4-Methylmethylenecyclohexane [bp 124–125° (724 mm), $n^{25}\text{D}$ 1.4425, $d^{25}{}_4$ 0.7966; lit.[29] bp 122–123°, $n^{22}\text{D}$ 1.4446, d^{22} 0.7925; lit.[11] $n^{20}\text{D}$ 1.4447] was prepared from 4-methylcyclohexanone *via* the Wittig reaction,[11,30] or by the pyrolysis of the acetate of 4-methylcyclohexylmethanol as is described in the following procedure for the preparation of 3-methylmethylenecyclohexane.[3]

3-Methylmethylenecyclohexane.—Sodium *m*-toluate (29.5 g of toluic acid, 9.5 g of sodium hydroxide, and 40 ml of water) was reduced catalytically (about 7 g of Raney nickel) in a 300-ml rocking autoclave for 4 hr at 175° with an initial pressure of hydrogen of 2500 psi. The product was obtained as a mixture of *cis* and *trans* isomers of 3-methylcyclohexanecarboxylic acid which distilled at 89–99° (1 mm) (90%).

The acid was reduced with lithium aluminum hydride, as customary for the reduction of ether soluble compounds,[32] to yield the mixed alcohols, bp 101–106° (23 mm), which were converted by gentle heating with acetyl chloride to the mixed acetates, bp 92–97° (13 mm).

The acetate was passed at a rate of 4–5 drops per minute through a heated (475–500°) Pyrex tube (50 cm by 30 mm) packed with Pyrex chips. The crude mixture was dissolved in ether, washed with a saturated solution of sodium bicarbonate and dried. The solvent was removed by distillation through an efficient column and the product distilled at 119–120° (726 mm), $n^{20}\text{D}$ 1.4461, $n^{25}\text{D}$ 1.4429, $d^{25}{}_4$ 0.7882; lit.[33] bp 123–124°, $n^{20}\text{D}$ 1.4461, d^{20} 0.794; see also Smith and Trotter.[34]

1,3-Dimethylcyclohexene.—2,6-Dimethylcyclohexanol, prepared by hydrogenating 2,6-dimethylphenol over Raney nickel according to the directions of Carlin,[35] was converted to the palmitate which was pyrolyzed as suggested by Birch.[36]

Palmitoyl chloride (121 g) was added to 2,6-dimethylcyclohexanol (50 g) in 300 ml of dry dimethylaniline at 20°. The mixture was stirred for 1 hr at 20° and then on a steam bath for 5 hr. Afterwards, it was poured into 1200 ml of iced 2 *M* hydrochloric acid. The ester was extracted with ether. The extract was washed with a saturated solution of sodium bicarbonate, dried over sodium sulfate, and concentrated. The concentrate was heated to 375° (bath temperature); pyrolysis took place. An ether extract of the distillate was washed with a solution of sodium bicarbonate, dried over magnesium sulfate, and distilled to yield 23 g of the crude 1,3-dimethylcyclohexene, bp 115–125°. Careful fractionation of this material (Todd column) yielded 19 g of the pure olefin, bp 123.5–124° (727 mm), $n^{25}\text{D}$ 1.4467, $d^{25}{}_4$ 0.7996; lit.[37] bp 124–126°, $n^{25}\text{D}$ 1.4480, d^{25} 0.807; lit.[34] bp 130–131° (750 mm), $n^{25.5}\text{D}$ 1.4465, $d^{25}{}_4$ 0.799.

The same product was also obtained by the pyrolysis of the acetate at 470–480°.[31,36]

2,3-Dimethylcyclohexene was separated by preparative chromatography on a 25 ft by 0.5 in. o.d. column of 20% polyethylene glycol 1000 monostearate on 60–80 mesh firebrick at 95° from a mixture of 25% 2,4-dimethylcyclohexene and 75% of 3,5-dimethylcyclohexene which had been obtained from the pyrolysis of 2,4-dimethylcyclohexyl acetate.[31] The compound has been carefully characterized recently by Smith and Trotter.[34]

Procedures for hyrogenation and the analysis of the products have been described previously.[4,6] In each experiment, 0.2 ml of the olefin, 5 ml of acetic acid, and 10–20 mg of platinum oxide were used. Experiments at 1-atm pressure and below were done in a constant-pressure apparatus, those in the intermediate range (2–5 atm) in a Parr low pressure hydrogenation apparatus, and at high pressure in a rocker type high pressure bomb. A 25 ft by 0.25 in. o.d. column containing 20% polyethylene glycol 1000 monostearate on 60–80 mesh firebrick and operated at 90–100° was used for the analysis of mixtures other than those from the hydrogenation of 1,4-dimethylcyclohexene and 4-methylmethylenecyclohexane for which a 15 ft by 0.25 in. o.d. column was adequate. Separations of all products and reactants were satisfactory, the peaks being symmetrical and well separated.

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(29) O. Wallach and E. Evans, *Ann.*, **347**, 345 (1906).

(30) *Org. Syn.*, **40**, 66 (1960).

(31) D. H. Froemsdorf, C. H. Collins, G. S. Hammond, and C. H. DePuy, *J. Am. Chem. Soc.*, **81**, 643 (1959).

(32) W. G. Brown, *Org. Reactions*, **VI**, 487 (1951).

(33) O. Wallach and E. Beschke, *Ann.*, **347**, 342 1(960).

(34) G. V. Smith and P. J. Trotter, *J. Org. Chem.*, **28**, 2450 (1963).

(35) R. B. Carlin, *J. Am. Chem. Soc.*, **67**, 928 (1945).

(36) A. J. Birch, *J. Chem. Soc.*, 1964 (1947).

(37) M. Mousseron, R. Richard, and R. Granger, *Bull. Soc. Chim. France*, **13**, 222 (1946).

Aliphatic Polynitro Compounds. I. Synthesis of 1,1,1-Trinitrochloroethane and Its Rearrangement to Dipotassium Tetranitroethane[1]

FRANK G. BORGARDT, ALLAN K. SEELER, AND PAUL NOBLE, JR.

