[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY]

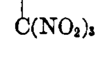
Addition Reactions of Trinitromethane and α,β-Unsaturated Ethers

HAROLD SHECHTER AND HARRY L. CATES, JR.[1]

Received May 11, 1960

Addition of trinitromethane to α,β-unsaturated ethers occurs in ether solvents to give α-trinitromethyl ethers. Dioxane and trinitromethane form a crystalline adduct having the molecular formula, $C_4H_8O_2.2HC(NO_2)_3$; the adduct serves as a convenient source of trinitromethane. The preparation and properties of five α-trinitromethyl ethers are described. The direction of addition of trinitromethane to isobutyl vinyl ether was determined by reduction of the adduct, isobutyl 1-methyl-2,2,2-trinitroethyl ether, with lithium aluminum hydride to 2-isobutoxypropylamine. 2-Isobutoxypropylamine was synthesized by reduction with iron and hydrochloric acid of isobutyl 1-methyl-2-nitroethyl ether prepared by base-catalyzed addition of isobutyl alcohol to 1-nitro-1-propene. Reduction of isobutyl 1-methyl-2,2,2-trinitroethyl ether with iron and hydrochloric acid yielded 2-isobutoxypropionamide.

Trinitromethane (nitroform), a strong acid ($K_{ion(H_2O)} \sim 10^{-1} - 10^{-2}$),[2] undergoes 1,4-addition with conjugatively-unsaturated aldehydes,[3a] ketones,[3a,b] acids,[3a] esters,[3a] nitriles,[3a] and nitro[3c,d] compounds to give the corresponding trinitromethyl derivatives. It is now reported that reaction of equimolar quantities of α,β-unsaturated ethers and trinitromethane (Equation 1) occurs in



$$RCH{=}CH{-}OR + HC(NO_2)_3 \longrightarrow RCH_2{-}\underset{\textstyle C(NO_2)_3}{\underset{|}{CH}}{-}OR \quad (1)$$

satisfactory yields (> 50–81%) to give α-trinitromethyl ethers.[4] The additions take place readily at room temperature, with little polymerization, in basic solvents such as dioxane and ethyl ether. Upon mixing dioxane and trinitromethane, heat is evolved, and a white crystalline adduct containing two equivalents of trinitromethane and one of dioxane is precipitated (Equation 2).[5] The solid adduct is fairly stable and can be distilled at reduced pressures. In water the adduct decomposes quantitatively to dioxane and trinitromethane. The addition-complex is dissociated in various solvents and may be used as a convenient source of trinitromethane.[6]

$$O(CH_2{-}CH_2)_2O + 2HC(NO_2)_3 \rightleftarrows (O_2N)_3CH{\cdot}O(CH_2{-}CH_2)_2O{\cdot}HC(NO_2)_3 \quad (2)$$

Trinitromethane has been added (Table I) to ethyl vinyl ether, isopropyl vinyl ether, isobutyl vinyl ether, 2-methoxyethyl vinyl ether, and 2,3-dihydropyran. The adducts were isolated and purified without serious hazard by use of conventional distillation techniques at reduced pressures. 2,3-Dihydro-5-methylfuran reacted readily with trinitromethane; the product could not be purified adequately however because of its thermal instability.

The structure of the adduct of isobutyl vinyl ether and trinitromethane, isobutyl 1-methyl-2,2,2-trinitroethyl ether, was determined by characterizing its reduction products. Reduction of the adduct with iron and hydrochloric acid occurred slowly to give 2-isobutoxypropionamide (Equation 2)[7a,b]; with lithium aluminum hydride, the trinitromethyl ether was reduced to 2-isobutoxypropylamine[7c] (Equation 3).

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[1] (a) Abstracted from the Ph.D. dissertation of Harry L. Cates, Jr., The Ohio State University, 1951. (b) This research was supported by the Office of Naval Research.

[2] A. Hantzsch and K. Rinckenberger, *Ber.*, **32**, 635 (1899).

