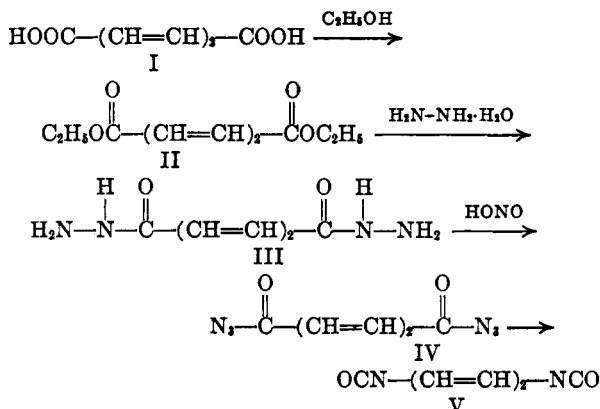


Some Carbamate Derivatives of 1,3-Butadienyl 1,4-Diisocyanate¹

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In connection with other studies in these laboratories, the preparation of new 1,3-butadienyl 1,4-diisocyanate (V) was accomplished through a four-step reaction sequence starting with muconic acid (I):



Although one of the intermediates muconyl dihydrazide (III) has been reported in the literature,² no experimental conditions or yields were given for its preparation from diethyl muconate (II) and hydrazine hydrate in *p*-dioxane as shown herein.

The extreme instability of V upon exposure to air prevented obtaining satisfactory elemental analyses. An attempted Dumas nitrogen analysis on muconyl diazide (IV) resulted in detonation of the combustion tube. In the absence of the elemental analyses on V, a series of carbamate derivatives characterized the diisocyanate.

EXPERIMENTAL³

Diethyl muconate (II). The preparation included the following: Addition of 53 g. of muconic acid⁴ to 200 ml. of absolute ethanol in a 500-ml. flask equipped with a reflux condenser and drying tube, then stirring and adding 10 ml. of concd. sulfuric acid with reflux of the mixture overnight; evaporation of the resulting solution almost to dryness *in vacuo* and the treatment of the residue with a saturated solution of sodium bicarbonate until basic to litmus; filtration of the product, thorough washing with water and drying; yield 73 g. (90%), m.p. 61–63°. Recrystallization

from ethanol-water gave 57 g. of colorless plates, m.p. 63–64° (lit., m.p. 64°).⁵

Muconyl dihydrazide (III). To diethyl muconate (43 g.) dissolved in 200 ml. of dioxane was added 33 ml. of 85% hydrazine hydrate. The resulting turbid solution was stored in a refrigerator (3°) for 72 hr. with periodical shaking. Then, the separated solid material was filtered, washed with ether followed by cold water, and dried; yield 23 g. (62%), m.p. 268° dec. Recrystallization of the analytical sample from a large volume of water gave white glistening plates, m.p. 274° dec. (lit., m.p. 274°).²

Muconyl diazide (IV). Muconyl dihydrazide (7.2 g.) was dissolved in 500 ml. of water containing 10 ml. of concd. hydrochloric acid. The resulting clear solution was cooled to 15°. With vigorous mechanical stirring of the solution, 8.4 g. of sodium nitrite was added in one portion. A small sample of the white flocculent precipitate which separated was isolated and dried on filter paper; m.p. 111–114° dec. The infrared spectrum in chloroform showed major bands at 2140 (N≡N stretching), 1685, 1605 (C=C), 1080, and 1000 cm.⁻¹.

