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FRANK J. SEILER RESEARCH LABORATORY

One-step Synthesis of Polynitroaliphatic Acetals and Ethers

Robert E. Cochoy

Raymond R. McGuire

and Scott A. Shackelford

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AIR FORCE SYSTEMS COMMAND

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A general, one-step, high yield reaction has been demonstrated that produces a variety of polynitroaliphatic acetal and ether products. Reaction conditions are mild; purification is simple; and, no costly high pressure or high temperature laboratory techniques are necessary to produce a variety of new polynitroaliphatic compounds not available from previously described synthetic methods. These novel energetic polynitroaliphatic acetals and ethers could provide precursor compounds for eventual application as energetic binder or plasticizer components in solid propellant and/or explosive formulations. A variety of activated alkenes and one alkyne reacted with polynitroaliphatic alcohols directly to produce novel new acetal and ether compounds. Difunctional polynitroalcohols reacted similarly with divinyl ether to produce low molecular weight acetal prepolymer compounds which were either vinyl or hydroxyl terminated. In one case, fluorodinitromethane was added to an alkene, however, the resultant product proved unstable at room temperature and gradually decomposed.

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Attempted addition of one polynitroaliphatic amine to divinyl ether proved to be unsuccessful and suggested the scope of the reactions outlined does not extend into polynitroaliphatic amine chemistry.

The reactions described serve to introduce a new concept in the synthetic production of 2,2,2-fluorodinitro and geminal dinitroaliphatic compounds. The scope appears to be fairly general and offers the possibility that novel extensions may produce a variety of interesting new energetic aliphatic materials. These reactions also suggest concrete options in reaction condition modification for transitioning into other new classes of energetic organic compounds. One case in point has been demonstrated in the one-step synthesis of polynitroaliphatic vinyl ether monomers which are suitable for polymerization and development into new energetic binders in solid propellant and/or explosive formulations.

18. Continued 7. energetic alkenes
8. 2-fluoro-2,2-dinitroethyl vinyl ether

PREFACE

Reported is a new nonaqueous synthesis method which permits the direct high yield production and easy isolation of polynitroaliphatic orthoester, acetal, and ether compounds via a one–step mercury salt catalytic addition of beta–substituted polynitroalphatic alcohols to alkyne and alkene hydrocarbons. In one case, the first reported direct addition of 2–fluoro–2, 2–dinitromethane to an alkene is discussed. The synthesis of energetic polynitroaliphatic acetal and ether compounds is severely limited by a geminal 2–polynitroalcohol reactant's inherent instability in alkaline or acid solution as well as their very weak nucliophilic character. Therefore, new synthetic methods are continually sought to expand the scope of available energetic polynitroaliphatic compounds. This is especially true for the ether compounds which could provide specific energetic plasticizer or binder materials applicable to composite propellant or plastic bond explosive use.

Since completion of this project, two coauthors are no longer located at the Directorate of Chemical Sciences in the F.J. Seiler Research Laboratory (FJSRL/NC). Colonel Robert E. Cochoy is currently a resident student at the Air War College, Maxwell AFB, Montgomery, AL. Dr Raymond R. McGuire is currently Technology Leader, High Explosives (Code L–324), Lawrence Livermore National Laboratory (LANL), P.O. Box 808, Livermore, CA 94550.

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SUMMARY

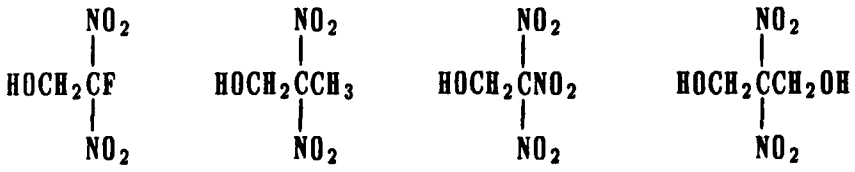
A general, one–step, high yield reaction has been demonstrated that produces a variety of polynitroaliphatic acetal and ether products. Reaction conditions are mild; purification is simple; and, no costly high pressure or high temperature laboratory techniques are necessary to produce a variety of new polynitroaliphatic compounds not available from previously described synthetic methods. These novel energetic polynitroaliphatic acetals and ethers could provide precursor compounds for eventual application as energetic binder or plasticizer components in solid propellant and/or explosive formulations. A variety of activated alkenes and one alkyne reacted with polynitroaliphatic alcohols directly to produce novel new acetal and ether compounds. Difunctional polynitroalcohols reacted similarly with divinyl ether to produce low molecular weight acetal prepolymer compounds which were either vinyl or hydroxyl terminated. In one case, fluorodinitromethane was added to an alkene, however, the resultant product proved unstable at room temperature and gradually decomposed. Attempted addition of one polynitroaliphatic amine to divinyl ether proved to be unsuccessful and suggested the scope of the reactions outlined does not extend into polynitroaliphatic amine chemistry.

The reactions described serve to introduce a new concept in the synthetic production of 2,2,2–fluorodinitro and geminal dinitroaliphatic compounds. The scope appears to be fairly general and offers the possibility that novel extensions may produce a variety of interesting new energetic aliphatic materials. These reactions also suggest concrete options in reaction condition modification for transitioning into other new classes of energetic organic compounds. One case in point has been demonstrated in the one–step synthesis of polynitroaliphatic vinyl ether monomers which are suitable for polymerization and development into new energetic binders in solid propellant and/or explosive formulations.

INTRODUCTION

A convenient, one-step addition reaction of non-nucleophilic polynitroaliphatic alcohols[1] and the highly acidic fluorodinitromethane molecule to unsymmetrically substituted alkenes has been defined. This mercury ion catalyzed S_n2 addition reaction proved to be a general method for addition to unsymmetrical alkenes; however, addition to an alkyne bond required a strong electron donating substituent on the acetylenic site. Depending upon the structure of the unsaturated hydrocarbon reactant and the reaction conditions, a variety of polynitroaliphatic acetals and ethers were obtained. In one case, a polynitroaliphatic acetal prepolymer of high molecular weight was synthesized in excellent yield by a convenient one-step reaction.

The synthesis of polynitroaliphatic acetals and ethers has been limited because of inherent chemical constraints which available starting materials exhibit. Such alcohols as 2-fluoro-2,2-dinitroethanol 1, 2,2-dinitropropanol 2, 2,2,2-trinitroethanol 3, and 2,2-dinitropropanediol 4 suffer from poor nucleophilic properties and a chemical instability in alkaline solution.[2]



1 2 3 4

This alkaline instability of alcohols 1-4 readily promote deformylation and subsequent decomposition of the original polynitroaliphatic alcohol. Thus, many well-defined synthesis procedures applicable to normal alcohols cannot be employed with this special class of polynitroaliphatic reactants. Another novel

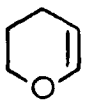
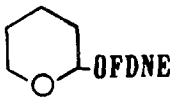
polynitroaliphatic compound, 2-fluoro-2,2-dinitromethane, 21, likewise displays a chemical instability in the kind of alkaline media that would enhance its nucleophilic properties.[3,4] In limited cases, polynitroaliphatic alcohols have been employed to convert routine organic compounds into more energetic polynitroaliphatic products.[2,5-10] The synthetic approaches, while novel and unique, are somewhat restricted in scope and sometimes require several steps. The catalytic, one-step process described is wide in scope and potentially allows the convenient, high-yield syntheses of many polynitroaliphatic compounds not available by these other procedures. Convenient, high-yield synthesis procedures for energetic polynitroaliphatic compounds are necessary to produce new energetic materials that offer improved mechanical properties to solid propellant and explosive formulations without sacrificing energy performance. Inclusion of certain polynitroliphatic compounds into solid propellant and explosive formulations as binder or plasticizer components could possibly increase the overall energy output of propulsion and detonation events while simultaneously offering an enhanced flexibility in mechanical property attenuation. Additionally, the excellent deflagration to detonation transition (DDT) properties attributed to the 2-fluoro-2,2-dinitroethyl moiety[11] suggest these compounds to be attractive components in a variety of energetic formulations.