Lockheed Palo Alto Research Laboratories,
Lockheed Missiles and Space Company, Palo Alto, California 94304

Received May 2, 1966

A general procedure for the conversion of β-polynitro-substituted alcohols to their corresponding halides is described, which consists of the treatment of the alcohol with thionyl chloride containing catalytic amounts of pyridine or pyridine hydrochloride. 1,1,1-Trinitrochloroethane undergoes a novel rearrangement reaction to dipotassium tetranitroethane upon treatment with nitrite ion in basic media. A study of the chemistry of 1,1,1-trinitrochloroethane permits some conclusions regarding possible mechanisms for this rearrangement.

During the course of a program investigating the chemistry of polynitro compounds attention was directed toward studying the little known β-halogen-substituted aliphatic polynitro compounds. Although a few reports of the synthesis of some of these compounds have appeared, the chemistry of these compounds has been largely unexplored. The recent appearance in the literature of a few compounds previously studied in our laboratories prompts the reporting of our results at this time. Novikov and Shvekgheimer[2] have reported the synthesis of 1,1,1-trinitrochloroethane (I) and 2,2-dinitrochloropropane (II) by treating the mixed acetal product of the reaction of corresponding polynitro alcohols and ethyl vinyl ether with phosphorus pentachloride. The yields of chlorides from the mixed acetals were 40 and 57%, respectively. Kissinger and co-workers[3] reported the synthesis of 2,2-dinitro-1,3-dichloropropane (III) and 2,2-dinitrochloropropane (II) from reactions of the corresponding nitro alcohols with sulfuryl chloride and pyridine in yields of 57 and 62%, respectively. Ungnade and Kissinger[4] have recently reported a reaction

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(1) This work has been carried out as a part of the Lockheed Independent Research Program.

(2) S. S. Novikov and G. A. Shvekgheimer, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 2026 (1960).

(3) L. W. Kissinger, T. M. Benziger, H. E. Ungnade, and R. K. Rohner, *J. Org. Chem.*, **28**, 2491 (1963).

(4) H. E. Ungnade and L. W. Kissinger, *ibid.*, **31**, 369 (1966).

TABLE I

CHLORINATION STUDIES OF 2,2,2-TRINITROETHANOL

Chlorinating agent	Catalyst[a]	Reaction time, hr	Product	Yield, %	Mp or bp (mm), °C
$SOCl_2$	. . .	70	$[(O_2N)_3CCH_2O]_2SO$ (VI)	34	96–96.5 (mp)
$SOCl_2$	Pyr–$SOCl_2$	6	$(O_2N)_3CCH_2Cl$ (I)	80–95	67–68 (10)
$SOCl_2$	Pyr·HCl	6	I	81	109–110 (60)
$SOCl_2$	Quin–$SOCl_2$	6	I	49	67–68 (10)
$SOCl_2$	Pic–$SOCl_2$	6	I	53	65–66 (10)
$SOCl_2$	Pip·HCl	7	$[(O_2N)_3CCH_2O]_2SO$ (VI)	85	87–90 (mp)
$SOCl_2$	$FeCl_3$	5	$(O_2N)_3CCH_2OSOCl$ (VII)	88	68–69 (0.05)
SO_2Cl_2	Pyr·HCl	20	$(O_2N)_3CCH_2OSO_2Cl$[b] (VIII)	66	84–85 (0.05)
SO_2Cl_2–pyr[c]	. . .	10	$(O_2N)_3CCH_2Cl$ (I)	56	36–37 (0.5)

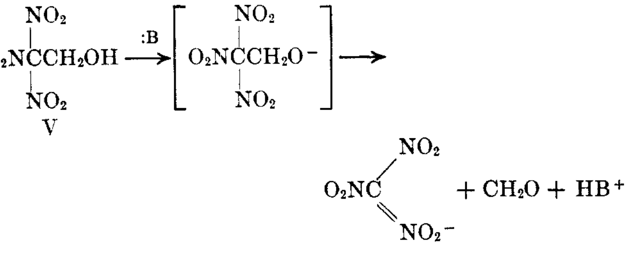
[a] About 5% by weight of the nitro alcohol was used; pyr = pyridine; quin = quinoline; pip = piperidine; pic = 4-picoline. [b] A trace of 1,1,1-trinitrochloroethane was recovered in the forerun of the distillation. [c] Pyridine (1 mole)/mole of nitro alcohol was used; methylene chloride was the solvent in this reaction. All other reactions used the chlorinating agent as solvent.

of 1,2-dichloro-1,1-dinitroethane (IV) with potassium iodide in alcohol solution yielding 2,2-dinitroethyl methyl ether. This reaction is analogous to those of 2-bromo-2,2-dinitroethyl acetate with bases.[5]

$$ClC(NO_2)_2CH_2Cl + KI \longrightarrow KC(NO_2)_2CH_2Cl \longrightarrow C(NO_2)_2{=}CH_2 \xrightarrow{ROH} HC(NO_2)_2CH_2OR$$

$$R = CH_3,\ C_2H_5,\ CH_2CH_2Cl,\ CH_2CH_2Br$$

Synthesis of 1,1,1-Trinitrochloroethane.—It has been found that most ordinary methods used to effect the conversion of alcohols to halides fail with polynitro alcohols. For example, the reaction of 2,2,2-trinitroethanol (V) with phosphorus pentachloride leads to the formation of phosphorus esters of V and thionyl chloride reacts with V to give the sulfite ester.[6] Reactions which rely on base to promote the conversion fail because of the fast reverse Henry reaction which takes place preferentially[7] between the nitro alcohol and base. In the case of V this leads to the formation of nitroformate ion and formaldehyde.