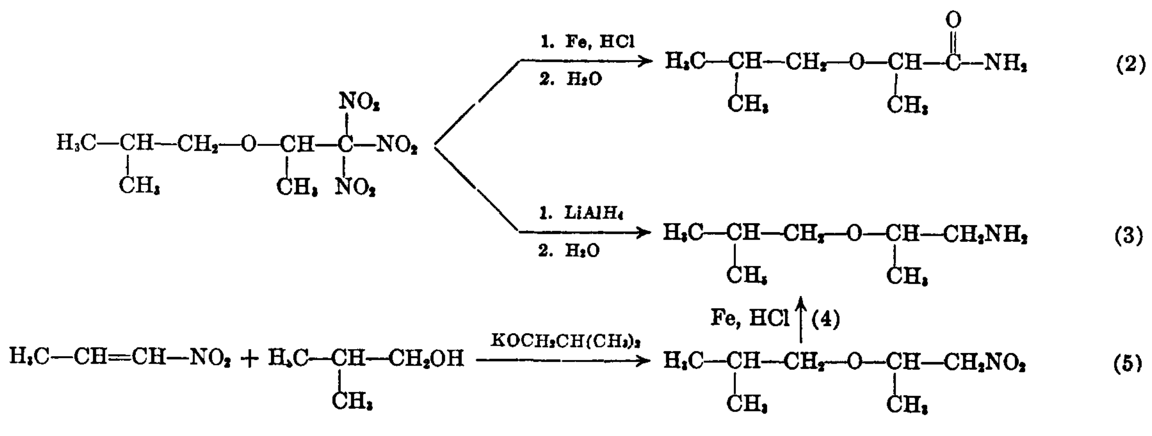
[3] (a) K. Schimmelschmidt, Ger. Patent **852,684**, Oct. 16, 1952; (b) S. S. Novikov, I. S. Korsakova, and N. A. Yatskovskaya, *Doklady Akad. Nauk S.S.S.R.*, **118**, 954 (1958); (c) S. S. Novikov, I. S. Korsakova, and K. K. Babievsky, *Iszv. Acad. Nauk S.S.S.R.*, **10**, 1847 (1959); (d) S. S. Novikov, K. K. Babievsky, and I. S. Korsakova, *Doklady Akad. Nauk S.S.S.R.*, **125**, 560 (1959).

[4] Additions of trinitromethane to α,β-unsaturated compounds are acid catalyzed. Reactions of the intermediate conjugate acids with the ambident trinitromethane anion by carbon rather than oxygen-alkylation probably stem from thermodynamic factors.

[5] Heat is evolved upon mixing trinitromethane with tetrahydrofuran or dimethyl Cellosolve; however, no solid product could be isolated.

[6] The acid-base reactions of trinitromethane and dioxane and the properties of the adduct are analogous to those of dioxane and sulfur trioxide; C. M. Suter, P. B. Evans, and J. M. Kiefer, *J. Am. Chem. Soc.*, **60**, 538 (1938).

[7] (a) This is the first example of reduction of a 1,1,1-trinitro compound to an amide. The basic organic products from this reduction were not identified because of their complexity. (b) T. Henderson and A. K. Macbeth, *J. Chem. Soc.*, **121**, 892 (1922) have reported that reduction of tetranitromethane with titanous chloride yielded guanidine. V. Meyer and J. Locher, *Ann.*, **180**, 172 (1876) obtained formic acid, hydrogen cyanide, ammonium chloride, hydroxylamine, and oxides of nitrogen from reduction of tetranitromethane with zinc and hydrochloric acid. It is thus possible that reduction of isobutyl 1-methyl-2,2,2-trinitroethyl ether with iron and hydrochloric acid yielded 2-isobutoxypropionamidine which then hydrolyzed to 2-isobutoxypropionamide and ammonia. (c) Reduction of a 1,1,1-trinitro compound to its corresponding amine by lithium aluminum hydride has not been reported previously.



The amine and its derivative, 1-(2-isobutoxypropyl)-3-phenyl-2-thiourea, are identical with that prepared by reduction of isobutyl 1-methyl-2-nitroethyl ether with iron and hydrochloric acid (Equation 4) and reaction of the product with phenyl isothiocyanate. Isobutyl 1-methyl-2-nitroethyl ether was synthesized by reaction of 1-nitro-1-propene, isobutyl alcohol, and potassium isobutoxide (Equation 5). The direction of addition of trinitromethane to α,β-unsaturated ethers is thus analogous to that of vinyl ethers with hydrogen halides,[8] carboxylic acids, and alcohols,[8] respectively.