The simplified one-step synthesis procedures described herein potentially open the door to a variety of new polynitroaliphatic compounds. Their high-yields and simple purification procedure are important considerations to the potential production scale quantities required for the eventual employment of any polynitroaliphatic compounds in operational propellant and explosive applications.

RESULTS AND DISCUSSION

Addition of 2-Fluoro-2,2-Dinitroethanol. The addition of 2-fluoro-2,2-dinitroethanol 1 to unsaturated hydrocarbons proved to be a general reaction limited only in scope to use with activated unsymetrical alkenes and alkynes. The addition reactions were accomplished by dissolving the alkene or alkyne and 2-fluoro-2,2-dinitroethanol in methylene chloride or carbon tetrachloride solvent and adding the appropriate mercury salt catalyst to the stirred solution. The stirred reaction mixture was refluxed approximately 16 hours (overnight); however some reactions may reach completion sooner. Excellent product yields were obtained after a simple work-up and purification procedure. Several mercury salts were tried as the catalytic species (e.g. mercury (II) sulfate, mercury (I), sulfate, mercury (II) acetate, red mercury (II) oxide, phenyl mercury (II) chloride); but the former two generally afforded the best results for the addition products listed in Table I.[12] A survey of the compounds in Table I shows that all alkenes and the one alkyne reactant are unsymetrically substituted about their unsaturated bonds when an oxygen atom, methyl group, or vinyl group is adjacent to or in conjugation with the vinyl/alkyne bond participating in this addition. In the case of divinyl ether, addition across both carbon-carbon double bonds can be accomplished; or, reaction conditions may be modified to give a major product where addition occurs only once. Apparently, the activating influence of the ether's oxygen atom is not lost after the first molecule of 2-fluoro-2,2-dinitroethanol is added. However, butadiene which is devoid of the activating oxygen atom,

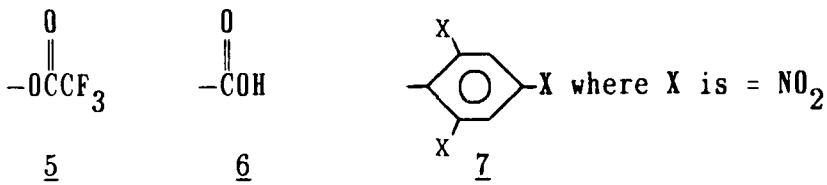
Table I. Products of 2-Fluoro-2-Dinitroethanol Addition

Reactants	Solvent	Products	Catalyst	% Yield
$H_2C{=}CHOCH{=}CH_2$	CH_2Cl_2	$H_2C{=}CHO\overset{OFDNE}{C}HCH_3$	$HgSO_4$	70 (Total)*
		$H_3C\overset{ENDFO}{C}HO\overset{OFDNE}{C}HCH_3$	Hg_2SO_4	74 (Total)*
				*Both Products
$H_2C{=}CHOCH_2CH_3$	CH_2Cl_2	$H_3C\overset{OFDNE}{C}HOCH_2CH_3$	$HgSO_4$	73
$H_2C{=}CH{-}OFDNE$	CH_2CL_2	$H_3C{-}\overset{OFDNE}{C}H$	$HgSO_4$	61
$H_2C{=}\overset{CH_3}{C}CH_2CH_2CH_3$	CH_2CL_2	$H_3C{-}\overset{CH_3}{C}(OFDNE)CH_2CH_2CH_3$	$HgSO_4$	74
			Hg_2SO_4	58
$H_2C{=}CH{-}CH{=}CH_2$	CCl_4	$H_2C{=}CH{-}\overset{OFDNE}{C}HCH_3$ $H_3CCH{=}CHCH_2OFDNE$	$HgSO_4$	53 (Total)*
	CCl_4		None	100
$HC{\equiv}COCH_2CH_3$	CH_2Cl_2	$H_3C{-}\overset{OFDNE}{C}(OFDNE)COCH_2CH_3$ $H_2C{=}\overset{OCH_2C_3}{C}(OFDNE)$	$Hg(OAc)_2$	95
				**

$$-OFDNE = -OCH_2\overset{NO_2}{\underset{NO_2}{C}}F$$

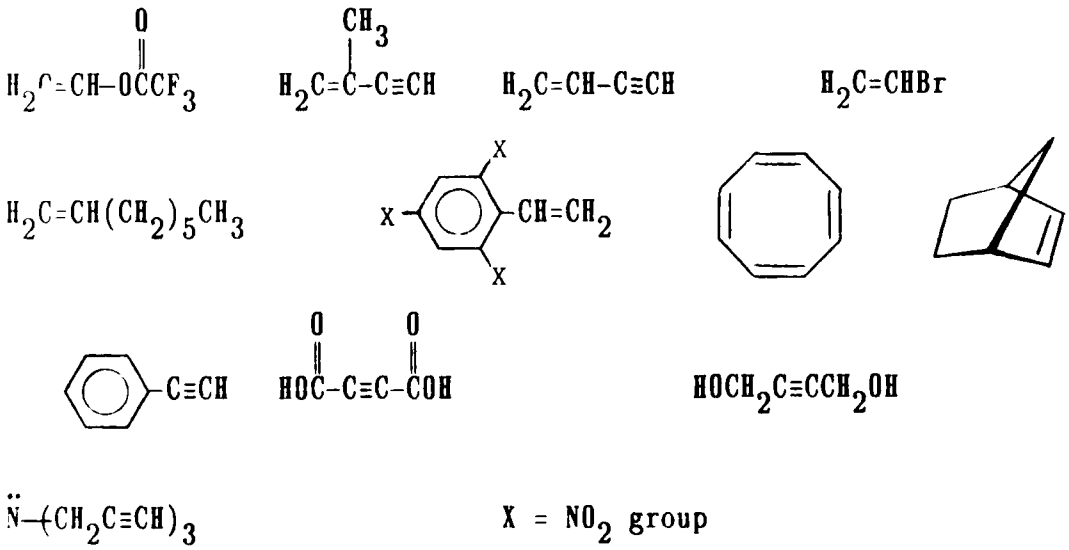
**This vinyl acetal was isolated as a minor product from the first reaction between 2-fluoro-2,2-dinitroethanol and ethoxyacetylene; however, all subsequent reactions under identical and a variety of other reaction conditions failed to reproduce this compound.

permits the addition of only one alcohol molecule. After the addition of one 2-fluoro-2,2-dinitroethanol molecule across one double bond, reaction ceases and the remaining carbon-carbon double bond becomes inert toward a second 2-fluoro-2,2-dinitroethanol addition. As expected with the butadiene reactant, both 1,2- and 1,4-addition products are found in an isomeric distribution of 77% and 23% respectively. Interestingly, the monoacetylene analogue of butadiene, butene-3-yne (Table II) failed to add an alcohol to either unsaturated bond. Note that 2,3-dihydropyran underwent addition without benefit of any mercury salt catalyst; it was the only unsaturated hydrocarbon found to do so. Several other alkene and alkyne compounds listed in Table II failed to react with the 2-fluoro-2,2-dinitroethanol under the reaction conditions cited. In most cases these compounds possess deactivating groups in conjugation with the alkene/alkyne bond, such as 5, 6, or 7, or are symmetrically substituted about the



