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DESENSITIZATION OF EXPLOSIVE MATERIALS

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Under the sponsorship of the Office of Naval Research, SRI International is studying the desensitization of explosive compounds by replacing hydrogen and other selected substituents with fluorine. The objectives are to demonstrate that "chemical" desensitization can be achieved with fluorine and, if possible, to determine the mode of desensitization.

Previous work at SRI has shown that bis(2,2,2-fluorodinitroethyl) formal (FEFO) is desensitized when the formal hydrogens are replaced with fluorine. We

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Work in the previous research period showed that some desensitization could be achieved in bis(trinitroethyl) formal and in the fluorodinitroethyl ether of ethylene glycol. Work during this second year emphasized preparation and testing of one difluoraminoaliphatic formal and its corresponding difluoroformal, two partially fluorinated nitrate esters and the corresponding unfluorinated ester, and two fluoronitroalkanes and the corresponding nitroalkane. At the conclusion of this research period, a partially fluorinated nitramine and two isomeric fluoronitroaliphatic formals were being prepared.

Sensitivity test have shown that the classes of explosive compounds studied so far generally exhibit desensitization when one or more of their substituents are replaced by fluorine. Various degrees of desensitization have been demonstrated for nitroalkyl formals, nitroalkyl ethers, nitroalkanes, difluoroaminoalkyl formals, and nitrate esters.

PREFACE

This report is submitted in partial fulfillment of the contractual obligation for Contract No. N00014-76-C-0810, entitled, "Desensitization of Explosive Materials." The report summarizes the work performed during the period May 15, 1977, through May 14, 1978.

The research program was performed by staff of the Chemistry Laboratory of the Physical Sciences Division under the supervision of Marion E. Hill and Donald L. Ross. John M. Guimont was the principal investigator and was assisted in part of the synthesis by William Blucher. Small scale screening tests and "wedge" tests were conducted under subcontract by Lawrence Livermore Laboratory under the supervision of Dr. Kenneth Scribner.

We wish to acknowledge Dr. Richard S. Miller for his valuable suggestions and encouragement given to this work.

SUMMARY

Under the sponsorship of the Office of Naval Research, SRI International is studying the desensitization of explosive compounds by replacing hydrogen and other selected substituents with fluorine. The objectives are to demonstrate that "chemical" desensitization can be achieved with fluorine and, if possible, to determine the mode of desensitization.

Previous work at SRI has shown that bis(2,2,2-fluorodinitroethyl) formal (FEFO) is desensitized when the formal hydrogens are replaced with fluorine. We are preparing and testing nitroaliphatic formals and difluoroformals similar to FEFO and we are introducing fluorine into other explosive structures such as difluoraminoaliphatic formals, nitramines, and alkyl nitrates. The results, if desensitization is confirmed, would provide insight into how compounds explode and the general theory of desensitization.

Work in the previous research period showed that some desensitization could be achieved in bis(trinitroethyl) formal, and the fluorodinitroethyl ether of ethylene glycol. Work during this second year emphasized preparation and testing of one difluoraminoaliphatic formal and its corresponding difluoroformal, two partially fluorinated nitrate esters and the corresponding unfluorinated ester, and two fluoronitroalkanes and the corresponding nitroalkane. At the conclusion of this research period, a partially fluorinated nitramine and two isomeric fluoronitroaliphatic formals were being prepared.

Sensitivity tests have shown that the classes of explosive compounds studied so far generally exhibit desensitization when one or more of their substituents are replaced by fluorine. Various degrees of desensitization have been demonstrated for nitroalkyl formals, nitroalkyl ethers, nitroalkanes, difluoraminoalkyl formals, and nitrate esters.

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GLOSSARY

BDNPF	Bis(2,2-dinitropropyl)formal
DFF	Bis(2,2,2-fluorodinitroethyl)difluoroformal
DNE	1,1-Dinitroethane
EN	Ethyl nitrate
ETN	1,1,1,3-Tetranitro-3-azapentane
FDN	1,1,1-Fluorodinitroethane
FDNEF	1,2-Difluoro-1,1-dinitroethane
FEFO	Bis(2,2,2-fluorodinitroethyl)formal
FEN	2-Fluoroethyl nitrate
FPFO	Bis(3-fluoro-2,2-dinitropropyl)formal
NFDF	Bis[2,2-bis(difluoroamino)propyl]difluoroformal
NFPF	Bis[2,2-bis(difluoroamino)propyl]formal
NPFF	Bis(2,2-dinitropropyl)difluoroformal
TFEN	2,2,2-Trifluoroethyl nitrate
TFETN	1,1,1-Trifluoro-3,5,5,5-tetranitro-3-azapentane

INTRODUCTION AND BACKGROUND

The Armed Services have continuing problems with explosive materials with regard to their optimum formulation, end-use fabrication, toxicity, irregular burning, and premature detonation. Of these problems, accidental initiation of explosives has been one of the most formidable for research and technology developments to overcome. Because many approaches to the solution of hazard problems have become standardized, few new advances have been made to desensitize explosive ingredients. However, in earlier work for Lawrence Livermore Laboratory, desensitization of bis(fluorodinitroethyl) formal (FEFO) was achieved by substituting the hydrogen of the aldehydic carbon, $-OCH_2O-$, with fluorine to produce bis(fluorodinitroethyl) difluoroformal (DFF).

$FC(NO_2)_2CH_2OCH_2OCH_2CF(NO_2)_2$ FEFO

↓

$FC(NO_2)_2CH_2OCF_2OCH_2CF(NO_2)_2$ DFF

DFF had energy equivalent to FEFO but was dramatically less sensitive, especially to initiation of low velocity detonation (LVD). In card gap tests at SRI the attenuation required to reduce shock input to initiate FEFO was much greater (more sensitive) by several orders of magnitude than that required to initiate DFF. Table 1 presents the physical properties of these two compounds.

In tests at Lawrence Livermore Laboratory with the wedge configuration, DFF not only showed much less sensitivity toward initiation than FEFO, but also exhibited a larger failure thickness than FEFO.[2] (The "wedge" test consists essentially of a controlled shock pressure delivered by a donor explosive into a thin wedge-shaped film of a liquid acceptor explosive). Thus, both high velocity detonation (HVD) and LVD were

Table 1

PHYSICAL PROPERTIES OF FEFO AND DFF

	$[FC(NO_2)_2CH_2O]_2CH_2$ FEFO	$[FC(NO_2)_2CH_2O]_2CF_2$ DFF
Mol. wt.	320.1	356.1
bp, ^oC (mm)	110 (0.3)	70 (0.003)
mp, ^oC	+14	-17
vp, μ (25^oC)	0.16	1.6
ρ, g/cc (^oC)	1.59	1.67 (27)
ΔH_f^o, kcal/mol	-178	-275
DTA, ^oC	exotherm starts 209	exotherm starts 228 max 250
CRT, cc	0.04-0.1	0.04-0.06
LVD[a]	1500-1800	225-325
HVD[a]	80-85	77
Wedge Test		
LVD, threshold[b] (% PETN)	45	90
HVD, threshold[c] (% PETN)	95	100
Impact, kg-cm	6	135
Sound speed, mm/μsec	1.25	1.15
Compressibility, cm^2/dyne, ($\times 10^{11}$)	4.03	4.53
Detonation pressure, kbar[d]	229	213
Shock velocity, m/sec[d]	7272	6849