EXPERIMENTAL

Materials. Trinitromethane was prepared by slowly adding concd. sulfuric acid to a cool suspension of potassium trinitromethane in petroleum ether (b.p. 60–90°). After potassium sulfate had been removed by filtration, trinitromethane was isolated by crystallization at −60 to −80°. Repeated recrystallization of the product from petroleum ether yielded very pure trinitromethane; white needles, m.p. 26.38°[9]; lit. m.p. 15°,[2] 22–23°.[10] Trinitromethane has been stored for months in Pyrex bottles at refrigerator temperatures without extensive decomposition. Distillation of trinitromethane can be effected at reduced pressures; however, a higher melting product is obtained by crystallization. Potassium trinitromethane was prepared by reduction of tetranitromethane with alcoholic potassium ethoxide.[11]

Vinyl ethers were supplied by the Carbide and Carbon Chemicals Corporation. Dihydropyran was obtained from E. I. du Pont de Nemours and Co. 1-Nitro-1-propene was prepared by dehydration of 1-nitro-2-propanol with phthalic anhydride.[12]

Isobutyl 1-methyl-2,2,2-trinitroethyl ether. A mixture of isobutyl vinyl ether (10.7 g., 0.107 mole) and dioxane (35 ml.) was added dropwise (2.5 hr.) to a stirred solution of trinitromethane (16.5 g., 0.109 mole) and dioxane (15 ml.) at 20°. The yellow mixture, after standing at room temperature for 4 days, was distilled to give isobutyl 1-methyl-2,2,2-trinitroethyl ether as a colorless liquid; b.p. 64–65° (0.7 mm.) (Table I); yield, 18.2 g. (75%).

Trinitromethane-dioxane adduct. Dioxane (4.4 g., 0.05 mole) was added dropwise to trinitromethane (15.1 g., 0.10 mole). Heat was evolved and cooling was necessary to keep the temperature of the mixture below 20°. On completion of the addition, the mixture solidified to a white crystalline mass. The product was distilled under reduced pressure to yield the pure trinitromethane-dioxane adduct as a white solid: b.p. 61–62° (9 mm.); m.p. 44–44.5°; yield, 18.0 g. (92%).

Anal. Calcd. for $C_6H_{10}N_6O_{14}$: C, 18.47; H, 2.58; N, 21.54. Found: C, 18.06; H, 2.77; N, 21.11.

The solid adduct dissolves in water to yield an acidic yellow solution which has a neutral equivalent of 193; the calculated neutral equivalent for $C_4H_8O_2.2CH(NO_2)_3$ is 195. Reaction of the adduct with an alcoholic solution of potassium hydroxide yields potassium trinitromethane and dioxane.

Ethyl 1-methyl-2,2,2-trinitroethyl ether. A solution of ethyl vinyl ether (6.0 g., 0.083 mole) and dioxane (20 ml.) was added dropwise (1 hr.) to a stirred solution of trinitromethane-dioxane complex (16.0 g., 0.041 mole) and dioxane (25 ml.) at 23°. After standing at room temperature for 4 days, the amber solution was distilled to give ethyl 1-methyl-2,2,2-trinitroethyl ether (Table I); b.p. 59–60° (0.6 mm.); yield, 13.4 g. (73%). The product was identical with that obtained from reaction of trinitromethane and ethyl vinyl ether.

Isobutyl 1-methyl-2,2,2-trinitroethyl ether and lithium aluminum hydride. A solution of isobutyl 1-methyl-2,2,2-trinitroethyl ether (55.1 g., 0.219 mole) and anhydrous ethyl ether (750 ml.) was added dropwise (6 hr.) to a stirred mixture of lithium aluminum hydride (40.0 g., 1.054 moles) and anhydrous ethyl ether (1000 ml.). The excess hydride was decomposed with water (30 ml.); 20% potassium sodium tartrate solution (900 ml.) was then added to the mixture. The ether layer was separated and washed with potassium sodium tartrate solution, water, and saturated sodium chloride solution. Distillation of the dried solution yielded 2-isobutoxypropylamine as a colorless liquid; b.p. 40–41° (7 mm.); n_D^{20} 1.4170; yield, 5.3 g. (18%). The amine was identical with that prepared by reduction of isobutyl 1-methyl-2-nitroethyl ether.