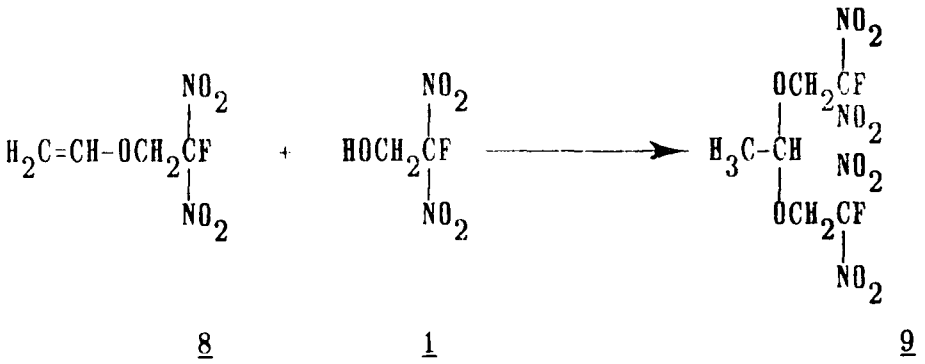
5 6 7

Table II. Reactants Inert to 2-Fluoro-2,2-Dinitroethanol Addition



unsaturated bond. While 2-methyl-1-pentene formed an addition product, its analogous unsubstituted compound, 1-pentene, failed to react without the activating influence of the methyl group. Furan, which exhibits a degree of aromaticity, is too deactivated to participate in this catalytic addition while highly activated the 2,3-dihydropyran reacts with 2-fluoro-2,2-dinitroethanol even without any catalytic assistance. Apparently an alkyne bond in conjugation with a vinyl is sufficiently deactivating to stop the desired addition to butene-3-yne (Table II), while a vinyl group in conjugation with another, butadiene, apparently defines the deactivating limit by allowing addition of one alcohol to the carbon-carbon double bonds under mildly stringent conditions (Table I). As evidenced by 2-methylbutene-3-yne (Table II), the deactivating effect of the carbon-carbon triple bond in conjugation with the vinyl bond must overcome the activating influence of the methyl group. This is demonstrated in comparing the reactivity of 2-methyl-1-pentene (Table I) and 1-pentene (Table II). A conjugated phenyl group also is sufficiently deactivating and prevents addition across the alkyne bond in phenylacetylene.

Interestingly, 2-fluoro-2,2-dinitroethanol 1 was added across the vinyl bond in 2-fluoro-2,2-dinitroethyl vinyl ether 8 to obtain the acetal 9 shown in Equation 1 and Table I. This reaction suggests the possibility of synthesizing



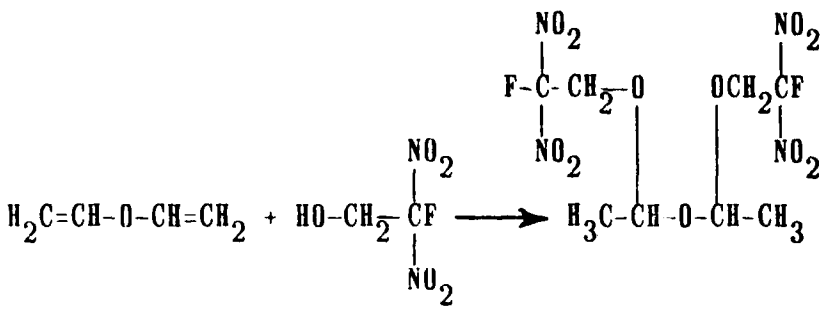
[1]

8 1 9

mixed energetic acetals by adding another polynitroaliphatic alcohol (e.g. 2,2-dinitropropanol 2) to vinyl ether 8. In the case of the vinyl ester, vinyl trifluoroacetate, the deactivating influence of the trifluoroacetate moiety totally inhibited addition by the energetic alcohol 1 (Table II).

Ethoxyacetylene was the only alkyne found which underwent addition of fluorodinitroethanol (1) and produced the saturated orthoester shown in Table I. Single addition of the alcohol with ethoxyacetylene produced a vinyl acetal product on the first reaction attempted; however, this result could not be reproduced despite attempting a wide variety of reaction conditions. Apparently, a strong electron donating group is necessary to produce the initial pi complex between the mercuric ion and alkyne bond prior to S_n2 attack by the alcohol;[13] and the same type of a metal ion pi complex with the intermediate vinyl acetal product apparently is too reactive to intercept. Interestingly, phenyl mercury (II) chloride, employed in the reaction between ethoxyacetylene and 2-fluoro-2,2-dinitroethanol, produced the orthoester product in 43 percent yield when the reaction was stirred at room temperature 21 hours. This catalyst, however, failed to give any addition product between divinyl ether and 2-fluoro-2,2-dinitroethanol even when refluxed in CH_2CL_2 5 hours after stirring at room temperature for 68 1/2 hours.

Additions to the divinyl ether reactant 10 could be controlled by varying reaction conditions to produce either the complex acetal diadduct, 11, or the normal acetal monoadduct, 12, as the major reaction product (Table III). This flexibility, shown in equation 2, makes available an unreacted vinyl bond for addition type polymerizations in the case of the monoadduct 12 for producing potential energetic acetal polymers. A two-fold excess of divinyl ether yields the maximum amount of monoadduct 12 (Table III); a three-fold excess did not significantly increase the amount of 12 formation.



[2]

10 11

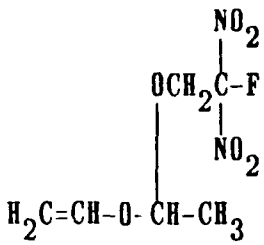


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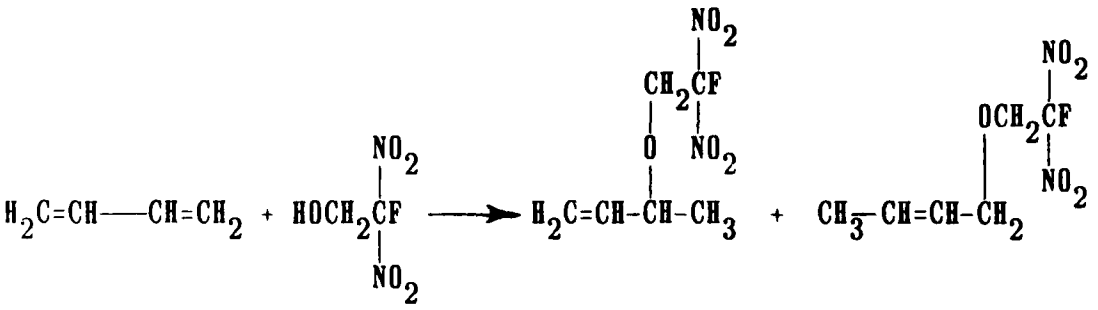
Table III. Product Percentages in Divinyl Ether (DVE) Addition Determined by Nuclear Magnetic Resonance

[DVE]/[FDNEOH] Ratio	Catalyst	% 11	% 12	Crude Overall % Yield
0.93	Mercury (II) sulfate	73	27	94
2.00	Mercury (II) sulfate	37	63	--
1.00	Mercury(I) sulfate[a]	63	37	66
2.00	Mercury(I) sulfate[a]	32	68	--