[a] Card gap test at SRI using 1/2-inch-diameter tubes.
[b] 1.6-mm wedge.
[c] 3.2-mm wedge.
[d] Estimated using TIGER Code; C_3H_3, C_2H_6, C_2H_2, C_3H_6, CH_2, CH, F_2, NF_3, F_2O, and F rejected as possible gaseous constituents.

initiated in FEFO at only 45 wt% PETN equivalent energy in the booster pellet at 1.6-mm film thickness. Neither the same energy nor indeed 100 wt% PETN would ignite DFF at the same film thickness. When the film thickness was increased to 3.2 mm, LVD in DFF was obtained at much higher input pressures, equivalent to 90 wt% PETN. Failure thickness for FEFO in the LVD mode was essentially zero at any thickness, and failure for DFF was at 0.2 mm at 3.2-mm initial thickness. Consequently these tests showed that pure undiluted FEFO was exceedingly dangerous (similar to nitroglycerin), but that DFF was much less hazardous by several orders of magnitude. Table 1 summarizes other physical property improvements obtained in DFF: lowered melting point and glass transition temperature higher density, decreased impact sensitivity, and lower toxicity.

We hypothesized that if "chemical" densensitization could be achieved by a simple replacement of H with F in one example of the formal class, then possibly other formals and other classes of explosive could be similarly desensitized with retention of energy. Such chemical desensitization is in contrast to the normal method of reducing hazard by diluting the energy with additional CH_2 groups in the molecule or by formulation of energetic explosives with desensitizing matrices (another method of dilution). Heretofore, ease of initiation followed in parallel with the energy of the explosive ingredient; that is, the most energetic compounds were the most sensitive. DFF sensitivity is an exception.

Subsequent work on this contract under the sponsorship of the Office of Naval Research (ONR) has confirmed the original observation and a study is now under way to ascertain whether desensitization by introducing fluorine into a molecule is a general phenomenon. The objectives of the current program are to: (1) prepare organic explosives having $-OCH_2O-$ and analogous $-OCF_2O-$ groups, and then extend the work to other explosives by modifying $-CH_2-$ and other selected groups; (2) verify that desensitization has been achieved by testing the compounds for sensitivity to initiation by shock wave, impact, and spark; (3) attempt to predict how desensitization may best be achieved by the introduction of fluorine into new molecules; (4) analyze the results in terms of molecular structure

to deduce how initiation is influenced by change in structure; and (5) develop an explanation of how sensitivity is affected by changes in chemical characteristics and physical properties.

All changes, including physical properties, caused by the introduction of fluorine are being studied to gain an understanding of the effect of replacing hydrogen or other groups in an explosive material. The relationship between various physical properties of an explosive and its sensitivity to initiation are not fully understood.

During the first year of this program, four compounds (two formals, two ethers) structurally similar to FEFO were prepared and tested; additional physical property measurements and theoretical calculations were completed for FEFO and DFF.[3] Tests have been run to compare the sensitivities of bis(trinitroethyl) formal, TEFO, and its fluorinated analog, TEDFO, with the sensitivities of FEFO and DFF. The results are shown in Table 2. The tests on TEFO and TEDFO for sensitivity to shock initiation by the card gap method were imprecise; however, we conclude that LVD can be initiated in each of these compounds with attenuation at least 64 inches in length. Both compounds were so sensitive that desensitization toward shock was difficult to distinguish. However, small-scale sensitivity and thermal stability tests showed reduction of sensitivity consistent with the trend in the formal class.

Analogous compound pairs of other classes of explosive liquids or low melting solids were also prepared in the initial research period. These include a pair of nitroaliphatic ethers, the bis(fluorodinitroethyl) ether of ethylene glycol, BFDEE, and its tetrafluoro analog, HTD.

$CF(NO_2)_2CH_2OCH_2CH_2OCH_2CF(NO_2)_2$ BFDEE

↓

$CF(NO_2)_2CH_2OCF_2CF_2OCH_2CF(NO_2)_2$ HTD

Table 2

COMPARISON OF PHYSICAL PROPERTIES OF TEST COMPOUND PAIRS

	FEFO	DFF	TEFO	TEDFO	BFDEE	HTD
mol wt	320.0	356.1	374.2	410.2	334.2	406.1
bp, °C (mm)	110(0.3)	70(0.003)	-	-	117-119 (0.01)	-
mp, °C	14	-17	65	16-18	30	33-35
vp, μ (25°C)	0.16	1.6	0.009	0.075	0.052	0.61
ρ, g/cm³ (25°C)	1.59	1.67	1.72	1.68	1.54	1.68
ΔH_f^o, kcal/mol (estimated)	-178	-275	-151	-243	-235	-421
DSC, °C, at 10°C/min	Exotherm 209	Exotherm 228	Endotherm 162	Nothing up to 207	Exotherm 167	Exotherm
Thermal stability, cm³/g	0.16-0.4[b]		0.36[c]	0.25[c]	0.12[c]	<0.01
LVD, cards[a]	1500-1800	225-325	>6400	>6400	None	None
HVD, cards[a]	80-85	77	Not determined		200-400	100-200
Impact, kg-cm	6	136	150	4-6 Liquid >250 Solid	50	>135
Sound Speed, mm/μsec	1.25	1.15	1.31	1.17	1.26	1.05
Compressibility, cm²/dyne, (c 10^{-11})	4.03	4.53	3.39	4.35	4.09	5.40
Detonation Pressure, kbar[d]	229	213	275	207	203	183
Shock Velocity, m/sec	7272	6849	7831	6860	7034	6384

[a] Card = 10 mil (0.254 mm).

[b] Values are for Lawrence Livermore CRT (chemical reactivity test) run on a 0.25-g sample at 120°C for 22 hr in an atmosphere of He.

[c] Values are for VTS (vacuum thermal stability test) run on a 0.25-g sample at 120°C for 22 hr at approximately 0.1 mm.

[d] Estimated using TIGER Code; C_3H_8, C_2H_6, C_2H_2, C_3H_6, CH_2, CH, F_2, NF_3, F_2O, and F rejected as possible gaseous constituents.

Desensitization was observed with these ethers in the sensitivity tests. In particular, HTD was less sensitive than BFDEE to shock initiation of LVD and HVD. Except for melting points of the latter compounds, the fluorinated analogs showed consistent improvements in physical properties and sensitivity characteristics when compared with hydrocarbons. The fluorinated analogs had higher density, higher vapor pressure, and lower melting point. They exhibited better thermal stability, decreased sensitivity to initiation by impact and shock wave, as well as slower sound speeds and greater compressibility.

Our goals during this second year have been to widen the scope of our program on desensitization by introduction of fluorine to include other classes of explosives and to determine the influence of selective introduction of fluorine into an explosive molecule. Thus, we have prepared and tested difluoroamino alkyl formals, nitroalkanes, and nitrate esters in order to determine if the desensitization effect is additive (more fluorine, more desensitization) and if the position of the fluorine in the molecule is a significant factor.