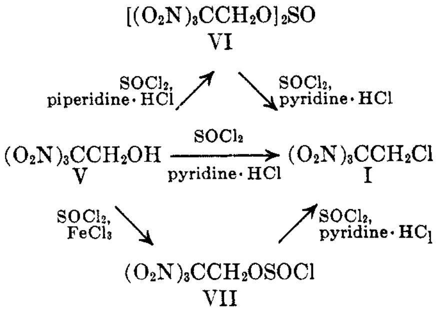


$$\underset{V}{O_2N\overset{NO_2}{\underset{NO_2}{C}}CH_2OH} \xrightarrow{:B} \left[O_2N\overset{NO_2}{\underset{NO_2}{C}}CH_2O^- \right] \longrightarrow O_2NC(NO_2)NO_2^- + CH_2O + HB^+$$

β-Dinitro-substituted alcohols are also readily dissociated in polar solvents.[8] Investigation of various chlorination techniques in these laboratories led to the discovery that the conversion of V to 1,1,1-trinitrochloroethane (I) could be effected easily and in yields of 85–95% by the use of thionyl chloride with pyridinium hydrochloride, or a previously made solution of catalytic amounts of pyridine in thionyl chloride.[9] Some of the more interesting observations made during the course of these studies are given in Table I.

The compounds, bis-2,2,2-trinitroethyl sulfite (VI) and 2,2,2-trinitroethyl chlorosulfite (VII), are converted in high yield to 1,1,1-trinitrochloroethane (I) by refluxing a short time in thionyl chloride containing a small amount of pyridine or pyridine·hydrochloride (Scheme I). These studies indicate that compounds of the pyridine family are the only effective catalysts in the conversion of V to I by thionyl chloride. When sufuryl chloride is used as the chlorinating agent it is necessary to use 1 mole of pyridine/mole of alcohol to effect the same conversion.

SCHEME I



The compounds, 1,2-dichloro-1,1-dinitroethane (IV), 1,3-dichloro-2,2-dinitropropane (III), 2,2-dinitrochloropropane (II), and 2,2-dinitro-1-chlorobutane (IX), were synthesized from their corresponding alcohols by the thionyl chloride–pyridine·hydrochloride procedure.

Several synthetic approaches were investigated for the attempted preparation of 1,1,1-trinitrobromoethane, all, however, were unsuccessful. For example, thionyl bromide–pyridinium hydrobromide, pyridinium hydrobromide–bromine complex, and pyridylpyridinium bromide hydrobromide gave negative results.

Reactions of 1,1,1-Trinitrochloroethane.—A study of the reactions of 1,1,1-trinitrochloroethane (I) led to the interesting discovery that certain bases and reducing agents cause an unusual rearrangement. Initially it was found that treatment of I (Scheme II) with an aqueous methanolic solution of potassium hydroxide produced a small amount of a bright yellow solid which was identified as dipotassium tetranitroethane (X). The yield of this reaction was greatly improved by the addition of nitrite ion. Potassium iodide and cyanide under similar conditions also gave X in low yields. Eventually it was found that the

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(5) M. B. Frankel, *J. Org. Chem.*, **23**, 813 (1958); L. J. Winters and W. E. McEwen, *Tetrahedron*, **19**, *Suppl.* **1**, 49 (1963).

(6) Private communication from H. Feuer, Purdue University, April 12, 1961.

(7) For leading references and further discussions of the chemistry of polynitro alcohols, see P. Noble, Jr., F. G. Borgardt, and W. L. Reed, *Chem. Rev.*, **64**, 19 (1964).

(8) T. Hall, *J. Org. Chem.*, **29**, 3587 (1964).

(9) P. Noble, Jr., W. L. Reed, and F. G. Borgardt, U. S. Patent 3,180,899 (April 27, 1965); *Chem. Abstr.*, **63**, 11359*e* (1965).

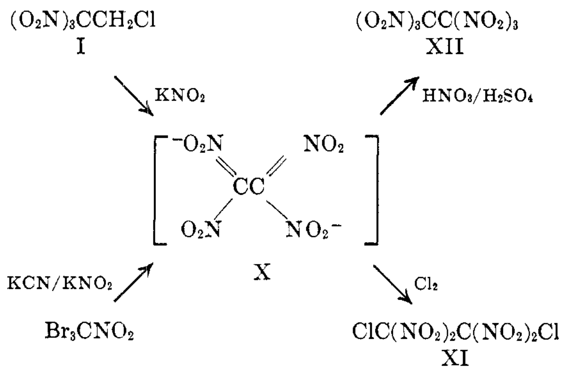
TABLE II

REACTIONS OF 1,1,1-TRINITROCHLOROETHANE WITH BASE

Reactants,[a] moles								Yield,
TNE–Cl	KNO_2	KOH	KOAc	KCN	KI	NH_3	Product	%
0.01	...	0.03					DKTNE[b]	21
0.01	0.01	0.03					DKTNE[b]	16
0.01	0.04	0.03					DKTNE[b]	31.5
0.01	0.04	...	0.02				DKTNE[b]	64
0.01	0.04	...	0.041				DKTNE[b]	65
0.01	0.04	...	0.041				DKTNE[b]	85[c]
0.01	0.04	...	...	0.02			DKTNE[b]	63
0.01	0.04	...	...	...	0.04		DKTNE[b]	64
0.01	0.04	...	...	...	...	*d*	DKTNE + KDNM[e]	*e*
0.01	0.047	...	...	...	...	...	DKTNE	55
0.01	0.094	...	...	...	...	...	DKTNE	91
0.01	...	...	0.082	...	...	...	KDNM	76
0.01	...	...	...	...	0.024	...	DKTNE	21
0.05	0.15	0.15	...	...	...	...	DKTNE	60
0.05	0.15	0.01	0.15	...	...	...	DKTNE	100[f]

[a] All reactions were run in aqueous methanol solution. [b] DKTNE = dipotassium tetranitroethane. [c] Solvent, aqueous ethanol. [d] Saturated solution. [e] KDNM = potassium dinitromethane; recrystallization of mixture from water gave DKTNE (53%). [f] Crude product.

