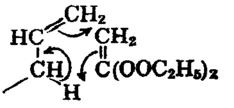
this adduct involves presumably a four-centered cyclic transition of this sort as has been shown in a previous publication from this laboratory.[5]



EXPERIMENTAL

Diethyl methylenemalonate.[11] A solution of 50 g. of diethyl ethoxymethylenemalonate (available from Eastman) in 100 ml. of ethanol was hydrogenated (in a Parr apparatus) at room temperature and 25 p.s.i. initial pressure, using 1.5 g. of 5% palladized carbon as the catalyst. The uptake of hydrogen, as indicated by the pressure gauge, was essentially over in approximately 0.5 hr. The reaction mixture was then filtered and the ethanol was distilled. The residue was then heated in an oil bath and the product, diethyl methylenemalonate, distilled at 205°, yield, 40 g.

Reaction of allylbenzene with diethyl methylenemalonate. Diethyl methylenemalonate (0.11 mole) and allylbenzene (0.49 mole) were heated together in a sealed glass bomb tube for 2 days at 190°. At the end of this time the tube was opened and the contents distilled. Eleven grams of a product, b.p. 141° at 1 mm., $n_D^{25°}$ 1.5117, was obtained (32% yield based on diethyl methylenemalonate).

Anal. Calcd. for $C_{17}H_{22}O_4$: C, 71.19; H, 7.56. Found: C, 71.11; H, 7.85.

The ultraviolet spectrum (major peak at 250μ and minor peaks at 285μ and 293μ) indicated that the double bond was now conjugated with the benzene ring.

Saponification. The 1:1 adduct (28 g.) was added to 150 ml. of 4*N* potassium hydroxide in 50% ethanol-water and the mixture was refluxed overnight. After acidification, extraction with ether, and evaporation of the ether, 19.5 g. of the free acid was isolated and recrystallized from nitromethane, m.p. 143°–144°.

Anal. Calcd. for $C_{13}H_{14}O_4$: C, 66.65; H, 6.03. Found: C, 66.65; H, 6.03.

Hydrogenation of the free acid. The free acid (2.408 g.) was hydrogenated in ethanol over palladium on charcoal. Hydrogen (245 ml.) was used up at room temperature. The saturated malonic acid prepared in this way was recrystallized from nitromethane, m.p. 111°–112°.

Anal. Calcd. for $C_{13}H_{16}O_4$: C, 66.08; H, 6.83. Found: C, 66.01; H, 7.01.

The neutral equivalent of the hydrogenated malonic acid was found to be 120 (theoretical neutral equivalent, 118).

Preparation of the barbiturate of the 1:1 adduct. The 1:1 adduct (20 g.) was added dropwise with stirring to a solution of 6 g. of sodium methoxide and 9.2 g. of urea, and dried at 60° overnight in 30 ml. of absolute methanol. The reaction mixture was refluxed for 6 hr. After this period of time the excess methanol was evaporated at reduced pressure and 67 ml. of ice water was added with vigorous stirring. Benzene was added, whereupon an emulsion benzene overnight. Three grams of a fine white powder that formed. After acidification, however, it was possible to separate the benzene layer in the form of a viscous semisolid slime. This was submitted to Soxhlet extraction with separated from the benzene extract were collected and an analytical sample was prepared by recrystallization from hot water, m.p. 188°–190°.

Anal. Calcd. for $C_{14}H_{14}O_3N_2$: C, 65.10; H, 5.46. Found: C, 64.89; H, 5.78.

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(8) C. J. Albisetti, N. G. Fisher, M. J. Hogsed and R. M. Joyce, *J. Am. Chem. Soc.*, **78**, 2637 (1956).

(9) C. S. Rondestvedt and A. H. Bilbey, *J. Org. Chem.*, **19**, 548 (1954).

(10) R. T. Arnold and J. F. Dowdall, *J. Am. Chem. Soc.*, **70**, 2590 (1948).

(11) This method of preparation was suggested by Prof. V. Boekelheide.