1,3-Butadienyl 1,4-diisocyanate (V). The reaction mixture containing the muconyl diazide stood for 30 min. at 10–15° before mechanical stirring was resumed. To the stirred mixture was added 150 ml. of purified chloroform⁶ and stirring continued until the precipitate dissolved completely. The organic layer was separated and washed with two 50-ml. portions of cold water. Anhydrous magnesium sulfate was added and the chloroform solution dried for 1 hr. at 10°. The contents of the flask were filtered. The filtrate was transferred to a 300 ml. flask equipped with a reflux condenser and drying tube and then heated at reflux for 6 hr. The slightly turbid solution was rapidly filtered and then evaporated to dryness *in vacuo* leaving a light yellow solid; yield 3.6 g. (73%, based on muconyl dihydrazide). Sublimation of the residue at 60–65°/0.15 mm. gave 2.8 g. of white crystals, m.p. 83–84°, which rapidly turned yellow on exposure to air. The infrared spectrum (carbon tetrachloride) showed major bands at 2240 (NCO) and 1620 cm.⁻¹ (C=C). The absorption of the C=C band was greatly intensified by conjugation with the isocyanate group as has been reported with 1-alkenyl isocyanates.⁷

Preparation of bis-1,4-(alkoxycarbonylamino)-1,3-butadienes. Approximately 0.2 g. of V was treated with 10 ml. of the appropriate anhydrous alcohol and then heated on the steam bath for 15 min. Evaporation of the solution to dryness on the steam bath and then recrystallization of the residue from ethanol using Norit-A yielded the following derivatives of the general formula, ROOCHN(CH=CH)₂NHCOOR:

R = CH₃, m.p. 238–239°. *Anal.* Calcd. for C₈H₁₂N₂O₄: N, 14.00. Found: 14.28.

R = C₂H₅, m.p. 232–233°. *Anal.* Calcd. for C₁₀H₁₆N₂O₄: N, 12.28. Found: 12.27.

R = *n*-C₃H₇, m.p. 214–216°. *Anal.* Calcd. for C₁₂H₂₀N₂O₄: N, 10.93. Found: 11.17.

R = *n*-C₄H₉, m.p. 203–206°. *Anal.* Calcd. for C₁₄H₂₄N₂O₄: N, 9.85. Found: 9.97.

R = *i*-C₅H₁₁, m.p. 189–191°. *Anal.* Calcd. for C₁₆H₂₈N₂O₄: N, 8.99. Found: 9.11.

A typical infrared spectrum (KBr disk) of these compounds is exemplified by R = C₂H₅ which showed major bands at 3265 (NH stretching), 1685 (C=O), 1640 (C=C), 1515 (NH deformation) and 1270 cm.⁻¹. The infrared spectra of the other derivatives resembled that of R = C₂H₅.

(1) This research was done under Army Ordnance Contract DA-01-021-ORD11919, Mod. 8.

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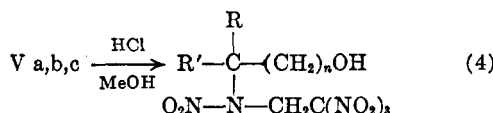
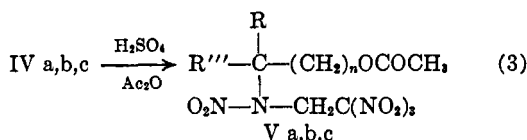
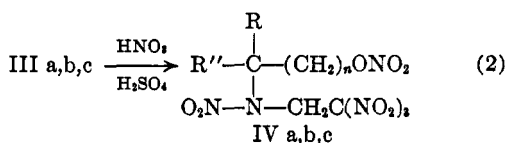
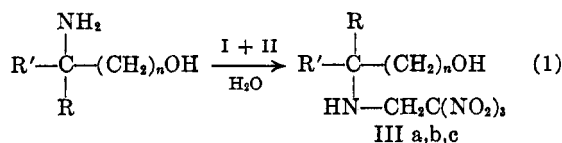
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Chemistry of Trinitromethane. IV. Preparation of *N*-Nitro-*N*-trinitroethylamino Alcohols

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N-Nitro-*N*-trinitroethylamino alcohols, representing a novel class of compounds, were prepared by treating amino alcohols with a mixture of trinitromethane (I) and formaldehyde (II) (step 1) followed by nitration (step 2), acetolysis (step 3), and hydrolysis (step 4).



- (a) R, R', R'', R''' = H; n = 1.
(b) R, R', R'', R''' = H; n = 2.
(c) R = CH₃; R' = CH₂OH; R'' = CH₂ONO₂; R''' = CH₂OCOCH₃; n = 1.