SCHEME II

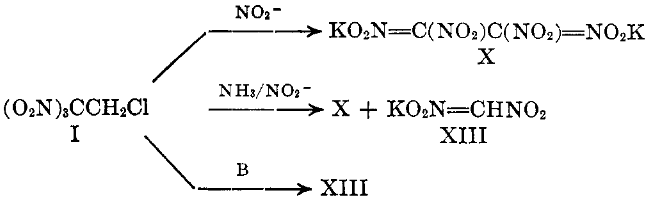


best yields were obtained with potassium nitrite alone in aqueous alcoholic solution.[9] A summary of the studies of these reactions is presented in Table II.

The only previously reported synthesis of X involved the coupling of bromopicrin by potassium cyanide and nitrite,[10] but only in low yields. This is an expensive procedure that gives only impure product at best.

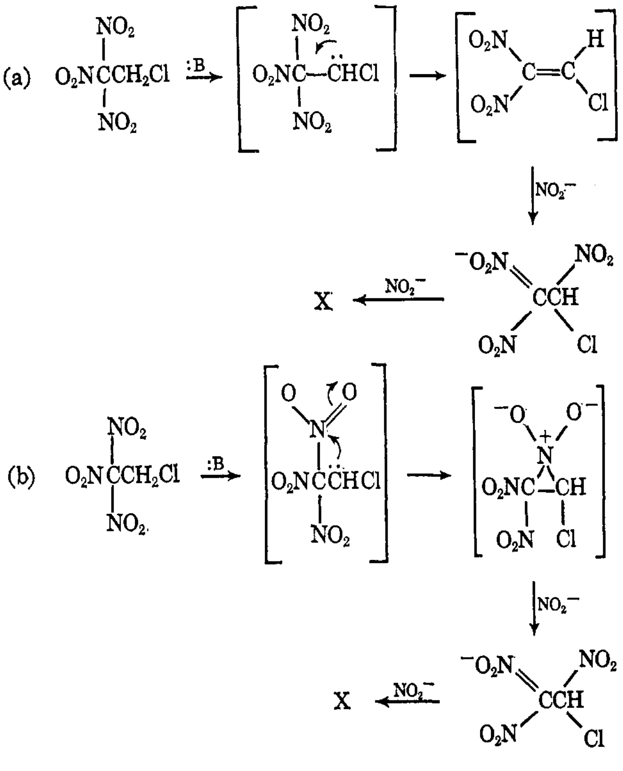
The chemistry of X remains virtually unexplored, with only the chlorination and nitration reactions, producing 1,2-dichlorotetranitroethane (XI) and hexanitroethane (XII), respectively, having been reported.[10]

When 1,1,1-trinitrochloroethane (I) is treated with ammonia in aqueous methanol, followed by addition of potassium ion to precipitate the products, a mixture of dipotassium tetranitroethane (X) and potassium dinitromethane (XIII) is formed. A similar reaction is observed with piperidine. The reaction of I with sodium methoxide also leads to the formation of dinitromethane, isolated as the potassium salt. Possible reaction paths by which the rearrangement of I to X might take place are shown in Scheme III. Reaction path a involves removal of an acidic proton by base, followed by elimination of nitrite ion to produce as a reactive transitory intermediate 1,1-dinitrochloroethylene. The Michael addition of nitrite ion to this olefinic intermediate would produce the mononitronate salt of 1,1,2-trinitrochloroethane, which would be expected to undergo the ter Meer reaction[7,11] in the presence of excess nitrite ion and base. Reaction path b involves the formation of a bridged nitro group, transfer of a nitro group by a concerted type process, and, finally,



B = piperidine, KOAc, ⁻OMe

SCHEME III



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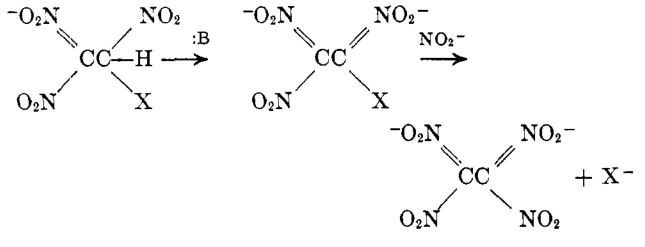
(10) W. Will, *Ber.*, **47**, 961 (1914); L. Hunter, *J. Chem. Soc.*, **123**, 543 (1923).

(11) E. ter Meer, Ann., **181**, 1 (1876); F. M. Hawthorne, *J. Am. Chem. Soc.*, **78**, 4980 (1956).

formation of the same 1,1,2-trinitrochloroethane salt as in path a.

In an attempt to determine the presence of an olefinic intermediate as a step in this rearrangement, the reaction was carried out in the presence of potassium phthalimide, which proved to be an effective trap for the 1,1-dinitroethylene intermediate in Frankel's[5] "dinitroethylation" reaction. However, no analogous intermediate could be isolated and only low yields of X were obtained. In this case, the above experiment does not preclude the existance of an olefinic intermediate because it is quite possible that the final step involving a ter Meer type base-catalyzed displacement with nitrite ion could take place with a phthalimidonitromethyl as well as a chloronitromethyl group.



X = halogen or phthalimido

The ter Meer reaction has been shown by Hawthorne[11] to be subject to general base catalysis with the rate-controlling step being the formation of the aci-nitro salt followed by nucleophilic displacement of X by nitrite ion at high nitrite concentration. The reaction, however, may be inhibited by excess strong base by causing competitive displacement of halogen by hydroxyl or by another 1-halo-1-nitroalkane anion and producing hydrolysis or coupled by-products. This deleterious effect of strong base is also noted in our work as shown in Table II. Attempts to provide more evidence bearing on the mechanism of this rearrangement are described in the second paper of this series.[12]

Reactions of Dipotassium Tetranitroethane.—It was found that the dipotassium salt of tetranitroethane X could be readily converted to the disodium or dilithium salts of tetranitroethane XIV and XV on a Dowex 50-X8 ion-exchange column. Evaporation of the water gives the solid mono or dihydrates of XIV and XV, all of which are very impact sensitive. The salts are quite soluable in polar organic solvents which may make the sodium and lithium salts useful intermediates in studies of the reactions of tetranitroethane dianion with organic materials. The calcium and beryllium salts have also been prepared by the ion-exchange technique, but have not been completely characterized. The dipotassium salt X is apparently stable indefinitely when stored as the dry salt at room temperature. The hydrated and anhydrous sodium salt and anhydrous lithium salt degrade slowly at room temperature; the hydrated lithium salt, however, appears to be fairly stable.