SENSITIVITY PROPERTIES

At the conclusion of the first year of this program, two pairs of ether type compounds--the bis(trinitroethyl) formal analogs and the analogous fluorodinitroethyl ethers of ethylene glycol--had been prepared, tested, and compared with data developed for FEFO and DFF, the "base pair". The test compounds showed the same general trend shown by the base pair in decreased sensitivity to shock initiation and impact initiation by introduction of fluorine. However, the structural similarity of the compounds limited any generalizations that could be made to the ether class. Our goals during this year have been to apply the desensitization concept to other classes of compounds and to correlate any results obtained from replacing functional groups, as well as hydrogen, by fluorine. Furthermore, it was desirable to ascertain if replacement of several hydrogens with fluorine (*a quantity effect*) was beneficial.

Because the demonstrable desensitizing effect so far has been with formals and ethers, one might infer that change in sensitivity is attributable to changing an $-OCH_2O-$ group to $-OCF_2O-$. Consequently, it seemed desirable to learn if placement of the fluorine on different kinds of carbon may correlate with changes in sensitivity properties. A useful approach to studying this is to prepare isomers of explosive compounds. The isomers should have similar energy content and any sensitivity differences should be attributable to the change in position of the fluorine. For example, we are preparing bis(2,2-dinitropropyl) difluoroformal (NPFF) for comparison with bis(3-fluoro-2,2-dinitropropyl) formal (FPFO); both will be compared with the well-known bis(2,2-dinitropropyl) formal, BDNPF.

$CH_3C(NO_2)_2CH_2OCH_2OCH_2C(NO_2)_2CH_3$ BDNPF

↓

$CH_3C(NO_2)_2CH_2OCF_2OCH_2C(NO_2)_2CH_3$ NPFF

↓

$FCH_2C(NO_2)_2CH_2OCH_2OCH_2C\ NO_2\ _2CH_2F$ FPFO

Another "practical change" can be achieved with substitution of fluorine on carbons with different substituents. For example, it is desirable to know if substitution of fluorine on a formal carbon has a different effect than on an alkane carbon, such as fluorine for hydrogen on a dinitromethyl group or for H on a CH_3 group.

Work on the nitramine class has been initiated. In this instance the methyl group of ethyl trinitroethyl nitramine will be replaced by a CF_3 group. Results from testing these will guide further work on nitramines. Attempts to prepare fluorinated RDX gave only unstable products or explosives.

The three new classes of compounds tested in this period, difluoraminoalkyl formals, nitrate esters, and nitroalkanes, all demonstrated some form of desensitization. We feel that the evidence accumulated so far does not contra-indicate that proper placement of fluorine in a molecular structure will achieve a degree of desensitization and, in some cases, almost complete desensitization.

Comparison of NFPF with NFDF

Impact sensitivity tests at LLL and SRI both showed that NFDF, bis[(2,2-bis(difluoroamino)propyl]difluoroformal, has reduced sensitivity to impact, compared with the hydrogen analog, NFPF, despite the reduced thermal stability shown by DSC measurements in a confined cell. Little change in boiling point or vapor pressure was noted with the introduction of fluorine, but the decrease of sound speed, increase in density, and increase in compressibility follow the general trend established previously.

No difference was observed in sensitivity of NFDF and NFPF to electrostatic discharge, although both were sensitive.

Small-scale screening tests at LLL revealed that these compounds were too sensitive to handle in the neat form required for wedge tests. Consequently, the wedge tests were not attempted.

Comparison of EN with FEN and TFEN

With the ethyl nitrate (EN), fluoroethyl nitrate (FEN), and trifluoroethyl nitrate (TFEN) series of compounds, we wanted to learn about the effect of the quantity of fluorine on various physical properties. The effect on sensitivity to impact seems to be progressive; one fluorine has a small effect and three fluorines have a larger effect. The effect of one fluorine on boiling point, vapor pressure, sound speed, and compressibility is the opposite of the expected trend, whereas the effect of three fluorines parallels the expected trend. Also the thermal stability of TFEN is less than either EN or FEN, which is the reverse of the expected trend.

Comparison of DNE with FDN and FDNEF

The physical property changes in the dinitroethane (DNE), fluorodinitroethane (FDN), and difluorodinitroethane (FDNEF) series follows the general trend, with the substitution effects becoming more pronounced when the second fluorine is introduced. Thermal stability is improved by introduction of the first fluorine but is not further improved by the second fluorine. The principal effect of the fluorine at the C-1 position derives from replacement of the very acidic hydrogen without much steric change. For impact sensitivity, the first fluorine has no effect and the second fluorine has some effect. For shock sensitivity, the first fluorine has a significant effect but the second does not.

With the data currently available to us, it is not possible to come to any sound conclusion on the manner of desensitization by fluorine. However, three important points are suggested by the data available.

(1) The impact desensitizing effect of fluorine appears to be additive in that the order of sensitivity for the nitrate esters is TFEN < FEN < EN. (2) The position in the molecule at which fluorine is introduced appears to be significant and appears so far to affect impact and shock sensitivity differently. That is, a comparison of DNE and FDN shows that shock sensitivity but not impact is reduced in FDN. Conversely, a comparison of FDN and FDNEF shows that impact sensitivity but not shock is reduced in FDNEF. Fluorine placed on the same carbon as the nitro groups has one effect, and fluorine placed on the other carbon has a different effect. (3) For all the compounds tested on this program, there appears to be a relationship between thermal stability in a confined cell and shock sensitivity; that is, those compounds with improved thermal stability have reduced shock sensitivity. However, no such relationship is apparent for impact sensitivity. In fact, for some pairs of compounds (NFPF/NFDF and EN/TFEN), the fluorinated analogs are less thermally stable and still less sensitive to impact.

Our original premise that desensitization can be achieved by selected substitution of fluorine for hydrogen in an explosive molecule is confirmed by results achieved so far for the classes that have been studied. However, the usefulness of the observation is based on the further premise that the phenomena is applicable to those analogs that have the same or nearly the same energy. FEFO and DFF, which have equivalent energy, are good examples. Thus, it is necessary to avoid diluting a molecule with less energetic bonds because the results then may correspond only to the "standard" method of achieving desensitization--that is, diluting the molecule or formulation with additional CH_2 groups to reduce the oxygen balance or to change physical properties. Consequently, energy calculations are made on each analogous series and, where possible, examples are chosen in which the fluorine introduced does not appreciably affect the energy. There are also some cases wherein the fluorinated molecule is more energetic than the hydrogen analog; however, proof of principle is the overriding consideration in choice of compounds.

Our test compounds are exemplary of explosive structures that are sensitive because of the position and quantity of the energetic groups. If substitution of F for H in a formal grouping (or in a nitroalkane, difluoramine compound, or other class of explosive) produces detectable desensitization, then one is tempted to infer that the desensitization effect is independent of the type of explosive group (e.g., nitro or nitrato group) in the molecule. This independence may be a phenomenon of "chemical" desensitization that influences the bond breaking step, or it may be due to a change in physical properties that are related to the ease with which a particular molecule absorbs energy. The molecule nonetheless begins to decompose and release energy exothermally over a brief time period--an explosion. Further work is needed to determine conclusively whether or not the effect of introducing fluorine at selected sites is a true chemical desensitization, affecting the intra-action of the molecular constituents, or whether or not it primarily has a physical property effect. It may be a combination of both. Consequently, any theory development has to be cognizant of physical property changes that may affect sensitivity.