[a]Less discoloration occurs in the reaction solution although overall yields are somewhat lower. (See also Table I)

Butadiene 13 offers a similar option in that it adds only one molecule of 2-fluoro-2,2-dinitroethanol 1 (Table I) both by 1,2- and 1,4-addition (14 and



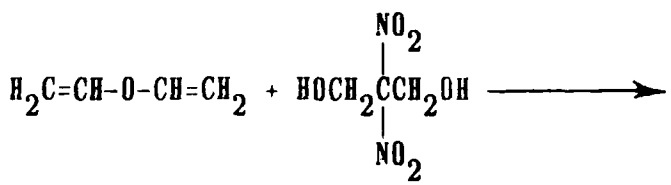
13 1 14 (77%) 15 (23%)

plus polymer

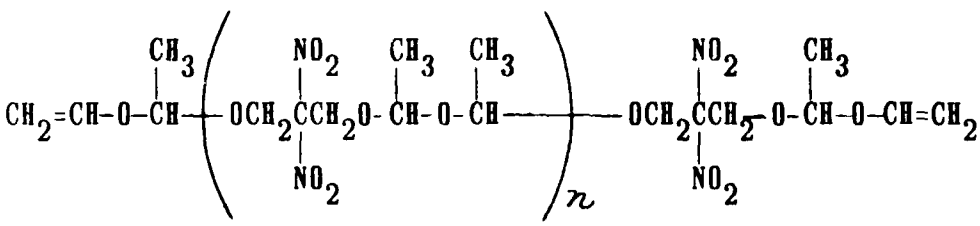
15 respectively) to produce more stable ether derivatives instead of the acetal products afforded by divinyl ether 10. Butadiene, however, requires stronger reaction conditions than divinyl ether (Experimental Section). This results in some starting material polymerization and requires more complex chemical

equipment. The higher yields obtained with divinyl ether additions and the easier handling techniques, plus the mono-/diadduct flexibility made 10 an attractive model compound upon which to conduct further investigations.

Addition of 2,2-Dinitropropane-1,3-Diol (ADIOL). The success of obtaining product 12 in the reaction between divinyl ether (DVE) and 2-fluoro-2, 2-dinitroethanol (FDNEOH) using excess DVE and the milder mercury (I) sulfate catalyst encouraged us to react difunctional 2,2-dinitropropanediol (ADIOL) 16 with divinyl ether 10 under the reaction conditions most likely to produce a vinyl terminated product. A three-fold excess of DVE with ADIOL 16 stirred in methylene chloride solvent with a catalytic amount of mercury (I) sulfate produced a 71% yield of the vinyl terminated polyacetal prepolymer 17 after 118 hours reflux time (bp CH_2CL_2 = 37^{0}C at FJSRL) and a silica-gel column chromatography work-up. Integration analysis by nmr showed the clear yellowish oil had an average n unit equal to 5-16 depending on the amount of reactants used in the reaction. Next, an attempt was made to produce an analogous hydroxy



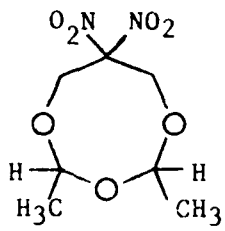
10 16



17

When n = 16 repeating units (average) MW = 4058 g/mol
density = 1.32 g/ml

terminated prepolymer by employing an excess of ADIOL. Instead of producing the desired long-chain hydroxyl terminated prepolymer, a cyclization reaction occurred to produce the novel eight-membered cyclooctane, 2,4-dimethyl-7,7-dinitro-1,3,5-trioxacycloctane 18 in reasonably good yield.

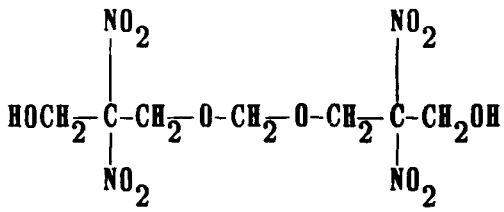


18

Interestingly, an attempted vacuum distillation of vinyl terminated prepolymer 17 at high temperature also resulted in the formation of 18 by thermochemical degradation and apparent cyclization. Mass spectral analysis of 18 revealed its fragmentation pattern[14] preferentially follows that exhibited by cyclic trioxane acetals in preference to a fragmentation analogous to geminal polynitroaliphatic and nitroalkane molecules.[15-17] A similar reaction substituting 1,3-propanediol for ADIOL produced the unnitrated trioxacyclooctane; however, a contaminent equivalent to one proton repeatedly co-distilled with this product.

Addition of 2,2,8,8-Tetranitro-4,6-Dioxa-1,9-Nonanediol (DINOL). A second prepolymer synthesis was attempted by the reaction of 2,2,8,8-tetranitro-4,6-dioxa-1,9-nonanediol (DINOL) 19 with divinyl ether (DVE) under reaction conditions similar to those used to produce the ADIOL/DVE prepolymer 17. This reaction was conducted with both DINOL monohydrate and anhydrous DINOL.

Reaction between DINOL monohydrate, excess divinyl ether, and



19

mercury(I) sulfate catalyst in refluxing methylene chloride solvent produced a high melting, cubic, white solid in 36 percent yield. Nuclear magnetic resonance and infrared analysis preliminarily suggest the product to be hydroxy-terminated prepolymer 20 where two DINOL portions appear to bond via H_2O elimination. Reaction between anhydrous dinol and excess divinyl ether under similar reaction conditions yielded a waxy white solid plus a light yellow oil, both of which appear to be vinyl terminated materials.

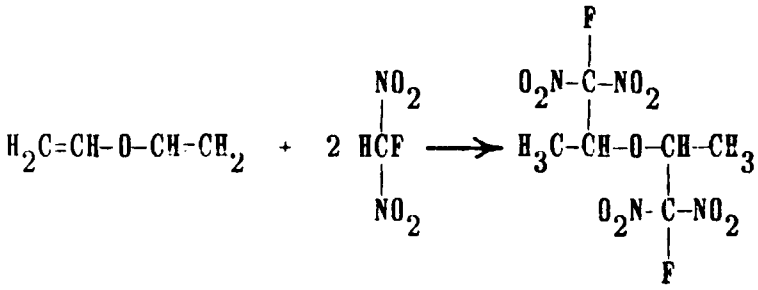
HO-DINOL[DVE(DINOL-DINOL)DVE]DINOL-OH

20 MW = 1499

mp = 237°C

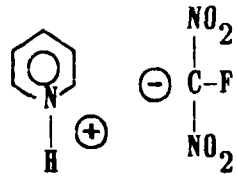
The structure of these two latter new materials is unknown; however, their total weight was 23 percent less than the weight yield of hydroxy-terminated prepolymer 20 using the same amount of reactants. While the yield of prepolymer 20 was only moderate, its high melting point represents a very attractive thermochemical feature. Further reaction modifications may lead to improved yields of this interesting energetic acetal prepolymer material.