Reduction of isobutyl 1-methyl-2,2,2-trinitroethyl ether with iron and hydrochloric acid. A solution of isobutyl 1-methyl-2,2,2-trinitroethyl ether (50.0 g., 0.199 mole) and ethyl ether (100 ml.) was added dropwise (4 hr.) to a stirred, refluxing suspension of clean iron filings (100.0 g., 1.791 moles) in water (200 ml.). Throughout the reduction, concd. hydrochloric acid (24 ml.) was added in 1-ml. portions every 10 min., and the aqueous mixture was kept refluxing by application of heat. The ethyl ether was removed by distillation and the mixture was refluxed for 9

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[8] (a) W. Reppe and K. Baur, Ger. Patent 566,033, March 15, 1938.

[9] The melting point was determined by Bro. V. J. Wottle, Ph.D. dissertation, The Ohio State University, 1951.

[10] K. v. Auwers and L. Harres, *Ber.*, **62**, 2296 (1929).

[11] E. Schmidt, R. Schumacher, and H. Kuhlmann, *Ber.*, **54**, 1483 (1921).

[12] G. D. Buckley and C. W. Scaife, *J. Chem. Soc.*, 1471 (1947).

hr. The mixture was then cooled and filtered under vacuum. The filtrate was extracted with ether. The combined ether extracts were washed with water, dried, and distilled under reduced pressure to yield 2-isobutoxypropionamide; b.p. 98° (3 mm.); yield, 4.7 g. (16%). Upon cooling the amide crystallized into a soft, white solid; m.p. *ca.* 30°. 2-Isobutoxypropionamide is insoluble in dilute hydrochloric acid and dilute sodium hydroxide; when heated with 10% sodium hydroxide solution, the amide evolved ammonia.

Anal. Calcd. for $C_7H_{15}NO_2$: C, 57.90; H, 10.41; N, 9.65. Found: 58.05; H, 10.47; N, 9.41.

No 2-isobutoxypropylamine was found in the acidic aqueous layer from the reduction mixture; the products isolated (in low yield) were high-boiling alkaline substances which were not identified; b.p. 85–102° (1 mm.); neut. equiv. 349–394.

Isobutyl 1-methyl-2-nitroethyl ether. A solution of 1-nitro-1-propene (19.8 g., 0.227 mole) and isobutyl alcohol (75 ml.) was added dropwise (2 hr.) to a stirred mixture of potassium (9.1 g., 0.233 mole) and isobutyl alcohol (100 ml.) in ethyl ether (75 ml.) at 0°. After being) warmed to 25°, the mixture was diluted with water (100 ml.) and acidified with 20% acetic acid (60 ml.). The two layers were separated, and the aqueous phase was extracted with ether. The ether extracts were combined with the isobutyl alcohol layer. After the solvents had been removed by distillation at 50 mm., isobutyl 1-methyl-2-nitroethyl ether was obtained as a colorless liquid; b.p. 55–59° (2 mm.); n_D^{20} 1.4210; d_{20}^{20} 0.9747; MRD (Calcd.) 41.79; MRD (Found) 41.90; yield 16.1 g. (44%). The residue (10.4 g.) from the distillation was a polymeric black oil.

Anal. Calcd. for $C_7H_{15}NO_3$: C, 52.15; H, 9.38; N, 8.69. Found: C, 52.22; H, 9.31; N, 8.68.

2-Isobutoxypropylamine. Concentrated hydrochloric acid (four 15-ml. portions) and isobutyl 1-methyl-2-nitroethyl ether (15.2 g., 0.094 mole) were added alternately in small portions, with stirring, to a refluxing mixture of water (35 ml.) and clean iron filings (20.0 g., 0.358 mole).[13] The mixture was stirred and refluxed for 4 hr. After having been cooled, the mixture was filtered, and solid sodium hydroxide (10.0 g.) was added to the filtrate. The addition of sodium hydroxide caused precipitation of iron hydroxides, but, after 12 hr., the basic mixture was easily separated from the solid by decantation. The alkaline solution was extracted with ether; the extracts were washed with water, dried, concentrated at atmospheric pressure and then distilled to give 2-isobutoxypropylamine as a colorless liquid; b.p. 46° (19 mm.); d_{20}^{20} 0.8311; n_D^{20} 1.4172; MRD (Calcd.) 39.72; MRD (Found) 39.72; neut. equiv. (calcd.) 131; neut. equiv. (found) 134; yield, 4.9 g. (40%).