Heterocyclic Polynitro Compounds

Milton B. Frankel[1]

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Aliphatic secondary amines containing *gem*-dinitro groups were prepared by the Mannich condensation of 2,2-dinitro-1-alkanols with ammonia, glycine, and hydrazine.[2] This work has now been extended to the synthesis of heterocyclic polynitro compounds. It was found that 2,2,4,4-tetranitro-1,5-pentanediol (I) condensed with ammonia to give 3,3,5,5-tetranitropiperidine (II). The condensation of I with 2,2,2-trifluoroethylamine, trimethylsilylmethylamine, 3-nitrazabutylamine, and 3,3,3-trinitropropylamine yielded the 1-substituted 3,3,5,5-tetranitropiperidines. The pronounced tendency for the formation of a six-membered ring takes precedence over the formation of the aliphatic secondary amines.[3] Nitration of II gave 1,3,3,5,5-pentanitropiperidine while the condensation of II with 2,2,2-trinitroethanol yielded 1-(2′,2′,2′-trinitroethyl)-3,3,5,5-tetranitropiperidine.

The reaction of 2,2-dinitro-1,3-propanediol with polynitro aliphatic primary amines and formaldehyde gave perhydropyrimidines.[4] Thus 1,3-bis-(3′,3′,3′ - trinitropropyl) - 5,5 - dinitroperhydropyrimidine and 1,3-bis(3′,3′-dinitrobutyl)-5,5-dinitroperhydropyrimidine were prepared from 3,3,3-trinitropropylamine and 3,3-dinitrobutylamine, respectively.

The condensation of methylenedinitramine and ethylenedinitramine with formaldehyde and 3,3-dinitrobutylamine gave 1-(3′,3′-dinitrobutyl)-3,5-dinitro-1,3,5-triazacyclohexane and 1-(3′,3′-dinitrobutyl)-3,6-dinitro-1,3,6-triazacycloheptane, re-

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(1) Present address: Stanford Research Institute, Menlo Park, Calif.

(2) M. B. Frankel and K. Klager, *J. Am. Chem. Soc.*, **79**, 2953 (1957).

(3) A similar type of reaction was observed by H. Feuer, G. B. Bachman, and W. May, *J. Am. Chem. Soc.*, **76**, 5124 (1954), who prepared *N*-carboxymethyl-3,3,5,5-tetranitropiperidine from the condensation of glycine with 2,2-dinitro-1,3-propanediol and sodium salt of 2,2-dinitroethanol.

(4) The formation of pyrimidines from the interactions of nitroparaffins with amines and formaldehyde has been reported by Senkus, *J. Am. Chem. Soc.*, **68**, 1611 (1946).

TABLE I

R	Yield, %	Recryst. Solvent	M.P.	Formula	Calcd. C	Calcd. H	Calcd. N	Calcd. Si	Found C	Found H	Found N	Found Si
1-Substituted 3,3,5,5-tetranitropiperidines												
H	53.7	Isopropyl alcohol	123–127	$C_5H_7N_5O_8$	22.65	2.66	26.42		23.06	2.94	26.61	
NO_2	46.8	Chloroform	120–125	$C_5H_6N_6O_{10}$	19.36	1.95	27.10		19.65	1.96	26.72	
CF_3CH_2	37.4	70% Nitric acid	95–96	$C_7H_8F_3N_5O_8$	24.22	2.32	20.17		24.23	2.31	19.66	
$(CH_3)_3SiCH_2$	17.1	Isopropyl alcohol–water	88–90	$C_9H_{17}N_5O_8Si$	30.77	4.88	19.94	7.99	30.84	4.69	19.97	7.78
$CH_3\overset{NO_2}{\overset{\vert}{N}}CH_2CH_2$	68.2	Ethylene dichloride	96–98	$C_8H_{13}N_7O_{10}$	26.16	3.57	26.70		26.33	3.75	26.71	
$(NO_2)_3CCH_2$	63.3	Benzene	163–168	$C_7H_8N_8O_{14}$	19.63	1.88	26.17		19.80	1.79	25.88	
$(NO_2)_3CCH_2CH_2$	37.3	70% Nitric acid	142–144	$C_8H_{10}N_8O_{14}$	21.73	2.28	25.34		21.33	2.29	24.72	
1,3-Substituted 5,5-dinitroperhydropyrimidines												
$CH_3C(NO_2)_2CH_2CH_2$	42.1	Methanol	127–128	$C_{12}H_{20}N_8O_{12}$	30.77	4.31	23.93		30.80	4.44	23.98	
$(NO_2)_3CCH_2CH_2$	40.8	Chloroform	119–121	$C_{10}H_{14}N_{10}O_{16}$	22.65	2.66	26.42		22.95	2.65	26.72	
1,3,5-Substituted perhydro-1,3,5-triazines												
								Mol. Wt.				Mol. Wt.
$CH_3C(NO_2)_2CH_2CH_2$	97.0	Ethyl acetate	131–132	$C_{15}H_{27}N_9O_{12}$	34.29	5.18	23.99		34.76	5.36	24.62	
$(NO_2)_3CCH_2CH_2$	99.4	Methanol	121–123	$C_{12}H_{18}N_{12}O_{18}$	23.31	2.93	27.19	618	23.78	2.88	27.21	600
1-(3′,3′-Dinitrobutyl)-3,5-dinitro-1,3,5-triazacyclohexane												
	89.8	Chloroform	118–120	$C_7H_{13}N_7O_8$	26.01	4.05	30.34		26.23	4.42	29.94	
1-(3′,3′-Dinitrobutyl)-3,6-dinitro-1,3,6-triazacycloheptane												
	99.3	Ethylene dichloride	146–147	$C_8H_{15}N_7O_8$	28.49	4.48	16.61		28.28	4.18	17.20	