Addition of Fluorodinitromethane. The addition of fluorodinitromethane 21 to an aliphatic alkene was first successfully accomplished using a cocatalytic reaction system. Reaction between fluordinitromethane 21, and divinyl ether 10 in refluxing carbon and divinyl ether 10 in refluxing carbon tetrachloride



10 21 22

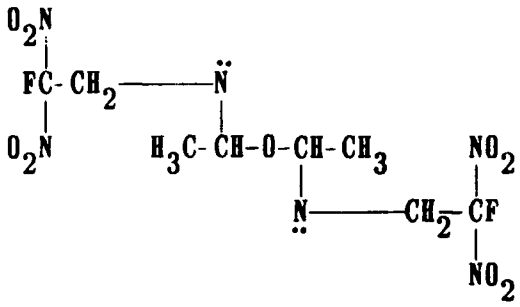
solvent produced symmetrical 1-fluorodinitromethyl ethyl ether 22 when mercury (I) sulfate and pyridine were present. Failure to use either cocatalytic component resulted in no reaction. Apparently, activation of the vinylic pi bond by mercury (I) sulfate was not a sufficient condition in itself, and the mild pyridine base was also necessary to activate the acidic fluorodinitromethane hydrogen atom for addition to proceed. Significantly improved yields of 22 were obtained by substituting a mercury trifluoroacetate catalyst wetted with trifluoroacetic acid. This catalytic salt was reproduceably synthesized from refluxing red mercury (II) oxide in trifluoroacetic acid/anhydride solvent and produced 22 in 47% yield.[18] When mercury (I) sulfate was employed as a cocatalyst, yields of 22 not only were lower, but purification was more difficult. A contaminant, which appeared to be a pyridinium salt of the fluorodinitromethide ion 23, was present in significant amounts and even co-distilled with 22 during molecular distillation. The smaller product yields and the presence of 23 in the crude reaction product



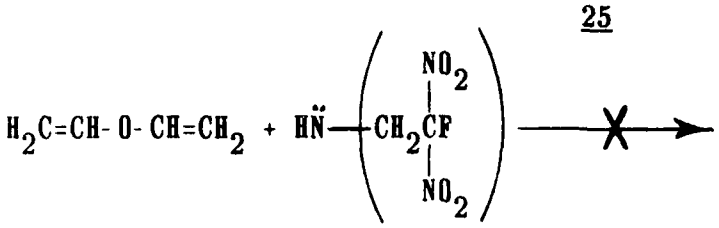
23

possibly suggests 23 to be an intermediate reaction species present because of incomplete reaction. This troublesome 23 species nearly disappears when the wetted mercury trifluoroacetate catalyst is used. Unfortunately, this novel energetic diadduct 17 of divinyl ether proved to be very unstable at room temperature probably because the fluorodinitromethyl moiety should be an excellent leving group.[19] Over several hours, this light yellow oil gradually decomposed with gas evolution to give a dark brown tar likely caused by a polymerization upon the loss of the fluorodinitromethyl moiety.

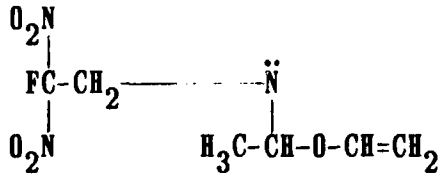
Addition of Bis-2-Fluoro-2,2-Dinitroethyl Amine. The bis-2,2,2-fluorodinitroethylamine 24 was prepared by a previously published procedure.[6] It was chosen over its primary amine analogue which proves to be a sensitive and unpredictable explosive material.[6] Attempts to prepare compounds 25 or 26 by the analogous mercury (I) and (II) sulfate catalyzed addition of 24 across divinyl ether 10 were unsuccessful.



25



10 24



26

Hence, the scope of this reaction does not appear to extend into polynitroaliphatic amines.

CONCLUSION

A general, one-step, high yield catalytic reaction has been demonstrated which produces a variety of polynitroaliphatic acetal and ether products. Reaction conditions are mild, purification is simple, and costly high pressure or high temperature laboratory techniques are usually unnecessary to produce a variety of new polynitroaliphatic compounds. These novel energetic polynitroaliphatic acetals and ethers could provide precursor compounds for eventual application as energetic binder or plasticizer components in solid propellant and/or explosive formulations. A variety of activated alkenes and one alkyne reacted with polynitroaliphatic alcohols directly to produce these

novel new acetal and ether compounds. Difunctional polynitroalcohols reacted similarly with divinyl ether to produce low molecular weight prepolymer compounds which were either vinyl or hydroxyl terminated. In one case, fluorodinitromethane was added to an alkene at a 2^0 carbon site; however, the resultant product proved unstable at room temperature and gradually decomposed. This decomposition is attributed to the fluorodinitromethyl moiety being an excellent leaving group. Attempted addition of one polynitroaliphatic amine to divinyl ether proved unsuccessful and suggested the scope of the reactions outlined does not extend into polynitroaliphatic amine chemistry.

The reactions described serve to introduce a new concept in the synthetic production of beta-substituted geminal fluorodinitro and dinitroaliphatic compounds. The scope appears to be fairly general and offers the possibility for novel extensions to produce a variety of interesting new energetic materials. These reactions also suggest concrete options for transitioning into other new classes of energetic organic compounds. One case in point has been demonstrated in the one-step synthesis of polynitroaliphatic vinyl ether monomers which are suitable for polymerization and development into new energetic binders in solid propellant and/or explosive formulations.[20-22] These new compounds could also find use as energetic plasticizer materials in a variety of future energetic material applications.

EXPERIMENTAL

General. The divinyl ether used was purchased from PCR, Inc., Gainesville, FL[23] and was used without further purification. Other alkenes and alkynes were distilled only when necessary. The 2-fluoro-2,2-dinitroethanol[24] was purchased from the Naval Surface Warfare Center/White Oak Laboratory, Silver Spring, MD as a 30 percent by-weight solution in dichloromethane solvent. Prior to use, the

dichloromethane was removed by rotary evaporation to yield a slightly yellow oil. (Caution! The 2-fluoro-2,2-dinitroethanol attains a sensitivity maximum during solvent removal and should be conducted behind appropriate shielding.) The neat 2-fluoro-2,2-dinitroethanol was fractionally vacuum distilled; over a wide vacuum range, this material distilled at 55°C. The distillate still contained the trace impurity, 2-fluoro-2,2-dinitroethyl methyl formal, but was used without additional purification. The mercury (I) and (II) sulfate catalysts were obtained from J.T. Baker Chemical Co. as "Baker Analyzed" reagent. The neutral aluminum oxide in the purification and work-up was "Baker Analyzed" reagent purity. Neutral aluminum oxide that provided a pH 6.9 or pH 7.3 water slurry was used. The dichloromethane and carbon tetrachloride solvents were MCB spectrametric grade. The 2,2-dinitropropanediol (ADIOL) was synthesized by previously reported procedures[25] as was the 2,2,8,8-tetranitro-4,6-dioxa-1,9-*nonadiol monohydrate* (DINOL monohydrate)[26] and was provided by NSWC/WOL. The fluoro- dinitromethane was prepared by chromic acid oxidation of 2-fluoro-2, 2-dinitroethanol. Caution! The polynitroaliphatic alcohols, 2-fluoro-2, 2-dinitroethanol, ADIOL, DINOL, and the bis-2,2,2-fluoror dinitroethyl amine employed in these studies can be explosive under the proper stimulus. The liquid 2-fluoro-2,2-dinitroethanol also causes severe burns to the skin. Proper shielding and gloves should be used when handling these pure compounds; gloves should be worn when handling 2-fluoro-2,2-dinitroethanol or when working up any reaction containing this reagent. Nuclear magnetic resonance spectra were taken either on a Varian A-60 or T-60 instrument using $DCCl_3$ as a solvent (unless otherwise stated) and TMS as an internal reference. Infrared spectra were obtained as a liquid film on NaCl plates in a Beckman IR-20 spectrophotometer. Mass spectra were taken on a Dupont 21-491 double focusing mass spectrometer. Elemental analyses were performed by Galbraith

Laboratories, Knoxville, TN.