2-(*N*-Trinitroethylamino)ethanol (IIIa), and 3-(*N*-trinitroethylamino)-1-propanol (IIIb) were obtained as yellow solids, while 2-methyl-2-(*N*-trinitroethylamino)-1,3-propanediol (IIIc) was isolated as an oil, when I and II were condensed with the appropriate amino alcohol in a minimal amount of water. Since IIIa and IIIb decomposed slowly at ambient temperatures with the formation of I, they were treated with a mixture of concentrated sulfuric and fuming nitric acids at 10–25°.

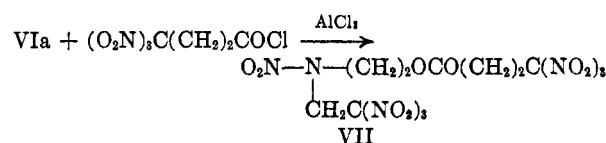
(1) (a) Abstracted from the Ph.D. thesis of W. A. Swarts, Purdue Univ., 1955. (b) This research was supported by the Office of Naval Research.

This afforded the stable 2-(*N*-nitro-*N*-trinitroethylamino)ethyl nitrate (IVa) and 3-(*N*-nitro-*N*-trinitroethylamino)-1-propyl nitrate (IVb).² When the unstable IIIc was nitrated with a mixture of acetic anhydride and fuming nitric acid, the dinitrate (IVc) was obtained as an oil which was used directly in subsequent reactions.

Direct hydrolysis, in acidic medium, of these nitrates led only to decomposition. Basic hydrolysis could not be applied because of the well-known³ instability of the trinitroethyl group in this medium. The desired alcohols, 2-(*N*-nitro-*N*-trinitroethylamino)ethanol (VIa), 3-(*N*-nitro-*N*-trinitroethylamino)-1-propanol (VIb) and 2-methyl-2-(*N*-nitro-*N*-trinitroethylamino)-1,3-propanediol (VIc) were, however, obtained by following the method of Wolfrom,⁴ which involved acetolysis with a mixture of acetic anhydride and concentrated sulfuric acid of the nitrate esters, followed by the acid hydrolysis of the acetates with methanolic hydrochloric acid.

The alcohols VIa and VIb reacted readily with phenyl isocyanate to give phenylurethanes, which had correct analyses, but which decomposed on standing at ambient temperatures. The reaction of the diol VIc with phenyl isocyanate gave a gummy solid which could not be purified.

The reaction of VIa with 4,4,4-trinitrobutanoyl chloride in the presence of aluminum chloride gave the expected ester VII.



EXPERIMENTAL

2-(*N*-Nitro-*N*-trinitroethylamino)ethyl nitrate (IVa). A mixture of 15.1 g. (0.1 mole) of trinitromethane (I), dissolved in 25 ml. of distilled water, 6.1 g. (0.1 mole) of ethanolamine and 8 ml. of 37% formalin solution (0.1 mole of formaldehyde) was stirred at about 5° for 1.5 hr. Since no precipitate appeared, the reaction mixture was placed overnight in the freezing compartment of the refrigerator.

The mixture was then allowed to melt slowly in the refrigerator, and 7.5 g. of a yellow solid was filtered off and dried on porous tiles. Repetition of the freezing and thawing process afforded only 0.1 g. more of 2-(*N*-trinitroethylamino)ethanol (IIIa); the total of 7.6 g. represented a 33.9% yield of IIIa.

A 100-ml. 3-necked round-bottomed flask equipped with a thermometer and a "Tru-Bore" stirrer was charged with a mixture of 25 ml. of concd. sulfuric acid and 25 ml. of fuming nitric acid, and cooled to approximately 15°. The dried IIIa was added to the mixture in fairly large

(2) CARE should be taken in handling these compounds for the impact sensitivity of IVa was found to be equal to that of lead azide and that of IVb to pentaerythritol tetranitrate.

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