Anal. Calcd. for $C_7H_{17}NO$: C, 64.07; H, 13.06; N, 10.67. Found: C, 64.08; H, 12.80; N, 10.88.

1-(2-Isobutoxypropyl)-3-phenyl-2-thiourea. 2-Isobutoxypropylamine (0.32 g.), prepared by reduction of isobutyl 1-methyl-2-nitroethyl ether, and phenyl isothiocyanate (excess) reacted to give 1-(2-isobutoxypropyl)-3-phenyl-2-thiourea as white needles; m.p. 64–65°, recrystallized from a mixture of ethanol and water; yield, 0.65 g. (100%).

Anal. Calcd. for $C_{14}H_{22}N_2OS$: C, 63.32; H, 8.32; N, 10.52. Found: C, 62.80; H, 8.30; N, 10.39.

2-Isobutoxypropylamine (0.24 g.), prepared by the reduction of isobutyl 1-methyl-2,2,2-trinitroethyl ether with lithium aluminum hydride, and phenyl isothiocyanate reacted to yield 1-(2-isobutoxypropyl)-3-phenyl-2-thiourea; m.p. 64–65°; yield, 0.30 g. (62%). The melting point of this derivative was not depressed by the addition of the substituted thiourea prepared from 2-isobutoxypropylamine obtained from isobutyl 1-methyl-2-nitroethyl ether.

Anal. Calcd. for $C_{14}H_{22}N_2OS$: C, 63.32; H, 8.32; N, 10.52. Found: C, 63.29; H, 7.85; N, 10.60.

COLUMBUS 10, OHIO

TABLE I

ADDUCTS FROM α,β-UNSATURATED ETHERS AND TRINITROMETHANE

Compound[a,b]	Yield, %	B.P.[d]	d_{20}^{20}	n_D^{20}	MRD Calcd.	MRD Found	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
Ethyl 1-methyl-2,2,2-trinitroethyl ether	68	63–64.5° (0.6 mm.)	1.3145	1.4386	43.8	44.6[c]	26.91	26.28	4.06	4.20	18.83	18.47
Isopropyl 1-methyl-2,2,2-trinitroethyl ether	73	65° (0.4 mm.)	1.2720	1.4390	48.4	49.0	30.38	29.90	4.68	4.48	17.72	17.55
Isobutyl 1-methyl-2,2,2-trinitroethyl ether	75	65° (0.7 mm.)	1.2227	1.4389	53.0	54.0	33.47	33.60	5.22	5.34	16.73	16.88
2-Methoxyethyl 1-methyl-2,2,2-trinitroethyl ether	50	102–103° (1.5 mm.)	1.3194	1.4468	50.1	51.2	28.46	28.01	4.38	4.36	16.60	16.29
2-Trinitromethyltetrahydropyran	81	103° (1.0 mm.)	1.3968	1.4708	—	—	30.64	30.92	3.86	4.02	17.87	17.09

[a] The adducts were obtained from trinitromethane and ethyl vinyl ether, isopropyl vinyl ether, isobutyl vinyl ether, 2-methoxyethyl vinyl ether, and dihydropyran, respectively. The reactions were conducted at room temperature over periods ranging from 4–34 days using equimolar quantities of the unsaturated ether and trinitromethane in dioxane. [b] The products have been kept for more than three years at 10° without appreciable decomposition. [c] No attempt was made to obtain maximum yields. The residues from reaction were discarded because of their instability. [d] The lower boiling trinitroethers distill without decomposition to yield colorless liquids: 2-trinitromethyltetrahydropyran and 2-methoxyethyl 1-methyl-2,2,2-trinitroethyl ether decompose slightly during distillation.

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(13) M. Senkus, *Ind. Eng. Chem.*, **40**, 506 (1948).