Addition of 2-Fluoro-2,2-Dinitroethanol (1) to Alkenes and Ethoxyacetylene (General Procedure). The alkene/alkyne was weighed into dichloromethane solvent contained in a 25 or 50 ml single-neck round bottom flask with a teflon coated stir bar. The 2-fluoro-2,2-dinitroethanol was added to the stirred solution; and next, the mercury salt catalyst was added. The reaction flask was fitted with a water-cooled reflux condenser topped with a Drierite filled drying tube. The reaction was stirred at room temperature, or sometimes was heated to reflux (bp CH_2Cl_2 at FJSRL - 37°C), for 16-19 hours. The reaction solution was filtered, and the solvent was removed by rotary evaporation. The remaining oil was taken up in several milliliters of CCl_4 (ca. 1-3 ml) and was eluted through a short neutral aluminum oxide (pH 6.9 or 7.2) column to remove any unreacted alcohol. This column was prepared by packing 2.5 g aluminum oxide slurried in CCl_4 into a 15 ml "course" glass sintered Buchner funnel. Rotary evaporation removed the CCl_4 and afforded the addition product(s). The product (always an oil) was further purified as necessary by vacuum distillation.

Addition of 2-Fluoro-2,2-Dinitroethanol (1) to Divinyl Ether (10).

a. A single-neck round bottom flask charged with 1.05 g (15 mmol) divinyl ether, 25 ml CH_2Cl_2, 3.08 g (20 mmol) 2-fluoro-2,2-dinitroethanol, and 200 mg $HgSO_4$, was stirred under reflux 16 hours. Vacuum distillation of the isolated oil afforded 0.4 g (12%) monoadduct 12. The pot residue was taken up in CCl_4 and passed through a short alumina (pH = 7.2) column to remove the colored impurities. Removal of CCl_4 by rotary evaporation gave 2.20 g (58%) pure diadduct 11 with density = 1.42 g/ml. Diadduct 11; nmr ($DCCl_3$) δ, (pent, 5.07, 2H), (dd, 4.57, 4H) with Jvic HF = 18 cps, (d, 1.39, 6H); ir (neat film) cm^{-1}, 3000, 2940 (sat. CH), 1600, 1310 (NO_2); Elemental Analysis (Calc. C 25.4,

H 3.20, N 14.8, F 10.1), (Found C 25.6, H 3.20, N 14.7, F 10.0).

b. A 100 ml single-neck round bottom flask charged with 2.0 g (28.6 mmol) divinyl ether, 60 ml CH_2Cl_2, 2.2 g (14.3 mmol) 2-fluoro-2,2-dinitroethanol, and 750 mg Hg_2SO_4, was stirred under reflux 26 hours. Work up produced 2.63 g crude oil product containing both the monoadduct 12 and diadduct 11. Short path vacuum distillation afforded 1.29 g (40%) monoadduct 12. The pot residue was dissolved in CH_2Cl_2 and eluted through a short alumina column. Removal of the CH_2Cl_2 gave 0.91 g (34%) diadduct 11. Monoadduct 12; nmr ($DCCl_3$) δ, (dd, 6.36, 1H), (quart, 5.14, 1H), (dd, 4.62, 2H) with Jvic HF = 18 cps, (m, 4.50, 2H), (d, 1.40, 3H); ir (neat film) cm^{-1}, 3120, 3070 (= CH), 3000, 2945 (sat. CH), 1645 (C = C), 1600, 1315 (NO_2); Elemental Analysis (Calc. C 32.2, H 4.05, N 12.5, F 8.48), (Found C 32.0, H 3.98, N 12.5, F 8.31).

Addition of 2-Fluoro-2,2-Dinitroethanol to Ethyl Vinyl Ether. A single-neck round bottom flask charged with 2.15 g (30 mmol) ethyl vinyl ether, 25 ml CH_2Cl_2, and 3.08 g (20 mmol) 2 fluoro-2, dinitroethanol, was stirred and cooled in an ice bath before 200 mg $HgSO_4$ was added. The solution was allowed to warm to room temperature and was stirred 16 hours. Work up produced 4.65 g of crude oil; vacuum distillation through a 6 in. Vigreaux column at 34-35^{0}C/0.10 mm produced 3.29 g (73%) product as a colorless oil; nmr ($DCCl_3$) δ, (quart, 4.92, 1H), (dd, 4.60, 2H) with Jvic HF = 18 cps, (m, 3.60, 2H), (m, 1.26, 6H); ir (neat film) cm^{-1}, 2995, 2940, 2900 (sat. CH), 1600,1315 (NO_2); Elemental Analysis (Calc. C 31.9, H 4.87, N 12.4, F 8.41), (Found C 31.9, h 4.69, N 12.2, F 8.35).

Addition of 2-Fluoro-2,2-Dinitroethanol to 2 Fluoro-2,2-Dinitroethyl Vinyl Ether (8). A 50 ml single-neck round bottom flask charged with 1.50 g (8.3 mmol), 2-fluoro-2,2-dinitroethyl vinyl ether,[22] 20 ml CH_2CL_2, 1.28 g (8.3 mmol) 2-fluoro-2,2-dinitroethanol, and 250 mg $HgSO_4$, was stirred under reflux 24

ours. After work up the crude oil was molecular distilled at 68.0-68.4^{o}C/0.2 mm to yield 1.71 g (61%) product. The product was a colorless oil with a density = 1.55 g/ml; nmr ($DCCl_3$)δ, (quart, 5.02, 1H), (dd, 4.61, 4H) with J<u>vic</u> HF = 17 cps, (d, 1.43, 3H); ir (neat film) cm^{-1}, 3000, 2950, 2900 (sat. CH), 1600, 1310 (NO_2), mass spec. 333 (M 1), 319 (M-15), 181 (M-153); Elemental Analysis (Calc. C 21.6, H 2.40, N 16.8, F 11.4), (Found C 21.6, H 2.5, N 16.6, F 11.2).

<u>Addition of 2-Fluoro-2,2-Dinitroethanol to 2-Methyl-1-Pentene</u>.

a. A single-neck round bottom flask charged with 2.52 g (30 mmol) 2-methyl-1-pentene, 25 ml CH_2Cl_2, 3.08 g (20 mmol) 2-fluoro-2,2-dinitroethanol, and 200 mg $HgSO_4$ was stirred under reflux 16 hours. The purple solution was worked up to provide 2.95 g crude product. Vacuum distillation at 47-48°C/0.2 mm through a 6 in. Vigreaux column gave 3.51 g (74%) nearly colorless oil. Analysis by nmr showed a slight impurity; so, redistillation 45°C/0.2 mm was accomplished through a 12 in. glass bead column; nmr ($DCCl_3$)δ, (dd, 4.42, 2H), (singlet amid a multiplet, 1.17, 13H); ir (neat film) cm^{-1}, 2970, 2940, 2880 (sat. CH), 1600, 1315 (NO_2); elemental Analysis (Calc. C 40.4, H 6.36, N 11.8, F 7.98), (Found C 40.4, H 6.37, N 11.7, F 7.76).

b. A 50 ml single-neck round bottom flask charged with 1.00 g (12 mmol) 2-methyl-1-pentene, 20 ml CH_2Cl_2, 1.85 g (12 mmol) 2-fluoro-2,2-dinitroethanol, and 550 mg Hg_2SO_4 was stirred under reflux 48 1/2 hours. Work up gave 1.58 g purple oil (58%); nmr ($DCCl_3$)δ, (dd, 4.42, 2H), (singlet amid a multiplet, 1.17, 14H).[27]