spectively.[5] In these reactions it is best to first prepare the diols *in situ* from the dinitramines and formaldehyde before the primary amine is added, since the primary amine and formaldehyde react very readily to form triazines. Thus, the condensation of 3,3-dinitrobutylamine and 3,3,3-trinitropropylamine with formaldehyde gave 1,3,5-tris(3′,3′-dinitrobutyl)perhydro-1,3,5-triazine and 1,3,5-tris(3′,3′,3′-trinitropropyl)perhydro-1,3,5-triazine, respectively. The results are summarized in Table I.

EXPERIMENTAL[6,7]

3,3,5,5-Tetranitropiperidine (III). A mixture of 4.0 g. (0.014 mole) of 2,2,4,4-tetranitro-1,5-pentanediol,[8] 4.0 g. (0.05 mole) of ammonium acetate, and 40 ml. of water was warmed to 40–50°. After several minutes an orange solid separated. The reaction mixture was cooled and the product collected and dried, 2.0 g. (53.7%) m.p. 108–112° dec. Recrystallization from isopropyl alcohol gave a white crystalline solid, m.p. 123–127° dec. This compound was stable when stored at −10° but decomposed on standing at ambient temperatures.

1,3,3,5,5-Pentanitropiperidine. A solution of 8 ml. of 100% nitric acid and 8 ml. of acetic anhydride was cooled to 5° and 0.4 g. of 3,3,5,5-tetranitropiperidine was added. The solution was kept at this temperature for 10 min. and poured onto ice. The white solid was collected, washed with water, and dried to yield 0.3 g. (46.8%) of product which was recrystallized from chloroform to give white needles, m.p. 120–125° dec.

1-(2′,2′,2′-Trinitroethyl)-3,3,5,5-tetranitropiperidine. A solution of 0.3 g. of 2,2,2-trinitroethanol,[9] 0.3 g. of 3,3,5,5-tetranitropiperidine, and 15 ml. of methanol was refluxed for 6 hr. The solution was concentrated *in vacuo* giving 0.45 g. (63.3%) of a cream-colored solid. Recrystallization from benzene gave white crystals, m.p. 163–168° dec.

1-(3′-Nitrazabutyl)-3,3,5,5-tetranitropiperidine. This preparation is given as typical for the condensation of primary amines with 2,2,4,4-tetranitro-1,5-pentanediol. A mixture of 2.84 g. (0.01 mole) of 2,2,4,4-tetranitro-1,5-pentanediol, 1.56 g. (0.01 mole) of 3-nitrazabutylamine hydrochloride,[10] and 50 ml. of water was warmed to 45-50° to effect solution. The solution was cooled to 25° and a solution of 0.82 g. (0.01 mole) of sodium acetate in 10 ml. of water was added dropwise. The cream colored solid which precipitated was collected, washed with water, and dried to give 2.5 g. (68.2%), of product, m.p. 92–94°. Recrystallization from ethylene dichloride raised the m.p. to 96–98°.

1,3-Bis(3′3,′3,′-trinitropropyl)-5-5-dinitroperhydropyrimidine. To a solution of 12.4 g. (0.075 mole) of 2,2-dinitro-1,3-propanediol,[11] 34.5 g. ′0.15 mole) of 3,3,3-trinitropropylamine hydrochloride,[8] and 75 ml. of water was added dropwise 30.7 ml. of 4.877*N* sodium hydroxide solution (0.15 mole). Since the trinitromethyl group is decomposed

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(5) Analogous condensations have been reported: F. Chapman, P. G. Owston, and D. Woodcock, *J. Chem. Soc.*, 1638 (1949) and G. S. Meyers and G. F. Wright, *Can. J. Res.*, **B27** (1949).