Acidification of the dipotassium tetranitroethane in a dry methylene chloride suspension with dry hydrogen chloride produces a solution of 1,1,2,2-tetranitroethane (XVI) which slowly decomposes at room temperature. Although the material cannot be isolated for analysis, the infrared spectrum is consistent with the assigned structure (carbon tetrachloride solution) and the nmr spectrum shows a single peak at 7.1 ppm (δ) from tetramethylsilane. Bromination of an ether suspension of X at $-20°$ leads to the formation of 1,2-dibromotetranitroethane, a white solid which decomposes rapidly at room temperature.

Preliminary attempts to prepare organic derivatives of X, XIV, XV, and XVI have thus far failed to yield identifiable products.

Experimental Section[13]

2,2,2-Trinitroethanol (V).—To a solution of 64.4 g (1.0 mole) of potassium hydroxide in 60 ml of water and 140 ml of ethanol was added dropwise 98 g (0.50 mole) of tetranitromethane with stirring, maintaining the temperature between 15 and 20°. The yellow precipitate of potassium nitroform was collected, washed with 50 ml of ice-water, 50 ml of ethanol, and finally, 50 ml of ice-water. (*Caution:* potassium nitroform cannot be stored.) The precipitate was immediately added to 160 ml of water and 45 ml of 38% formalin, and 50 ml of concentrated hydrochloric acid was added in one portion. The mixture was stirred for 2 hr at room temperature and extracted with methylene chloride. The methylene chloride extracts were dried with anhydrous magnesium sulfate and filtered, and the filtrate was distilled azeotropically to remove all possible water. Final concentration was accomplished by evaporation *in vacuo* with a rotary evaporator. Crystallization of the residue from carbon tetrachloride gave 78.8 g (86%) of colorless needles, mp 70–71° (lit.[14] mp 72°).

1,1,1-Trinitrochloroethane (I). **Method A.**—To a solution of 68 g (0.38 mole) of dry V in 70 ml of thionyl chloride was added 1.0 g of anhydrous pyridine·hydrochloride in several portions during a 6-hr refluxing reaction time. The excess thionyl chloride was removed by distillation *in vacuo* and the residue was fractionated under reduced pressure to give 61 g (81%) of I, bp 109–110° (60 mm), $n^{25}\text{D}$ 1.4651. A safer procedure involved washing a methylene chloride solution of the crude product with water, drying with anhydrous magnesium sulfate, evaporating the solvent, and then fractionating the residue at pressures below 10 mm: bp 64–65° (10 mm); the nmr spectrum (60 Mc) of *ca.* 10% solution of I in carbon tetrachloride showed a single peak at 4.77 ppm (δ); principal infrared adsorption (pure liquid film) at 1600 (s), 1420 (m), 1350 (m), 1300 (s), 860 (ms), 820 (ms), and 790 (ms) cm^{-1}; lit.[2] bp 59° (4 mm); $n^{20}\text{D}$ 1.4668.

Anal. Calcd for $C_2H_2ClN_3O_6$: C, 12.04; H, 1.01; Cl, 17.77. Found: C, 12.25; H, 0.97; Cl, 17.94.

Method B. From Sulfuryl Chloride (Modification of a Procedure by Kissinger).[3]—To 46.8 g (0.26 mole) of crude V was added 17.5 g (0.13 mole) of sulfuryl chloride, then 100 ml of methylene chloride. Pyridine (20.5 g, 0.26 mole) was then added dropwise with stirring. The resulting pale yellow solution was refluxed for 6 hr, cooled overnight, then refluxed for 4 hr more. The mixture was poured into ice-water, and the methylene chloride layer was separated and dried over anhydrous magnesium sulfate. The mixture was filtered, the solvent was removed under reduced pressure, and the residue was fractionated: yield 28.5 g (56%), bp 37–37° (0.5 mm). The pot residue weighed 7.8 g and contained some 2,2,2-trinitroethyl chlorosulfate, which can be converted to I by heating with pyridine·hydrochloride.

2,2-Dinitrochloropropane (II).—2,2-Dinitropropanol[15] (50 g, 0.33 mole) and 50 ml of thionyl chloride containing 2 g of pyridine was refluxed for 8 hr. A solution of 8 ml of thionyl chloride containing 2 ml of pyridine was added and refluxing was continued for 8 hr longer. The excess thionyl chloride was removed under vacuum and the residue was poured onto ice–water. The mixture was extracted with methylene chloride, and the methylene chloride layer was separated and dried over magnesium sulfate. The solvent was removed and the residue was fractionated under

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[12] F. G. Borgardt, P. Noble, Jr., W. L. Reed, and A. K. Seeler, in preparation.

[13] Melting points and boiling points are uncorrected. *Caution:* many of the compounds described are sensitive to friction and impact and must be handled with care. Microanalysis was by Berkeley Analytical Laboratories, nmr by Varian Associates.

[14] H. Feuer and T. J. Kucera, *J. Org. Chem.*, **25**, 2069 (1960).

[15] E. E. Hamel, J. S. Dehn, J. A. Love, J. J. Scigliano, and A. H. Swift, *Ind. Eng. Chem. Prod. Res. Develop.*, **1**, 108 (1962).

reduced pressure: yield 23.9 g (42%); bp 55–57° (3 mm); lit.[3] 73° (8 mm). The nmr spectrum (60 Mc) of *ca.* 10% of II in carbon tetrachloride showed a single peak at δ = 4.63 ppm.

Anal. Calcd for $C_3H_5ClN_2O_4$: C, 21.4; H, 3.0; N, 16.6; Cl, 21.0. Found: C, 21.24; H, 2.84; N, 16.32; Cl, 21.22.