<u>Addition of 2-Fluoro-2,2-Dinitroethanol (1) to 1,3-Butadiene (13)</u>. A Paar pressure bottle was charged with 40 ml CCl_4. The bottle was cooled in an ice bath before 4.2 g (7.8 mmol) 1,3-butadiene <u>13</u> was bubbled into the solvent. Next, 3.08 (2.0 mmol) 2-fluoro-2,2-dinitroethanol <u>1</u> and 0.1 g $HgSO_4$ were added to the Paar bottle. The bottle was stoppered with a teflon wrapped rubber

stopper and placed into the Paar bomb apparatus. The reaction was shaken at 55°C for 16 hours. The reaction solution was then poured through 23 g alumina (pH = 7.2) with a CCl_4 wash. The CCl_4 solution was removed by rotary evaporation, and the resultant product was again filtered through another 23 g alumina with a CCl_4 wash. Rotary evaporation of the CCl_4 provided 4.05 g of light reddish brown oil. The oil was vacuum distilled through a 6 in. Vigreaux column at 35°C/0.10 mm to give 2.19 g (53%) of light yellow oil. The distillate contained mainly the 1,2-adduct 14 but was contaminated with the 1,4-adduct 15. Distillation (51.0-51.5°C/1.6 mm) through a 12 in. glass bead column did provide nearly pure (90%) 1,2-adduct 14; the 1,4-adduct could not be distilled even with a diethyl succinate pot chaser. Analytical colorless oil samples of the two adduct isomers were obtained by preparative glpc using an 8 ft. by 1/2 in. 20% Dow 710 Silicon Oil column at 148°C. 1,2-Adduct 14; nmr ($DCCl_3$)δ, (m, 5.55, 3H), (dd, 4.48, 2H) with Jvic HF = 18 cps, (pent, 4.02, 1H), (d, 1.25, 3H); ir (neat film) cm^{-1}, 3090 (= CH), 2990, 2930, 2890 (sat. CH), 1600, 1310 (NO_2); Elemental Analysis (Calc. C 34.6, H 4.36, N 13.5, F 9.13), (Found C 34.85, H 4.39, N 13.3, F 9.16). 1,4-Adduct 15; nmr ($DCCl_3$)δ, (m, 5.62, 2H), (dd, 4.49, 2H) with Jvic HF = 18 cps, (d, 1.76, 3H); ir (neat film) cm^{-1} 3010 (= CH), 2985, 2960, 2920, 2870 (sat. CH), 1600, 1315 (NO_2); Elemental Analysis (Calc. C 34.6, H 4.36, N 13.5, F 9.13), (Found C 34.85, H 4.39, N 13.6, F 8.71).

Addition of 2-Fluoro-2,2-Dinitroethanol to 3,4-Dihydropyran. A single-necked round bottom flask charged with 1.00 g (11.9 mmol) 3,4-dihydropyran, 10 ml CCl_4, and 1.00 g (6.5 mmol) 2-fluoro-2,2-dinitroethanol was stirred under reflux 17 hours. Rotary evaporation of the CCl_4 solvent afforded 1.56 g (100%) light yellow oil which proved to be the 2-(2-fluoro-2, 2-dinitroethyl) tetrahydropyran; nmr ($DCCl_3$)δ,(m, 4.82, 1H), (dd, 4.70, 2H), (m, 3.72, 2H), (m, 1.68, 6H).

Addition of 2-Fluoro-2,2-Dinitroethanol to Ethoxyacetylene. A 50 ml single-neck round bottom flask charged with 1.05 g (15 mmol) distilled ethoxyacetylene, 25 ml CH_2Cl_2, 3.08 g (20 mmol) 2-fluoro-2,2-dinitroethanol and 100 mg mercury (II) acetate, was stirred at room temperataure overnight (c.a. 16 hr.). Solvent removal by rotary evaporation was accomplished and the resulting oil was filtered through 23 g alumina (pH = 7.2) with CH_2Cl_2. Rotary evaporation of the CH_2Cl_2 afforded 3.59 g (95%) clear yellow oil. Vacuum distillation $90^oC/0.05$ mm for 4 hours in a molecular still gave 3.26 g light yellow oil which was less pure than before distillation. Density of the yellow oil was 1.42 g/ml; nmr ($DCCl_3$)δ, (dd, 4.64, 4H) with Jvic HF = 17 cps, (quart, 3.57, 2H), (s, 1.54, 3H), (t, 1.22, 3H); ir (neat film Cm^{-1}, 2990, 2950, 2900 (sat. CH), 1600, 1310 (NO_2), Elemental Analysis (Calc. C 25.4, H 3.20, N 14.8, F 10.1), (Found C 25.4, H 3.19, N 14.7, F 10.1). The once isolated vinyl acetal (Table I) was separated by distillation $48^oC/0.2$ mm to provide 27% of the product mixture with the orthoester. This material was seen when mercury (II) acetate and 62% ethoxyacetylene reactant in hexane was placed into a reaction mixture with CH_2Cl_2 solvent; nmr ($DCCl_3$)δ, (dd, 4.94, 2H) with Jvic HF = 16.5 cps, (quart, 3.96, 2H), (quart, 3.37, 2H), (t, 1.33, 3H). Repeating the same and modified reaction conditions never again provided this material.

Addition of 2,2-Dinitropropanediol (16) to Divinyl Ether (10).

a. Prepolymer 17. A 1000 ml single-neck round bottom flask charged with 15.0 g (21.4 mmol) divinyl ether 10, 750 ml CH_2Cl_2, 11.85 g (7.14 mmol), 2,2-dinitro-1,3-propanediol (ADIOL) and 2.9 g Hg_2SO_4, was stirred under reflux 118 hours (5 days). Rotary evaporation of the CH_2Cl_2 left 13.42 g of slightly yellow oil containing some solid suspension. The oil was poured onto a silica column which was prepared by placing into a 150 ml fritted glass medium porosity funnel, 25 g (60/200 mesh) SiO_2 slurried in CCl_4 with a 1/4 in. sand overlay.

Next, the oil was eluted through the SiO_2 column with 350 ml CCl_4; rotary evaporations of the CCl_4 produced 12.11 g (71%) clear yellowish oil 17; nmr ($DCCl_3$)δ, (dd, 6.4, 2H), (m, 4.7, 53H), (d, 1.4, 51H); ir (neat film) cm^{-1}, 2980, 2940, 2890 (sat. CH), 1645, 1630 (C = C), 1570, 1320 (NO_2). This particular sample via nmr integration gave an average repeating (n) unit equal to sixteen. An attempted molecular still vacuum distillation of 17 produced the eight-membered trioxacyclooctane 18 which condensed out as a solid on the still's cold finger. Apparently, the prepolymer 17 decomposes thermally to cyclize into 18.

b. Trioxacyclooctane 18. A 50 ml single-neck round bottom flask charged with 0.23 g (3.3 mmol) divinyl ether, 20 ml CH_2Cl_2, 3.50 g (21 mmol) ADIOL, and 550 mg Hg_2SO_4, was stirred under reflux 24 hours. The reaction solution was filtered through a course glass sintered funnel, and the solvent was removed by rotary evaporation. The yellow tinted solid (much of it excess unreacted ADIOL) was coated onto alumina (pH 6.9) by dissolving this solid in acetone, adding 2.3 g alumina and stripping the acetone solvent by rotary evaporation. The coated alumina was placed onto a 1.5 x 10.0 cm^2 column. The column, packed with CH_2Cl_2, was eluted by the CH_2Cl_2 solvent. The combined CH_2Cl_2 column fractions were stripped of CH_2Cl_2 by rotary evaporation to yield 0.37 g (48%) light yellow oil. This oil was purified by vacuum distillation 70-71^oC/1.4 mm Hg in a molecular still and afforded 0.21 g (27%) colorless oil that solidified in a refrigerator to a solid (mp. 54.2-56.8^oC); nmr ($DCCl_3$)δ, (m, 4.87, 6H), (d, 1.49, 6H); ir (neat film) cm^{-1}, 2990, 2940, 2880 (sat. CH), 1570, 1315 (NO_2); mass spec. 235 (M-1), 221 (M-15), 193 (M-43), 191 (M-45), 177 (M-59); Elemental Analysis (Calc. C 35.6, H 5.1, N 11.9), (Found C 35.4, H 4.9, N 12.0).