Work to date has emphasized exchanging fluorine for hydrogen. However, we now are studying the effects of the exchange of fluorine for other atomic or group substituents, such as F for NO_2, F for OH, F for CH_3, and so on. Such comparisons will be only correlative at first to ascertain any apparent trends. Results of the correlations will be used to identify specific compound pairs to prepare for testing any theoretical explanation that is developed.

SYNTHESIS OF EXPLOSIVES FOR SENSITIVITY TESTS

At the end of the first year of this program, preparation of two difluoraminoalkyl formals was in progress. Both had been successfully prepared, but the overall yield of the synthetic route was poor. Thus, our initial effort during this second year was to attempt to improve the yields and to prepare enough material for testing.

Difluoraminoalkyl Formals

We expended considerable effort in preparing the difluoraminoalkyl formals because they represent a class of hazardous compounds for which desensitization has not been demonstrated. Difluoramino compounds are very sensitive to initiation by impact and shock; therefore, desensitization of these compounds not only would widen the scope of our desensitization approach, but also might permit incorporation of such compounds into explosive or propellant systems for which they are currently too sensitive.

Bis[2,2-bis(difluoramino)propyl]difluoroformal (NFDF) was synthesized by the route shown in Equations (1) to (5).

$$HOCH_2C(O)CH_3 \xrightarrow[(1)]{(CF_3CO)_2O} CF_3COOCH_2C(O)CH_3$$

$$\xrightarrow[(2)]{HNF_2} CF_3COOCH_2C(NF_2)_2CH_3 \xrightarrow[(3)]{CH_3OH}$$

$$HOCH_2C(NF_2)_2CH_3 \xrightarrow[(4)]{CSCl_2} [CH_3C(NF_2)_2CH_2O]C = S$$

$$\xrightarrow[(5)]{SF_4} [CH_3C(NF_2)_2CH_2O]_2CF_2$$

NFDF

Although the first four steps in the route are well known, none of them are exceptionally high yield reactions and the overall yield is only 15%. Equation (5) is a high yield reaction (80%) that entails the novel fluorination of a thionocarbonate under very mild conditions. Detailed information regarding this reaction is presented in Appendix A, which is a communication that will be submitted to Synthesis for publication. In addition to low yields, the synthesis is complicated by the hazardous properties of all the difluoramino-containing intermediates. Because of the hazard involved, only reaction (1) could be carried out on a large scale. A total of 20 g of NFDF was prepared, and most of that was consumed in the preliminary sensitivity testing. Because of poor yields in the synthetic route and the hazards involved, we concluded that preparation of sufficient material for shock sensitivity measurements would be prohibitively time-consuming and expensive.

Bis[2,2-bis(difluoramino)propyl]formal (NFPF), the hydrogen analog of NFDF, was prepared according to the following reaction.

$$CH_3C(NF_2)_2CH_2OH \xrightarrow[(6)]{HCHO/H_2SO_4} [CH_3C(NF_2)_2CH_2O]_2CH_2$$

NFPF

All the synthetic problems discussed in connection with NFDF apply here as well. The low yield is primarily due to difficulties with reaction (6). Success of reaction (6) is dependent on forcing the equilibrium between the difluoramino alcohol and formal to the product side in sulfuric acid solution. Unfortunately, all the reaction conditions that favor formation of the desired formal also favor decomposition of both the starting alcohol and formal through loss of the difluoramino groups.[4] A total of 12 g of NFPF was prepared for preliminary testing, but, as in the case of NFDF, preparation of large quantities required for shock sensitivity testing was prohibitively expensive and time-consuming.

Nitrate Esters

The second class of compounds tested this year are the nitrate esters ethyl nitrate (EN), 2-fluoroethyl nitrate (FEN), and 2,2,2-trifluoroethyl nitrate (TFEN). These compounds were chosen because they represent a new class of compounds for which desensitization with fluorine has not been demonstrated. They also present the opportunity to determine if the desensitization effect is additive--that is, if three fluorines will result in more desensitization than one fluorine. EN is available commercially, and FEN and TFEN were reported in the open literature; however, the latter two were prepared in moderate yields using nitronium tetrafluoroborate. After a brief investigation, we found that both FEN and TFEN could be prepared in high yield using a mixture of nitric and sulfuric acids, as shown in Equation (7).

$$RCH_2OH \xrightarrow[(7)]{HNO_3/H_2SO_4} RCH_2ONO_2$$

$$R = FCH_2-,\ CF_3-$$

A total of 100 g of each of FEN and TFEN was prepared and delivered to LLL for the wedge test after preliminary testing was completed at SRI.

Nitroalkanes

Three nitroalkanes were prepared and tested during this report period--1,1-dinitroethane (DNE), 1,1,1-fluorodinitroethane (FDN), and 1,2-difluoro-1,1-dinitroethane (FDNEF). All three compounds have been prepared previously,[6,7,8] and no difficulties were encountered in their syntheses, Equations (8) to (12).

$$CH_3C(NO_2)_2CH_2OH \xrightarrow[(8)]{KOH} KC(NO_2)_2CH_3 \xrightarrow[(9)]{H_2SO_4} HC(NO_2)_2CH_3$$

DNE

$$HC(NO_2)_2CH_3 \xrightarrow[(10)]{NaOH} NaC(NO_2)_2CH_3 \xrightarrow[(11)]{F_2} FC(NO_2)_2CH_3$$

FDN

$$FC(NO_2)_2CH_2OH \xrightarrow[(12)]{SF_4} FC(NO_2)_2CH_2F$$

FDNEF

After preliminary testing was completed at SRI, 150 g of DNE, 150 g of FDN, and 90 g of FDNEF were prepared and delivered to LLL for the wedge tests.

Nitramines

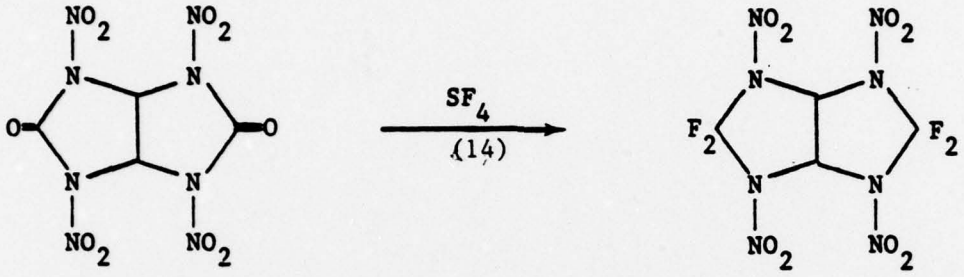
Several attempts were made to prepare fluorinated nitramines during this report period; for example, efforts to prepare perfluoro-RDX by reaction (13) resulted in an unstable, unidentified product.