2,2-Dinitropropanediol.—This compound was prepared by the oxidative nitration reaction of Shechter and Kaplan.[16] A mixture of 406 g (6.7 moles) of nitromethane, 1079 g of 36% formalin, and 919 g of water was cooled to 0°. To this solution was added with vigorous stirring a few drops of a solution of 306 g of sodium hydroxide in 800 ml of water with the acetone–Dry Ice bath removed. After the temperature had risen to 40°, the mixture was again cooled to 0° and the remainder of the sodium hydroxide solution was added in a steady stream, keeping the temperature between −5 and +5°. After addition, the mixture was allowed to stir for 1–2 hr at 0°. To this solution was added 460 g (6.7 moles) of sodium nitrite. This entire mixture was then added to a solution of 2263 g (13.3 moles) of silver nitrate in 3000 ml of distilled water, keeping the temperature below 25°. The mixture was sitrred for 2 hr, the silver was filtered, and the filtrate was extracted with five 1-l. portions of ether. The ether extracts were dried with magnesium sulfate overnight. The ether solution was evaporated to a volume of less than 1 l., methylene chloride was added, and the resulting solution was cooled to precipitate the product. The colorless crystalline product weighed 850 g (77%): mp 146–147°; lit.[17] mp 142°.

1,3-Dichloro-2,2-dinitropropane (III).—2,2-Dinitropropanediol (20 g, 0.12 mole) was dissolved in 50 ml of thionyl chloride. Pyridine hydrochloride (3 g) was added then the reaction mixture was refluxed for 72 hr. The excess thionyl chloride was removed *in vacuo* and the oily residue was fractionated under reduced pressure to give 19.6 g (81%) of product, bp 60–62° (5 mm). Sublimation of the product gave white waxy solid: mp 38–39°; lit.[3] mp 38–34°, bp 48° (2 mm); lit[18] mp 35–36°, bp 47–50° (0.2 mm). With a threefold increase in the amount of pyridine catalyst (pyridine premixed with $SOCl_2$), the reaction time was cut to 12–18 hr (yield of a comparable product was 77.5%).

2-Chloro-2,2-dinitroethanol.—To a solution of 166 g (1.0 mole) of 2,2-dinitropropanediol in 500 ml of absolute ethanol was added a solution of 71.2 g (1.1 mole) of potassium hydroxide in 100 ml of water. The temperature was maintained at 0–5° during the addition. The reaction mixture was stirred for 1.5 hr and then filtered. The precipitate was washed with absolute ethanol, then ether. The precipitate, potassium dinitroethanol, was slurried in 1 l. of ether and chlorine gas slowly introduced at a temperature of −5 to −10°. When the yellow salt had disappeared, the solution was filtered and evaporated, leaving a low-melting solid residue. Distillation under reduced pressure gave 143 g (85%) of 2-chloro-2,2-dinitroethanol: bp 68–70° (3 mm); lit.[4] mp 40–42°. This compound is very hygroscopic.

1,2-Dichloro-1,1-dinitroethane (IV).—To a solution of 36.3 g (0.214 mole) of 2-chloro-2,2-dinitroethanol in 50 ml of thionyl chloride was added 1 g of pyridine·hydrochloride in several portions over a 6-hr refluxing period. The mixture was refluxed overnight. The excess thionyl chloride was removed under reduced pressure and the residue was fractionated. The yield of IV was 33.5 g (83%): bp 45-47° (5 mm), $n^{25}D$ 1.4677; lit.[4] bp 60 (10 mm), $n^{25}D$ 1.4672.

Anal. Calcd for $C_2H_2Cl_2N_2O_4$: N, 14.83; Cl, 37.52. Found: N, 14.73; Cl, 37.42.

2,2,2-Trinitroethyl Sulfite (VI). Method A.[6]—A solution of 32 g (0.177 mole) of V in 80 ml of thionyl chloride was refluxed for 70 hr. The excess thionyl chloride was then removed by distillation under reduced pressure at 85° (bath temperature) and 0.01 mm. The crude sulfite ester VI was recrystallized from carbon tetrachloride giving 12.4 g (34.5%) of VI, mp 96–96.5°.

Anal. Calcd for $C_4H_4N_6O_{15}S$: C, 11.77; H, 0.99; S, 7.84. Found: C, 11.68; H, 0.92; S, 7.59.

Method B.—To a solution of 20 g (0.111 mole) of V in 20 ml of thionyl chloride was added a solution of 0.5 g (0.004 mole) of anhydrous piperidine·hydrochloride in 10 ml of thionyl chloride. The reaction mixture was refluxed for 7 hr; then the excess thionyl chloride was removed by distillation under reduced pressure as in A. The pot residue solidified on standing. The yield of crude VI was 23 g (85.5%): mp 87–90°; principal infrared absorption (KBr) at 1600 (s), 1300 (ms), 1210 (ms), 1050 (m), 1020 (m), 990 (m), 810 (ms), 788 (m), and 740 (m) cm^{-1}.

2,2,2-Trinitroethyl Chlorosulfite (VII).—To 20 g (0.11 mole) of V was added a mixture of 1 g of anhydrous ferric chloride in 30 ml of thionyl chloride. The mixture was refluxed for 5 hr then fractionated under reduced pressure. The fraction boiling at 68–69° (0.05 mm) was collected. The yield of trinitroethyl chlorosulfite was 25.5 g (88%): $n^{25}D$ 1.4988; principal infrared absorption (liquid film) at 1600 (s), 1430 (m), 1300 (s), 1230 (s), 1020 (s), 990 (s), 880 (m), 858 (ms), 810 (s), 785 (s), and 743 (s) cm^{-1}.

Anal. Calcd for $C_2H_2ClN_3O_8S$: C, 9.11; H, 0.77; Cl, 13.45; S, 12.14. Found: C, 9.21; H, 0.56; Cl, 13.47; S, 12.23.