(6) All melting points are uncorrected.

(7) Microanalyses by Elek Microanalytical Laboratories, Los Angeles, Calif.

(8) The preparation of this compound will be described in a subsequent publication.

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

(10) M. B. Frankel and K. Klager, *J. Am. Chem. Soc.*, **78**, 5428 (1956).

(11) H. Feuer, G. B. Bachman, and J. P. Kispersky, *J. Am. Chem. Soc.*, **73**, 1360 (1951).

by base, it is necessary to avoid an excess of alkali in the neutralization of the amine salt. After stirring for 15 min. a yellow solid had separated. The water was decanted and the product was water-washed by decantation. The solid was dissolved in 200 ml. of hot methanol, the solution cooled to 30° and 12.1 g. (0.15 mole) of 37% formaldehyde added. The reaction mixture was stirred for 1 hr. at which time a light yellow solid had separated. The product was collected and dried, 16.2 g. (over-all yield of 40.8%), m.p. 114–118°. Recrystallization from chloroform gave yellow rods, m.p. 119–121°.

1-(3',3'-Dinitrobutyl)-3,6-dinitro-1,3,6-triazacycloheptane. A solution of 0.8 g. (0.02 mole) of sodium hydroxide in 30 ml. of water was added to a suspension of 3.2 g. (0.02 mole) of ethylenedinitramine, 3.2 g. (0.04 mole) of 37% formalin, and 30 ml of water. After stirring for 15 min. the solid had dissolved. A solution of 4.0 g. (0.02 mole) of 3,3-dinitrobutylamine hydrochloride[6] in 20 ml. of water was added dropwise. There was an immediate precipitate of a white solid. The product was collected and dried, 6.7 g. (99.3%) m.p. 140–146°. Recrystallization from ethylene dichloride raised the m.p. to 146–147°.

1,3,5-Tris(3',3',3'-trinitropropyl)perhydro-1,3,5-triazine. To a solution of 34.5 g. (0.15 mole) of 3,3,3-trinitropropylamine hydrochloride, 75 ml. of water, and 12.1 g. (0.15 mole) of 37% formaldehyde was added dropwise a solution of 12.3 g. (0.15 mole) of sodium acetate in 50 ml. of water. A yellow solid was immediately precipitated. The product was collected, washed with water, and dried to give 30.7 g. (99.4%), m.p. 118–123°. Recrystallization from methanol gave yellow plates, m.p. 121–123°.

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The Preparation of Diethylphosphonoalkyl Acrylates

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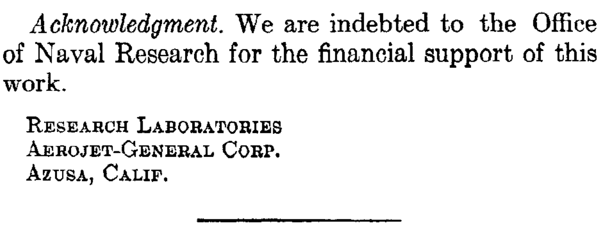
A recent patent by O'Brien, Park, and Lane[1] concerning the preparation of dialkylphosphonoalkyl acrylates prompts us to report our preparation of these compounds and simple polymers derived therefrom. We have found that the acrylate or methacrylate esters can be prepared directly from the sodium salts of the hydroxyalkylphosphonic esters[2] *via* the following sequence of reactions:



$$(RO)_2\overset{O}{\overset{\|}{P}}H \xrightarrow[\text{ether}]{Na} (RO)_2\overset{O}{\overset{\|}{P}}Na \xrightarrow{R'CHO} (RO)_2\overset{O}{\overset{\|}{P}}-CHR'ONa$$

$$(RO)_2\overset{O}{\overset{\|}{P}}-CHR'ONa \xrightarrow{CH_2=CR''\overset{O}{\overset{\|}{C}}Cl} (RO)_2\overset{O}{\overset{\|}{P}}-CHR'O\overset{O}{\overset{\|}{C}}-CR''=CH_2$$

In the reactions studied, R' and R'' was either H or CH_3. These compounds have been polymerized using free radical initiators. The polymerization and copolymerization behavior of these materials is currently under study and will be reported in detail at a later date.