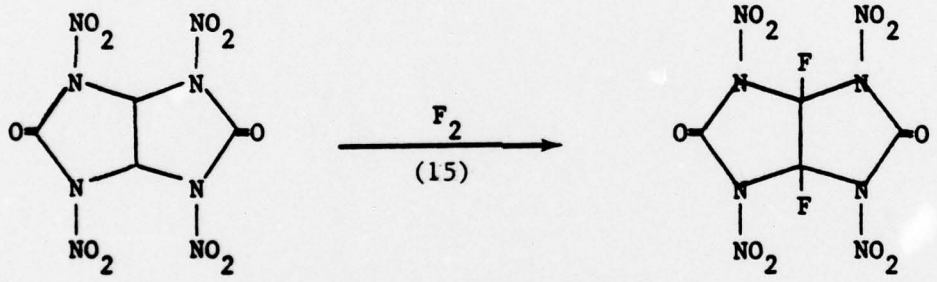
$$(FCN)_3 + 3NO_2F \xrightarrow[(13)]{} (CF_2NNO_2)_3$$

perfluoro-RDX

Our experimental procedure was based on vague information provided by the reported reaction of cyanuric fluoride with chlorine monofluoride.[9] The reaction consumed a theoretical amount of nitryl fluoride to give a product that reacted vigorously with sodium chloride plates and slowly decomposed to volatile products after standing at ambient temperature.

Several attempts were made to fluorinate tetranitroglycoluril (TNGU), Eqs, (14) and (15), using sulfur tetrafluoride and elemental fluorine, respectively.





The first reaction with sulfur tetrafluoride using titanium tetrafluoride as a catalyst at 100°C gave no reaction, and a second attempt at 120° resulted in detonation of the mixture after a 20-min reaction time. Work on this reaction has been discontinued for safety reasons. Fluorinations using elemental fluorine, and with hydrofluoric acid as a solvent, were unsuccessful in the past. We have since tried reaction (15) using acetonitrile as a solvent and also as a solid phase reaction by mixing TNGU with sodium fluoride. Both resulted in no reaction.

Efforts to prepare fluorinated RDX or TNGU as examples of desensitized nitramines were suspended when we learned that an example of a fluorinated nitramine had been prepared by Dr. Milton Frankel[10] (Rocketdyne) and had been found to be less sensitive to initiation by impact than its hydrogen analog.

We have prepared 1,1,1-trifluoro-3,5,5,5-tetranitro-3-azapentane (TFETN) and 1,1,1,3-tetranitro-3-azapentane by the routes shown in (16) to (17) and (18) to (19), respectively.

$$CF_3CH_2NH_2 \cdot HCl + C(NO_2)_3CH_2OH \xrightarrow[(16)]{NaOAc/H_2O} CF_3CH_2NHCH_2C(NO_2)_3$$

$$\xrightarrow[(17)]{HNO_3/Ac_2O} CF_3CH_2N(NO_2)CH_2C(NO_2)$$

TFETN

$$CH_3CH_2NH_2 + C(NO_2)_3CH_2OH \xrightarrow[(18)]{AcOH/H_2O} CH_3CH_2NHCH_2C(NO_2)_3$$

$$\xrightarrow[(19)]{HNO_3/Ac_2O} CH_3CH_2N(NO_2)CH_2C(NO_2)_3$$

ETN

TFETN was easily prepared using experimental details provided in the referenced patent, but no details or physical properties were given for ETN. After several unsuccessful attempts to prepare ETN following the same general procedure used to prepare TFETN, we found that reaction (18) yielded the secondary amine in an acetic/water mixture at a pH of 4.1 to 5.1. Optimum conditions for the reaction have not been determined, but we were able to prepare ETN in sufficient quantity to complete preliminary testing, which is in progress. Reaction conditions will be optimized before we prepare larger quantities for shock sensitivity tests.

Nitroalkyl Formals

We have begun to investigate three nitroalkyl formals--bis(2,2-dinitropropyl)formal (BDNPF), bis(2,2-dinitropropyl)difluoroformal (NPFF), and bis(3-fluoro-2,2-dinitropropyl)formal (FPFO) to provide proof of principle in the isomer approach. BDNPF is well known. NPFF was prepared under an earlier contract[11], by Equations (20) and (21), and preparation of additional material has presented no major problems.

$$CH_3C(NO_2)_2CH_2OH \xrightarrow[(19)]{COCl_2} [CH_3C(NO_2)_2CH_2O]_2CO$$

$$\xrightarrow[(21)]{SF_4/HF} [CH_3C(NO_2)_2CH_2O]_2CF_2$$

NPFF

The sensitivity properties of NPFF should be different than those of BDNPF because the formal/difluoroformal structural relationship directly parallels the FEFO/DFF pair for which desensitization has already been demonstrated.

FPFO was prepared by Equations (22) and (23) to compare its sensitivity to BDNPF and NPFF and to determine if the position of fluorine in the molecule affects desensitization.

$$HOCH_2C(NO_2)_2CH_2OH \xrightarrow[(22)]{SF_4} FCH_2C(NO_2)_2CH_2OH$$

$$\xrightarrow[(23)]{HCHO/H_2SO_4} [FCH_2C(NO_2)_2CH_2O]_2CH_2$$

FPFO

3-Fluoro-2,2-dinitropropanol, the precursor to FPFO, was previously prepared[12] from A-Diol using sulfur tetrafluoride and hydrofluoric acid at high temperature in an autoclave, but the yield was poor (18%). Several attempts to prepare the alcohol in better yield led to the discovery that sulfur tetrafluoride could be used as an effective fluorinating agent at ambient temperature in pyridine-polyhydrogen fluoride reagent. Complete details of our investigation of the reaction are presented in Appendix B, which is a note that will be submitted to the Journal of the American Chemical Society for publication. Conversion of the alcohol to the formal, FPFO presented no difficulties, and enough material is on hand to conduct preliminary tests.

The physical properties of the compounds prepared during this report period are shown in Table 3 (see next section).

CHARACTERIZATION AND SENSITIVITY TESTING

All the compounds prepared during this program have been or will be well-characterized by physical property and sensitivity measurements. Vapor pressures, densities, melting points, boiling points, thermal stabilities, sound speeds, and sensitivities to initiation were all experimentally determined in our laboratories. Heats of formation, compressibilities, detonation pressures, and shock velocities were all estimated using well-established techniques. The measured and estimated properties of the subject compounds are shown in Table 3.

Physical Properties

The physical property measurements and calculations (vapor pressure, density, sound speed, and compressibility) were made using the same procedures as reported previously.[3] The changes in physical properties due to introduction of fluorine follow the same trend as determined for FEFO/DFF, with the exception of the vapor pressure, sound speed, and compressibility of FEN.

Thermal Stability

The thermal stability of the test compounds was determined by two methods. First, differential thermal analyses (DTA) were run using an open pan in air; however, most of the new compounds are low boiling and exhibited only endotherms at the boiling point. An exception was dinitroethane, which decomposed at 100°. Second, differential scanning calorimetry (DSC) was run at LLL on each compound under a nitrogen atmosphere in a sealed holder. Because the sample holders were sealed, the materials could be heated beyond their boiling points to observe their decomposition temperature. All the compounds decomposed exothermally with DSC.

