol) over 2 min. After 3 h at room temperature, the mixture was poured onto ice (30 g) and the solid was filtered, washed with water and dried to give 995 mg (93.5%) of white crystals: mp - softens at ~ 100°C and melts to a foam at 125-130°C. Recrystallization from ethanol gave colorless crystals: mp 182-187°C. ^{1}H NMR (Me_2CO-d_6) δ 1.37(m, 6H, CH_3), 4.47(m, 4H, CH_2), 6.37(m, 2H, CH)ppm.

4,8-Dibromo-2,6-dinitro-3,7-dioxo-2,6-diazabicyclo[3.3.0]octane (41). - A 1:1 (V:V) mixture of nitric acid (98%) and conc sulfuric acid (8 mL) was cooled in an ice bath during the addition, with stirring of 36 (1.19 g, 4 mmol) over 2 min. After 1 h at room temperature the mixture was poured into ice and water (40 mL) and the solid was filtered, washed with water and dried to give 950 mg (61.8%) of white product: mp 230-231°C (dec). Recrystallization from CH_3CN gave colorless crystals: mp 235-236°C (dec). ^{1}H NMR (Me_2SO-d_6) δ 5.51(m, 4H, CHBr and CHN) ppm; mass spectrum (CI, CH_4) m/z 46(100), 48(52), 83(31), 387(5), 389(8), 391(M+1, 4, Br = 81). Anal. Calcd. for $C_6H_4Br_2N_4O_6$: C,

18.57; H, 1.04; N, 14.44; Br, 41.20. Found: C, 18.87; H, 1.27; N, 14.38; Br, 41.26.

4,8-Dibromo-3,7-dihydroxy-2,6-dinitro-2,6-diazabicyclo[3.3.0]octane (42). - Borane in tetrahydrofuran (4.5 mL of 1 M) was added to a suspension of 41 (388 mg, 1.0 mmol) in dry tetrahydrofuran (15 mL), and the mixture was refluxed for 2 h. The solution was then concentrated under reduced pressure to ~ 5 mL, water (15 mL) was added, and the oily mixture adjusted to pH 2 with conc HCl. After stirring at room temeprature for 15 min a solid separated, which was filtered to yield 220 mg (56.1%) of white product: mp 167-168°C (dec). Recrystallization from ethylene dichloride gave white plates of the same mp. ^{1}H NMR (Me_2SO-d_6) δ 4.78(m, 2H, CHBr); 5.44(m, 2H, CHN), 6.11(s, 2H, CHOH), 8.28(br s, 2H, OH)ppm; mass spectrum (CI, CH_4) m/z 43(100), 45(68), 47(66), 63(60), 81(34), 169(28), 373(2), 375(4), 377(M+1-H_2O, 2, Br = 81). Anal. Calcd. for $C_6H_8Br_2N_4O_6$: C, 18.38; H, 2.06; N, 14.29; Br, 40.77. Found: C, 18.86; H, 2.15; N, 14.33; Br, 40.43.

Diethyl-4,8-dibromo-2,6-dimethyl-3,7-dioxo-2,6-diazabicyclo[3.3.0]octane-4,8-dicarboxylate (43). - A stirred solution of 30 (31.23 g, 0.10 mol) in 1:10 pyridine-$CHCl_3$ (350 mL) was cooled in an ice bath during the rapid addition of bromine (32.76 g, 0.205 mol) in $CHCl_3$ (150 mL). After stirring overnight at room temperature, the solution was refluxed for 1 h, cooled and extracted once with water (100 mL), twice with 5% aqueous $NaHCO_3$ (100 mL), dried ($MgSO_4$) and evaporated under reduced pressure to leave a white residue. The product was triturated with ethyl acetate (150 mL), refrigerated overnight and filtered to yield 30.9 g of white solid: mp 172-175°C. Concentration of the filtrate to 50 mL and cooling yielded an additional 8.24 g of solid: mp 165-169°C (total yield 83.26%). The analytical sample, recrystallized from ethyl acetate as colorless prisms, had mp 179-181°C. ^{1}H NMR ($CDCl_3$) δ 1.41(t, 6H, CH_3), 3.07(s, 6H, CH_3N), 4.47(q, 4H, CH_2), 4.91(s, 2H, CH)ppm; mass spectrum (CI, CH_4) m/z 43(100), 47(34), 81(8), 83(7), 261(1), 313(2), 469(3), 471(5), 473(M+1, 3, Br = 81), 501(M+29, 0.4, Br = 81), 513(M+41, 0.2, Br = 81). Anal. Calcd. for $C_{14}H_{18}Br_2N_2O_6$: C, 35.76; H, 3.86; N, 5.96; Br, 34.00. Found: C, 35.80; H, 3.97; N, 5.97; Br, 33.76.

Diethyl-2,6-dimethyl-4,8-dinitro-3,7-dioxo-2,6-diazabicyclo[3.3.0]octane-4,8-dicarboxylate (44). - A mixture of 43 (2.35 g, 5 mmol), sodium nitrate (2.76 g, 40 mmol) and DMSO (20 mL) was stirred at room temperature for 3 days, then poured into a mixture of ice and water (70 mL) and extracted with $CHCl_3$ (3X50 mL). The combined extracts were washed with water (50 mL), 5% aqueous $NaHCO_3$ (50 mL), dried ($MgSO_4$) and evaporated under reduced pressure to leave a green-yellow oil. The oil was triturated with ether (15 mL) and the resulting precipitate filtered to give 1.25 g of yellow solid: mp 133-136°C. ^{1}H NMR analysis ($CDCl_3$) showed that this product consisted of a mixture of 44 and 29 in a ratio of about 4:1. The solid was dissolved in a stirred mixture of CH_3CN (5 mL) and water (2 mL) followed by the addition of sodium borohydride (50 mg). The color of the mixture changed from deep green to yellow in about 2 min, and after 5 min the mixture was diluted with water (25 mL). After stirring in an ice bath for 20 min, the precipitated solid was filtered to give 750 mg (31.3%) of fairly pure product (44): mp 129-132°C. Recrystallization from benzene-isopropyl ether gave colorless prisms: mp 133-135°C. ^{1}H NMR ($CDCl_3$) δ 1.38(t, 6H, CH_3), 3.18(s, 6H, CH_3N), 4.44(q, 4H, CH_2), 5.63(s, 2H, CH)ppm; mass spectrum (CI, CH_4) m/z 356(16), 357(100), 358(27), 403(M+1, 42), 431(M+29, 12), 443(M+41, 10). Anal. Calcd for

$C_{14}H_{18}N_4O_{10}$: C, 41.79; H, 4.51; N, 13.93. Found: C, 41.99; H, 4.65; N, 13.90.

Ditetrazolo[1,5-a:1,5-c]pyrazine (45). - Sodium azide (16.25 g, 0.25 mol) was added in portions over 10 min to a stirred solution of 2,3-dichloropyrazine (14.9 g, 0.1 mol) in DMSO (100 mL). The mixture was stirred at room temperature for 18 h and the resulting gel was then poured into a mixture of ice and water (350 mL) and the precipitated solid filtered, washed with water and air-dried to yield 12.43 g (76.7%) of yellow product: mp 260°C (violent dec).

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