EXPERIMENTAL[3]

Diethyl hydroxymethylphosphonate. This alcohol was prepared by the method of Abramov[2] except that acetic acid was used instead of hydrochloric acid to acidify the sodium salt. From 11.5 g. (0.5 g.-atom) of sodium, 69 g. (0.5 mole) of diethyl hydrogen phosphite and 18 g. (0.6 mole) of paraformaldehyde, there was obtained on distillation in vacuum, 55 g. (65%) of colorless product, b.p. 112–115° (1.5 mm.); n_D^{25} 1.4310 (b.p. 123° (3 mm.), no yield reported, n_D^{20} 1.4322).[2]

Anal. Calcd. for $C_5H_{13}O_4P$: C, 35.72; H, 7.81; P, 18.42. Found: C, 35.47; H, 7.87; P, 18.22.

Diethyl 1-hydroxyethylphosphonate. This alcohol can be prepared as described above except that acetaldehyde is used in place of paraformaldehyde. Another convenient method is that of Fields.[4] To a stirred solution of 69 g. (0.5 mole) of diethyl hydrogen phosphite and 10.1 g. (0.1 mole) of triethylamine was added slowly and with external cooling, 27 g. (0.6 mole) of acetaldehyde. After addition of the aldehyde, the solution was heated at 75° for 0.5 hr. using a Dry Ice-condenser. Vacuum distillation gave 64 g. (70%) of a colorless liquid, b.p. 116–119° (1.5 mm.); n_D^{25} 1.4298 (b.p. 139–140° (6 mm.); n_D^{20} 1.4308).[2]

Diethylphosphonomethyl acrylate. The acrylic esters can be prepared directly from the sodium salt of the corresponding alcohol without prior isolation of the alcohol. To the ice-cooled ether solution of sodium diethyl hydroxymethylphosphonate, 45 g. (0.5 mole) of acrylyl chloride containing 0.1% cuprous chloride, was added dropwise. The reaction mixture was stirred for 1 hr. after which time it was refluxed an additional 0.5 hr. The precipitate was removed and the ether evaporated. The resulting yellow oil was distilled in the presence of *t*-butylcatechol to give 39 g. (35%) of a colorless liquid, b.p. 108–110° (0.6 mm.); n_D^{25} 1.4340.

Anal. Calcd. for $C_8H_{15}O_5P$: P, 13.94. Found: P, 13.90.

1-Diethylphosphonoethyl acrylate. The acrylic ester of diethyl 1-hydroxyethylphosphonate was prepared as described above. Distillation gave 35 g. (30%) of a colorless liquid, b.p. 90–93° (0.05 mm.); n_D^{25} 1.4333.

Anal. Calcd. for $C_9H_{17}O_5P$: P, 13.11. Found: P, 12.82.

Diethylphosphonomethyl methacrylate. The methacrylate derivative can be prepared as described above, using 52 g. (0.5 mole) of methacrylyl chloride in place of acrylyl chloride. This procedure affords 54 g. (46%) of a clear liquid, b.p. 92–94° (0.3 mm.); n_D^{23} 1.4398.

Anal. Calcd. for $C_9H_{17}O_5P$: P, 13.11. Found: P, 12.73.

Polydiethylphosphonomethyl acrylate. Polymerizations were carried out in an evacuated sealed tube at 75° for 12 hr., using 0.1 mole % of azobisisobutyronitrile as an initiator. A white, rubbery, benzene-soluble polymer was obtained after precipitation from ether and freeze-drying from benzene; [η], 0.13 in benzene at 28.2°.

Anal. Calcd. for $C_8H_{15}O_5P$: C, 43.24; H, 6.81; P. 13.94. Found: C, 43.25; H, 7.05; P, 13.79.

Poly-1-diethylphosphonoethyl acrylate. Polymerization as described above gave a white, rubbery, benzene-soluble polymer; [η], 0.33 in benzene at 28.2°.

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(1) J. L. O'Brien, E. Park, and C. A. Lane, U. S. Patent **2,934,555** (to Rohm and Haas Co.), April 26, 1960.

(2) V. S. Abramov, *J. Gen. Chem.*, **22,** 647 (1952); *Chem. Abstr.*, **47,** 5351 (1953).

(3) Analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

(4) E. K. Fields, U. S. Patent **2,579,810** (to Research Corp), December 25, 1951; *Chem. Abstr.*, **46,** 6140 (1952).