Table 3

COMPARISON OF PROPERTIES OF TEST COMPOUNDS

	Difluoramino		Nitrate Esters			Nitroalkanes			Nitramines		Dinitropropyl Formals		
	NFPF	NFDF	EN	FEN	TFEN	DNE	FDN	FDNEF	ETN	TFETN	BDNPF	NPFF	FPFO
Mol. wt	336.21	379.19	91.07	109.06	145.05	120.07	138.06	156.06	253.15	307.12	312.2	348.2	348.2
bp, °C (mm)	67(0.15)	48(0.15)	86(760)	127(760)	66(760)	55(4)	55(35)						
mp, °C									64	59	33	18	41
vp, mm (25°C)	0.025	0.020	64	7.6	150	0.56	9	17					
ρ, g/cm³ (25°C)	1.45	1.51	1.10	1.33	1.48	1.35	1.41	1.55	1.66	1.86	1.56	1.51	1.63
ΔH°_f, kcal/mol {calculated	-177	-269	-47	-93	-185	-41	-87	-133	-50	-189	-142.7	-252.5	-252.5
DTA[a]	237 Endo	214 Endo	70° Endo	113 Endo	55 Endo	100 Exo	115 Endo	105 Endo					
DSC[b]	187 Exo	114 Exo	175 Exo	176 Exo	140 Exo	88 Exo	206 Exo	204 Exo					
LLL Impact, cm[c] (2.5 kg)	11.9	27.5	>177	>177	>177	>177	>177	>177					
SRI Impact, kg-cm[d]	2-3	6	1-2	4-5	20-22	35-40	35-40	45-50					
Wedge Test, % PETN in Donor at Threshold (thickness)	-	-	>100(1/8)	>100(1/8)	>100(1/8)	50-55(1/16)	60-70(1/8)	55-60(1/8)					
Sound Speed, mm/μsec	1.06	0.95	1.12	1.24	0.86	1.34	1.09	1.02					
Compressibility, cm²/dyne, (x 10^{-11})	6.14	7.34	7.30	4.93	9.17	4.16	6.02	6.21					
Detonation Pressure, kbar	170	e	132	163	138	192	182	182	289	276	246	193	226
Shock Velocity, m/sec	6365	e	6679	6640	5717	7259	6763	6473	8170	7571	7841	6979	7360

[a] Run in open aluminum pan with heating rate of 10°/min.
[b] Run in a sealed pan under nitrogen with heating rate of 10°/min.
[c] LLL drop-hammer standards; nitroglycerine (19.8 cm) and FEFO (50 cm); sample impacted on an open plate.
[d] SRI impact standards; HMX (34 kg-cm) and propyl nitrate (4.5 kg-cm); impacted in sealed holder.
[e] TIGER Code unable to calculate, probably because of high fluorine content or discontinuities in the Hugoniot due to phase changes.

Introduction of fluorine improved the thermal stability of FDN and FDNEF compared with DNE, but FDN and FDNEF were essentially the same. Introduction of one fluorine did not improve the stability of FEN over EN, but introduction of three fluorines caused a decreased thermal stability of TFEN compared with EN and FEN. Introduction of fluorine also reduced the stability of NFDF compared with NFPF. THe general trend of improved thermal stability with introduction of fluorine observed in other compounds during the first year of this program has not been corroborated by this new series of compounds. With the limited amount of data available, we can propose no sound rationale for the effects observed.

Vacuum thermal stability tests could not be run due to volatility of this group of compounds.

Impact Sensitivity

Impact sensitivity measurements were made using two types of machines having different physical arrangements. Tests at SRI were conducted with the liquid samples confined in a steel chamber sealed with an O-ring and rupture disc. Tests at LLL were run using a machine in which the sample is placed on an open plate. No real parallel can be drawn between the two test methods. The data show that sensitivity to impact initiation of samples of the same compound under differing conditions is being measured.

Most of the materials were too insensitive to impact to be initiated by the LLL method; however, NFDF was shown to be less sensitive, which agrees with the SRI test. The SRI test indicates that nitrate esters show reduced sensitivity as one and the three fluorines are introduced into EN. For the nitroalkanes, introduction of one fluorine into DNE apparently has no effect (at least in the position it was introduced), but the second fluorine does result in desensitization. It appears that two fluorines are needed to produce desensitization or that the fluorine must be in the correct location in the molecule.

Spark Sensitivity

All the subject compounds were tested for sensitivity to electrostatic discharge as described in our previous annual report. Only NFPF and NFDF were sensitive, and both exhibited a threshold at 16 mj.

Shock Sensitivity

In our last annual report we discussed several difficulties that were encountered in measuring sensitivity to shock initiation with the card gap test. Consequently, we have adopted the wedge test as our criterion for judging shock sensitivity of liquid compounds.

The test arrangement consists of a flat shot tray of 6061-T6 aluminum alloy plate 12.7 mm thick, 50.8 mm wide, and 380 mm long. Polymethylmethacrylate (PMMA) was used on the sides and a 0.5-mm-thick piece of epoxy was fixed to one end to confine the liquid on the plate. A PMMA fixture was used to align the detonator-booster assembly on the closed end of the plate with its center on the liquid-aluminum interface.

The shot tray was leveled on the table and then shimmed so that the open end was elevated either 1.6 or 3.2 mm. Liquid was added to form a long, thin wedge tapering from either 1.6 or 3.2 mm thickness at the initiator end to zero at a position 305 mm along the plate. The aluminum base became a witness plate that clearly showed the various reactions occurring during the test.

The donor system consisted of an exploding bridgewire detonator filled with low-density PETN (ρ = 0.95 g/cm^3), a booster pellet 12.7 mm in diameter by 12.7 mm long, and a 0.5-mm epoxy attenuator. The booster pellets consisted of blends of PETN and pentaerythritol pressed to 90.0 $\pm$ 0.5% of their theoretical maximum density. The PETN concentration ranged from 20 to 100 wt% in 5% increments, giving a variable output donor. Lower concentrations of PETN could not be made to detonate reliably. The input pressures of the donors were previously determined and ranged from 50.7 to 185 kbar.

The results of each shot are based on the condition of the aluminum plate after the shot. High velocity detonations (HVD) leave a definite depression in the plate, low velocity detonations (LVD) cause scratching and pitting of the plate, burning of the sample leaves the plate dry, and a "no go" leaves a wet plate. Samples that will not detonate using a 1.6 mm wedge (presumably because of a greater failure thickness) are subjected to testing with the 3.2 mm wedge. Results of all the shots are given in Table 4.

None of the nitrate esters exhibited an HVD or LVD with maximum input pressure, but several shots resulted in a dry plate, indicating that the sample had burned.

All the nitroalkanes detonated in the high velocity mode when subjected to shock. The threshold for DNE (50-55% PETN) is clearly below (more sensitive) that of FDN (60-70% PETN), especially since the wedge thickness had to be increased to 1/8 in. to observe detonation for FDN. The threshold for FDNEF (55-60% PETN) at 1/8 in. is about the same as FDN, but it is clearly less sensitive to shock than DNE.

Detonation Pressure and Velocity Calculations

Detonation pressures and velocities were calculated using TIGER Code. In general, the introduction of fluorine into a molecule to replace hydrogen results in reduced detonation pressure and velocity due to the more negative heat of formation. The nitrate ester series is an interesting exception. FEN has a higher pressure than EN, where TFEN has about the same pressure as EN.

It is difficult to weigh the various parameters, which change upon introduction of fluorine, but it appears that the increase in pressure is due to the increased density of FEN over EN and the ability of fluorine to convert residual carbon to gaseous CF_4 upon detonation. When two more fluorines are introduced (TFEN), the increase in pressure achieved by FEN is lost. Solid carbon is virtually eliminated from the detonation products and the density is a little higher, but these factors are apparently overcome by the large decrease in heat of formation.