2,2,2-Trinitroethyl Chlorosulfate (VIII).—To a solution of 20 g (0.11 mole) of V in 40 ml of sulfuryl chloride was added approximately 1 g of pyridinium·hydrochloride. The resulting solution was refluxed 20 hr. The excess sulfuryl chloride was removed under reduced pressure and the residue was distilled fractionally. A small amount (0.5 g) of a low-boiling forerun was obtained which was identified as 1,1,1-trinitrochloroethane (I). The main fraction, bp 84–85° (0.05 mm), $n^{25}D$ 1.4735, gave 20.2 g (66%) of VIII: principal infrared absorption (thin film) at 1600 (s), 1440 (m), 1300 (s), 1230 (s), 1030 (s), 995 (s), 883 (m), 860 (m), 815 (s), 785 (s), and 740 (s) cm^{-1}.

Anal. Calcd for $C_2H_2ClN_3O_9S$: C, 8.59; H, 0.72; Cl, 12.69; S, 11.45. Found: 8.79, 8.89; H, 0.64, 0.61; Cl, 12.87, 12.92; S, 11.47, 11.51.

1,1-Dinitropropane (Shechter and Kaplan Reaction).[16]—1-Nitropropane (178 g, 2.0 mole) was added dropwise to a solution of 80 g (2.0 mole) of sodium hydroxide in 300 ml of water maintaining the temperature at 10°. The resulting solution was stirred for 1 hr then a solution of 138 g (2.0 mole) of sodium nitrite in 400 ml of water was added. The resulting solution was poured into a solution of 680 g (4.0 moles) of silver nitrate in 2 l. of water which was cooled to 10°. Water (1 l.) was added. During the reaction the temperature rose to 22°. The resulting mixture was stirred 1.5 hr and then filtered. The filtrate was extracted with four 200-ml portions of ether. The combined ether extracts were dried over anhydrous magnesium sulfate overnight. Filtration and evaporation of the ether solutions produced a colorless residue which was distilled under reduced pressure giving 230 g (85.8%) of 1,1-dinitropropane: bp 67-68° (2.5 mm), $n^{25}D$ 1.4321; lit.[19] 77° (11 mm), $n^{20}D$ 1.4334.

1-Chloro-2,2-dinitrobutane (IX).—To a solution of 21.5 g (0.16 mole) of 1,1-dinitropropane in 20 ml of 37% formalin was added 10 ml of 5 *N* hydrochloric acid. After 24 hr the mixture was extracted with methylene chloride. The methylene chloride extracts were dried over anhydrous magnesium sulfate. The solvent was removed on a rotary evaporator leaving crude 2,2-dinitro-1-butanol as the residue. Thionyl chloride (19.4 g, 0.16 mole) containing 1 g of pyridine was added to the butanol and the resulting solution was heated to reflux. Thionyl chloride (10 ml) containing 1 g of pyridine was added after 6 hr. Refluxing was continued for another 4 hr. The excess thionyl chloride was removed under reduced pressure and the residue was poured into ice–water. The crude product IX was extracted with methylene chloride. The methylene chloride extracts were dried, filtered, and then evaporated. The residue was distilled under reduced pressure, giving 19 g (65.5%), bp 30° (0.5 mm), $n^{26}D$ 1.4455.

Dipotassium Tetranitroethane (X).—A solution of 2.0 g (0.01 mole) of I and 8.0 g (0.09 mole) of potassium nitrite in 25 ml of 60% aqueous methanol was allowed to stand at room temperature for 24 hr. The precipitate was collected and washed with two portions of methanol. The yield of dipotassium tetranitroethane was 2.6 g (91%): mp 293–294° (dec); lit.[10] 275° (dec); additional experimental conditions are tabulated in Table II; principal infrared absorption (KBr) at 1470 (*asym*-NO_2), and 1265 cm^{-1} (*sym*-NO_2).

Anal. Calcd for $C_2N_4K_2O_8$: C, 8.39. Found: C, 8.38, 8.42.

1,2-Dichlorotetranitroethane (XI).—A suspension of 8 g (0.028 mole) of X in 150 ml of ether was cooled to −5°. Chlorine gas was slowly introduced maintaining the temperature at −10 to −5°. After the chlorine uptake had ceased, the reaction mixture was filtered. Evaporation of the ether left a white solid residue which was sublimed: yield 7 g (89.9%); mp 104–105° (dec). The chlorination can also be effected in aqueous solution

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[16] R. B. Kaplan and H. Shechter, *J. Am. Chem. Soc.*, **83**, 3535 (1961).

[17] H. Feuer, G. B. Bachman and J. P. Kispersky, *ibid.*, **73**, 1360 (1951).

[18] S. S. Novikov, V. M. Belikov, and L. V. Epishina, *Izv. Akad. Nauk SSR, Otd. Khim. Nauk*, 1111 (1962).

[19] L. V. Ershova, V. N. Gogitidze, V. M. Belikov, and S. S. Novkov, *ibid.*, 943 (1959).

at 5-10°. The white solid product is insoluble in water; no extraction is necessary.

Anal. Calcd for $C_2Cl_2N_4O_8$: C, 8.61; Cl, 25.42; N, 20.09. Found: C, 8.65, 8.80; H, 0.11, 0.20; Cl, 25.22, 25.38; N, 19.95, 20.02.

Hexanitroethane (XII).—To a vigorously stirred slurry of 19.6 g (0.069 mole) of X in 50 ml of methylene chloride was added dropwise 100 ml of cold (−10°) concentrated sulfuric acid, maintaining the temperature at −10–0° during the addition. To this solution was added slowly the nitration mixture consisting of 35 ml of concentrated sulfuric acid and 35 ml of white fuming nitric acid ($d = 1.52$). After the nitrating mixture was added, the reaction temperature was raised to 50° and maintained for about 30 min. The methylene chloride layer was separated, dried over anhydrous magnesium sulfate, and evaporated under reduced pressure. Cooling afforded 19 g (92%) of XII, mp 150° (dec).