Addition of 2,2,8,8-Tetranitro-4,6-Dioxa-1, 9-Nonadiol (DINOL) (19) to Divinyl Ether (10). (a). Dinol monohydrate. (b). Dinol anhydrous.

a. A 100 ml single-neck round bottom flask charged with 0.50 g (7.1 mmol) divinyl ether, 50 ml CH_2Cl_2, 2.46 g (7.1 mmol) dinol monohydrate, and 250 mg Hg_2SO_4, was stirred at room temperature 8 1/4 hours, followed by 41 1/4 hours of reflux. Solvent removal by rotary evaporation produced a solid black material which was dissolved in a minimum amount of CH_2Cl_2 and liquid chromatographed on a 2.0 x 20.0 cm SiO_2 (60/200 mesh) column using CH_2Cl_2 elutant. The CH_2Cl_2 fraction was collected until the yellow color on the column just reached the bottom of the silica gel. Rotary evaporation of the CH_2Cl_2 afforded 0.55 g of a white solid (mp 235.0-238.6^{0}C). The solid was recrystallized in $CHCl_3$ for analysis; nmr (d_6 - DMSO)δ, (quart, 5.17, 1H), (s, 4.88, 2H), (d, 4.54, 8H), (d, 1.32, 3H);[28] ir (KBr pellet) cm^{-1}, 3500 (OH)[29], 3000, 2955, 2900 (sat. CH), 1570, 1325 (NO_2); mass spec. 193 (largest fragment). A reaction using only 1.23 g dinol monohydrate afforded 5.3 g white solid from the silica gel column, recrystallization from $CHCl_3$ gave 4.8 g of white solid material.

b. Anhydrous dinol was prepared by charging a 100 ml single-neck round bottom flask with 1.23 g (3.3 mmol) dinol monohydrate, 50 ml, 1,2-dichloroethane and a teflon coated stir bar. The flask was fitted with a Dean-Stark tube topped with a water-cooled reflux condenser and Drierite fitted drying tube. The solution was stirred under reflux to azeotrope [92/8: $H_2O/(CH_2Cl)_2$] off the water for 21 1/2 hours. The 15 ml dichloroethane trapped in the side arm with the water layer was discarded, and a fresh 15 ml portion of solvent was added to the 100 ml single-neck round bottom raction flask. Next, the anhydrous dinol solution was charged with 0.5 g (7.1 mmol) divinyl ether and 100 mg Hg_2SO_4. The reaction was stirred under reflux for 79 hours, then was filtered. Rotary evaporation of the 1,2-dichloroethane solvent afforded a brown oily residue which was placed on a silica get (60/200 mesh) column packed with CH_2Cl_2. Elution with CH_2Cl_2 fractioned the crude residue into two materials. The first

product isolated was a waxy white solid (0.28 g) which appeared to be a vinyl terminated polymeric material; nmr ($DCCl_3$)δ, (dd, 6.44, 1H), (m and s overlap, 4.80, 12H), (sharp m, 4.46, 30H), (two combined d, 1.34, 17H); ir (neat film) cm^{-1}, 3000, 2940, 2910 (sat. CH), 1645, 1620 (C = C), 1570, 1320 (NO_2).

Addition of Divinyl Ether 10 with Fluorodinitromethane 21. A 50 ml single-neck round bottom flask charged with 0.50 g (7.1 mmol) divinyl ether 10, 20 ml CCl_4, 0.89 g (7.2 mmol) fluorodinitromethane 21, 100 mg Hg_2SO_4 and 50 mg pyridine, was stirred under reflux 17 hours. The reaction solution was then cooled to room temperature for an additional 1 1/2 hours. Rotary evaporation afforded 0.22 g (19%) yellow oil. This oily product was dissolved in approximately 1 ml CH_2Cl_2 and eluted through a short 2.0 cm x 1.5 cm SiO_2 column previously packed as a CH_2Cl_2 slurry. The 10 ml CH_2Cl_2 filtrate was removed by rotary evaporation to provide a light yellow oil 22.

A much higher yield of the diadduct 22 was obtained when another catalyst was substituted for the Hg_2SO_4. The new catalyst was prepared reproduceably by placing 2.0 g HgO in a 100 ml single-neck round bottom flask along with 10 ml trifluoroacetic anhydride. The single-neck flask was fitted with a water-cooled reflux condenser topped with a Drierite containing drying tube. The suspension was stirred under reflux 2 1/2 hours. Then 5 ml additional trifluoroacetic anhydride was added and an additional 2 1/2 reflux followed. Next, 2 ml trifluoroacetic acid was added and reflux continued. Thirty minutes later an additional 3 ml trifluoroacetic acid was added. After another 15 minutes, all material dissolved to give a yellow solution. Then, 5 ml additional trifluoroacetic anhydride was added and an additional 15 minute reflux followed. The solvent was removed by rotary evaporation leaving a wetted off-white solid. By ir and x-ray analyses, this solid was confirmed as being mercury (II) trifluoroacetate wetted with trifluoroacetic acid.[30] This sample was then used

in place of the Hg_2SO_4. A 50 ml single-neck round bottom flask was charged with 0.5 g (7.1 mmol) divinyl ether 10, 20 ml CH_2Cl_2, 0.89 g (7.2 mmol) fluorodinitromethane 21, and 100 mg wetted mercury (II) trifluoroacetate. The reaction was stirred under reflux 18 1/2 hours, but no reaction occurred. Next, 100 mg pyridine was added, and the reaction was stirred under reflux for an additional 20 1/2 hours. A reddish brown solution resulted which was filtered and stripped of solvent by rotary evaporation. The reddish brown oil was eluted through a short 3.0 cm x 1.5 cm SiO_2 (60/200 mesh) column, prepared from a CCl_4 slurry, with CCl_4 until the yellow color just reached the bottom of the column (Fraction 1). The column was then eluted with 35 ml CH_2Cl_2 (Fraction 2). Solvent removal from both fractions 1 and 2 afforded a total of 0.43 g (47%) diadduct 22 product; nmr ($DCCl_3$)δ, (d, quart, 5.14, 2H), (d, 1.44, 6H) with a singlet (2H) at δ 3.25 which exchanged with D_2O. This diadduct 22 appears to be hydroscopic and often appears with this singlet thought to be one water of hydration even when vacuum distilled 37.6-38.4^{o}C/0.1 mm; ir (neat film) cm^{-1}, 3500 (OH), 3000, 2950, 2900 (sat. CH), 1600, 1310 (NO_2); density = 1.46 g/ml. As this light yellow (nearly colorless) oil 22 stands at room temperature, it gradually turns more yellow and eventually decomposes.

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