Table 4

WEDGE TEST RESULTS

Sample	Wedge Thickness	% PETN in Donor	Result[a]
DNE	1/16	100	HVD-Partial LVD
DNE	1/16	60	HVD only
DNE	1/16	30	No go
DNE	1/16	40	No go
DNE	1/16	50	No go
DNE	1/16	60	HVD only
DNE	1/16	55	HVD only
FDN	1/16	55	No go
FDN	1/16	65	No go
FDN	1/16	100	No go
FDN	1/8	100	HVD only
FDN	1/8	80	HVD and LVD
FDN	1/8	70	HVD only
FDN	1/8	50	No go
FDN	1/8	60	No go
FDNEF	1/8	70	HVD and LVD
FDNEF	1/8	50	No go
FDNEF	1/8	60	HCD and LVD
FDNEF	1/8	55	No go
EN	1/8	100	Burn
EN	1/8	100	Burn
EN	1/8	75	Burn
FEN	1/8	100	No go
FEN	1/8	100	No go
TFEN	1/8	100	Burn

[a] HVD = High velocity detonation
LVD = Low velocity detonation.

Replacement of hydrogen with fluorine appears to give a more energetic explosive, provided the density increase is large and the hydrogen analog has a significant amount of residual carbon after detonation.

EXPERIMENTAL DETAILS

The following experiments are given in detail because they describe the synthesis of either new compounds or key intermediates. Elemental analyses were performed by Georgina Hum using a Perkin-Elmer Autosampler, infrared spectra were run using a Perkin-Elmer 247 Spectrophotometer, ^{1}H-nmr spectra were run using a Varian EM-360 Spectrometer, and ^{19}F-nmr were run using a Varian XL-100 Spectrometer.

2-Fluoroethyl Nitrate (FEN)

2-Fluoroethanol (17.5 g, 0.27 mol) was placed in a 200 ml, three-neck flask fitted with a thermometer, addition funnel, and magnetic stirrer, and was cooled to 5°. 100% nitric acid (34 g, 0.54 mol) was added dropwise at 5-10° followed by 100 g of 97% sulfuric acid, also at 5-10°. The reaction was stirred at 10° for 15 min, and then poured onto 300 g of ice. The organic phase was separated, washed three times with an equal volume of water, and dried over calcium chloride. Ir (film): 1640, 1280 (s, ONO_2), 1060, 910, 860 cm^{-} (S, CF). Pmr ($CDCl_3$): 4.4 and 5.08, unresolved multiplets.

1,1,1,3-Tetranitro-3-Azapentane (ETN)

To a solution of 1.81 g (10 mmol) of trinitroethanol in 20 ml of water was added 0.3 g (5 mmol) of acetic acid at 25°. To this was added dropwise, at 25°, 0.65 g (11 mmol) of 70% aqueous ethyl amine. The mixture was stirred for 1 hr at 25° and then evaporated to dryness. The residue was dissolved in 10 ml of acetic anhydride and cooled to 0°. To this was added dropwise 15 ml of 100% nitric acid at 0-5°. After stirring for 1 hour at 0-5°, the reaction mixture was poured onto 50 g of ice, and the product was removed by filtration and dried to yield 0.55 g, 22% yield. After recrystallization from chloroform/hexane, ETN melted at 64°. IR (KBr): 1580, 1530, 1280, 1260 cm^{-} (S, NO_2). Pmr ($CDCl_3$): 5.45 (S, $C\underline{H}_2CNO_2$), 3.87 (q, J = 7 Hz, $C\underline{H}_2$), and 1.30 δ (T, J = 7 Hz, $C\underline{H}_3$).

Bis (3-Fluoro-2,2-Dinitropropyl) Formal (FPFO)

A previously prepared solution of 0.6 g (20 mmol) of paraformaldehyde in 5 ml of 97% sulfuric acid was added dropwise at 25° to a solution of 2.35 g (20 mmol) of 3-fluoro-2,2-dinitropropanol in 10 ml of methylene chloride. The reaction mixture was stirred vigorously for 30 min after which the methylene chloride phase was separated. The acid phase was extracted three times with 10-ml portions of methylene chloride, which were combined with the original methylene chloride solution, dried over magnesium sulfate, and evaporated, leaving 2.35 of pale-yellow oil that crystallized on cooling. Recrystallization from chloroform/hexane yielded 1.3 g (52% yield) of FPFO, which melted at 41°. IR (film): 1560, 1320 (S, NO_2), 1040 cm^{-1} (S, CO). Pmr ($CDCl_3$): 5.30 (d, J = 45 Hz, $FC\underline{H}_2$), 4.85 (S, $OC\underline{H}_2O$), 4.50 δ (d, J = 3 Hz, $C\underline{H}_2O$).

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Appendix A

PREPARATION OF DIFLUOROFORMALS FROM THIONOCARBONATES

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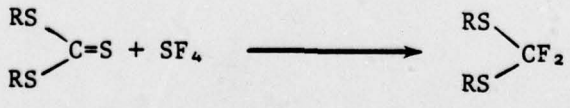
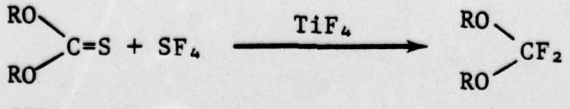
Preparation of difluoroformals by the action of sulfur tetrafluoride on dialkyl carbonates has been reported.[1,2] The procedures require large quantities of hydrofluoric acid, which acts as both solvent and catalyst, and temperatures in excess of 200°C. The presence of hydrofluoric acid and high temperatures limit the scope of the reaction in that dialkyl carbonates containing sensitive functional groups are likely to degrade under the reaction conditions. Several times in the past[3] we have attempted to prepare difluoraminoalkyl difluoroformals from difluoraminoalkyl carbonates, but we were unsuccessful due to incompatibility of the highly reactive N,N-difluoraminoalkyl group with hydrofluoric acid at elevated temperatures. Since thiocarbonates (1) have been fluorinated under milder conditions using Lewis acid catalysts or no catalyst at all,[4] it seemed reasonable that thionocarbonates (2) could be fluorinated under mild conditions to give difluoroformals (3).



(1)



(2) (3)

3a, R = $FC(NO_2)_2CH_2$-

3b, R = $CH_3C(NF_2)_2CH_2$-

We wish to report the synthesis of difluoroformals by fluorination of thionocarbonates with sulfur tetrafluoride in the presence of catalytic titanium tetrafluoride at relatively low temperatures. Thus, bis(1,1,1-fluorodinitroethyl) thionocarbonate and di[2,2-bis(difluoramino)propyl] thionocarbonate were fluorinated to yield the corresponding difluoroformals (3a and 3b). The use of thionocarbonates in place of carbonates permits the use of much lower reaction temperatures and eliminates the need for hydrofluoric acid.

We have not investigated the reaction mechanisms; however, the presence of elemental sulfur in the reaction product strongly suggests that the mechanism is the same as that proposed by Harder and Smith,[4] which involves disproportionation of the byproduct SSF_2 to S° and SF_4.