Hexanitroethane is also obtained by the nitration of dipotassium trinitropropionaldehyde.[20]

Potassium Dinitromethane (XIII).—A solution of 5 g (0.059 mole) of piperidine in 10 ml of methanol was slowly added to a solution of 2 g (0.01 mole) of I in 10 ml of methanol–water solution (80:20) at 5°. The solution was allowed to stand for 2 hr and then a solution of 5 g (0.05 mole) of potassium acetate in 10 ml of 60% methanol was added. The yellow precipitate which formed was immediately collected, washed with methanol, and the crude product was crystallized from water, giving 83.3% of XIII, mp 225° (dec). This product was identical with an authentic sample of XIII prepared from 2,2-dinitropropanediol by the method of Feuer and co-workers.[17]

XIII is also obtained as a product of the reaction of I with ammonia, sodium methoxide, potassium acetate, and potassium phthalimide under similar reaction conditions.

Other Salts of *sym*-Tetranitroethane.—An ion-exchange column of approximately 280 ml of Dowex 50-X8 was washed with sulfuric acid, followed by sodium hydroxide (twice), according to established procedure to charge the column with sodium ion. A solution of 50 g (0.182 mole) of dipotassium tetranitroethane in water was allowed to flow slowly through the column. When the column eluate was colorless, the collected solution of disodium tetranitroethane (XIV) was evaporated on a rotary evaporator. The residue was finally dried *in vacuo* over P_2O_5. The yield of the dihydrate of XIV was 47 g (93%).

Anal. Calcd for $Na_2C_2N_4O_8 \cdot 2H_2O$: C, 8.28; H, 1.39; N, 19.32. Found: C, 8.44; H, 1.47; N, 19.56.

Drying the dihydrate above at 60° over P_2O_5 in a drying pistol *in vacuo* produced the monohydrate of XIV.

Anal. Calcd for $Na_2C_2N_4O_8 \cdot H_2O$: C, 8.83; H, 0.7; N, 20.59. Found: C, 8.88; H, 1.44; N, 20.70.

The melting point (for both mono and dihydrate) was 295° (experimental). The dilithium tetranitroethane (XV) was prepared by an analogous procedure from a lithium ion charged ion-exchange column. Drying the residue at room temperature over P_2O_5 *in vacuo* produced the dihydrate of XV. The berylium and calcium salts of tetranitroethane were also prepared by this technique. The hydrates of salts of tetranitroethane are not stable for storage for long periods of time at room temperature, as contrasted to the dipotassium salt which appears to be stable indefinitely.

Anal. Calcd for $Li_2C_2N_4O_8 \cdot 2H_2O$: C, 9.31; H, 1.56; N, 21.73. Found: C, 8.88, 9.04; H, 1.49, 1.63; N, 21.34, 21.50.

***sym*-Tetranitroethane (XVI).**—Solutions of *sym*-tetranitroethane may be prepared by suspending X in an anhydrous organic solvent (preferably alkanes or halogenated alkanes) and introducing dry hydrogen chloride slowly at −15 to −20°. After yellow salt disappears the white precipitate (KCl) is filtered off, leaving a colorless solution of XVI. If this solution is allowed to warm to 10°, it turns yellow and produces bubbles. The infrared spectrum showed principal bands at 1610 (*asym*-NO_2) and 1310 cm^{-1} (*sym*-NO_2). The nmr (60 Mc) spectrum in carbon tetrachloride showed a single peak at $\delta = 7.12$ ppm.

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[20] J. A. Gallaghan and W. L. Reed, U. S. Patent 3,101,379 (Aug 20, 1963); *Chem. Abstr.*, **60**, 1588c (1964).

Electron Spin Resonance Studies of a Stable Arylnitroso–Olefin Adduct Free Radical[1]

A. B. SULLIVAN

Monsanto Company, Organic Chemicals Division,
Rubber Chemicals Research Laboratories, Nitro, West Virginia

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An extremely stable alkenylaryl nitroxide has been prepared and studied by esr techniques. The free radical is formed by what appears to be a novel pseudo Diels–Alder reaction between nitrosobenzene and its derivatives with an olefin such as 2,3-dimethyl-2-butene. The N^{14} and proton hyperfine interactions have been used to interpret the esr spectra. Assignments of hyperfine coupling constants have been confirmed in part by deuterium substitution and are consistent with published results on similar radicals. The effect of substitution in the aromatic entity on N^{14} coupling constants has been considered, and correlations similar to those observed by other workers with substituted nitrobenzene anion radicals have been found. The kinetics of the formation of these nitroxides have been studied in some detail using esr techniques. The reaction was found to be over-all second order. The structure of the adduct free radical has been essentially confirmed by separation and identification of reduction products. A reaction mechanism is proposed.

The study of organic free radicals containing nitrogen using esr techniques has received considerable attention in recent years. Nitrobenzene anion radicals have been the object of considerable interest in this regard. Weissman, *et al.*,[2] observed the spectrum of the anion radical prepared by reduction of nitrobenzene with metallic sodium. Spectra were observed on similar systems by Geske and Maki[3] using constant potential electrolysis directly inside the esr microwave cavity as the means of radical generation.

In contrast, the nitroxide-type odd electron compounds have received somewhat less systematic attention by workers in the field. This type of free radical was first reported in 1914 by Weiland and Offenbacker.[4] The esr spectrum of di-*p*-anisylnitric oxide free radical was observed in 1950 by Holden, *et al.*[5] Diphenylnitric oxide radical was first observed by Hoskins in 1956 using

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[1] Presented at the Sixteenth Annual Southeastern Regional Meeting of the American Chemical Society, Charleston, W. Va., Oct 1964.

[2] T. E. Chu, G. E. Pake, D. E. Paul, J. Townsend, and S. I. Weissman, *J. Phys. Chem.*, **57**, 504 (1953).

[3] David H. Geske and August H. Maki, *J. Am. Chem. Soc.*, **82**, 2671 (1960); A. H. Maki and D. H. Geske, *J. Chem. Phys.*, **33**, 825 (1960).

[4] H. Weiland and H. Offenbacker, *Ber.*, **47**, 2111 (1914).

[5] A. N. Holden, C. Kittle, F. R. Merritt, and W. A. Yager, *Phys. Rev.*, **77**, 147 (1950).