The compounds described in this paper are explosives; fluorodinitromethyl compounds cause severe burns on contact with skin, and all gaseous reactants and products are highly toxic. Therefore, all materials should be handled with extreme caution.

Bis (2-fluoro-2,2-dinitroethyl) Difluoroformal (3a)

Bis(2-fluoro-2,2-dinitroethyl) thionocarbonate (1.0 g, 3 mmol) and titanium tetrafluoride (0.04 g, 0.3 mmol) were placed in an 18-ml Monel high-pressure reactor. The reactor was cooled to -78°C and charged with 2 g (18 mmol) of sulfur tetrafluoride. The reaction was heated to 110°C for 48 hr with shaking. The reactor was cooled and vented, and the contents were removed in methylene chloride. The solution was washed with water, treated with NaF and $MgSO_4$, and filtered; the solvent was removed, leaving 0.74 g of liquid product (70% yield, DFF), bp. 70°C at 3 μ.

$C_5H_4F_4N_4O_{10}$	Calc.	C 16.87	H 1.13	N 15.73	F 21.34
356.1	Found	C 16.94	H 1.01	N 15.65	F 21.56

^{1}H-N.M.R. ($CDCl_3$): δ = 4.91 (doublet, 2H, J_{HF} = 15 Hz)

^{19}F-N.M.R. ($CDCl_3$): ϕ = 132 (broad triplet), 89 (triplet) referenced to $CFCl_3$

Di [2,2-bis(difluoramino)propyl]difluoroformal (3b)

Di [2,2-bis(difluoramino)propyl] thionocarbonate (0.5 g, 1.4 mmol and titanium tetrafluoride (0.05 g, 0.4 mmol) were placed in an 18-ml Monel high-pressure reactor. The reactor was cooled to -78° and charged with 5 g (46.3 mmol) of sulfur tetrafluoride. The reactor was then heated to 65° on a shaker for 18 hr. After the reactor was cooled and vented, the product was washed out with methylene chloride. The methylene chloride solution was stirred for 24 hr with mercury to remove residual sulfur, filtered, and evaporated to a pale-yellow liquid that was distilled at 48° (0.15 mm); 0.24 g (48% yield)

$C_7H_{10}F_{10}N_4O_2$ Calc. C 22.59 H 2.71 N 15.06

360.2 Found C 22.22 H 2.62 N 14.76

^{1}H-N.M.R. ($CDCl_3$): δ = 1.70 (quint, 3H, J = 2Hz), 4.40 ppm (quint, 2H, J = 2Hz)

^{19}F-N.M.R. ($CDCl_3$): δ = 27.6 (d, J = 6 Hz), -65.9 ppm (s) Referenced to $CFCl_3$.

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Appendix B

SF_4 FLUORINATION AT ATMOSPHERIC PRESSURE[1]

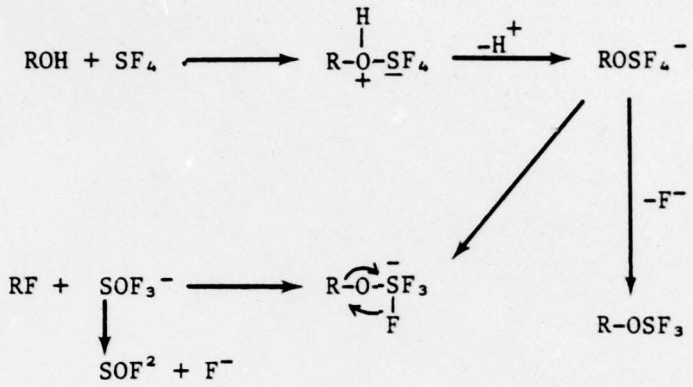
Sir:

The usefulness of sulfur tetrafluoride as a fluorinating agent for nitroaliphatic alcohols has been demonstrated.[2,3] The drawback in the use of sulfur tetrafluoride has been the need for high-pressure stainless steel reactors and auxilliary safety equipment required for high-pressure reactions. Aliphatic alcohols can be fluorinated[4,5] by a far less complicated procedure using polyhydrogen fluoride/pyridine solution, but attempts to fluorinate alcohols with electron attracting substituents have been unsuccessful.[6] We wish to report the fluorination of a nitroaliphatic alcohol using sulfur tetrafluoride at atmospheric pressure.

2,2-Dinitro-1,3-propanediol was fluorinated to yield 83% 3-fluoro-2,2-dinitropropanol[7] by passing sulfur tetrafluoride gas through a solution of the diol in polyhydrogen fluoride/pyridine at ambient temperature and pressure. The reaction is worked up by pouring the mixture into ice water, stirring until the solution is clear, and extracting the product from the aqueous solution with ether. When the reaction is poured into water, an insoluble oil is initially obtained, and immediate separation of this phase gives a 44% yield of 3-fluoro-2,2-dinitropropoxysulfur trifluoride. Extraction of the aqueous phase gave a 39% yield of the alcohol. Isolation of an alkoxysulfur trifluoride has been previously reported.[3]

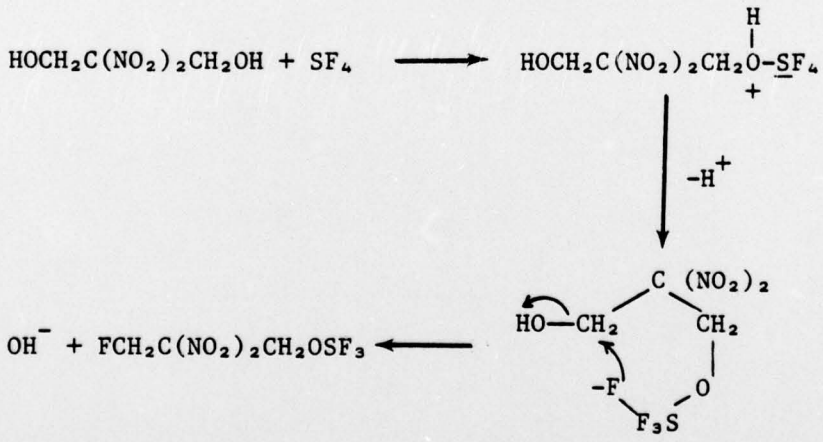
We have been unable to isolate any 1,3-difluoro-2,2-dinitropropane from this reaction. Absence of the doubly fluorinated product suggests that the reaction mechanism using this procedure precludes its formation and is contradictory to the mechanism previously proposed by Baum for the high-pressure fluorination of 2-fluoro-2,2-dinitroethanol,[3] Scheme I.

Scheme I



If Scheme I was the prevailing mechanism for our procedure, a statistical distribution of difluoro, fluoropropoxysulfur trifluoride, and propoxy-1,3-disulfur trifluoride would be expected. Scheme II shows a possible mechanism in which 3-fluoro-2,2-dinitropropoxysulfur trifluoride is the sole product. This mechanism is

Scheme II



in agreement with Baum's finding that the alkoxysulfur trifluoride is not an intermediate to formation of the alkyl fluoride and is in fact applicable to Baum's fluorination of 2-fluoro-2,2-dinitroethanol if displacement of the hydroxide anion is invoked as an intermolecular step. Additional experiments clearly are needed to verify either of the proposed mechanisms.

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1. This work was supported, in part, by the Office of Naval Research.

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