to a 2,4-dinitrophenylhydrazone, m.p. 221–222° (reported,[12,21] m.p. 224–225°), which showed no depression in melting point upon admixture with an authentic sample[12] of the hydroxy ketone 2,4-dinitrophenylhydrazone derivative.

The aqueous acid solution obtained from the above hydrolysis was made basic and extracted with ether. The ether extract was dried over anhydrous potassium carbonate, the ether removed under reduced pressure (aspirator–steam bath) and the residue was fractionated *in vacuo*. The amino ketone XIII, 2.22 g. (57%), was obtained as an oil, b.p. 82–86° (8 mm.), $n^{32}D$ 1.4611, d^{25}_4 0.9481. The infrared spectra indicated a single carbonyl absorption band at 5.85 μ.

Anal. Calcd. for $C_{10}H_{19}NO$: C, 70.96; H, 11.31. Found: C, 70.66; H, 11.55.

The hydrochloride salt was recrystallized from methanol–ether, m.p. 158.5–160°.

Anal. Calcd. for $C_{10}H_{20}ClNO$: C, 58.38; H, 9.80. Found: C, 58.64; H, 9.84.

Oxidation of Amino Ketone XIII to Geronic Acid.—Two-tenths gram (0.0012 mole) of XIII was dissolved in 24 ml. of 2 *N* sodium metaperiodate solution. The reaction mixture was allowed to stand at room temperature for 20 hr. At the end of this period the periodate solution was made strongly alkaline, extracted with ether, and the ether extract discarded. The aqueous portion was acidified, and extracted twice with ether and once with chloroform. The extracts were combined, dried over anhydrous sodium sulfate, and the solvent removed under reduced pressure. The residue was treated with 2,4-dinitrophenylhydrazine to yield 0.26 g. (62%) of the derivative, m.p. 135.5–137° (reported m.p. 135.5–137°[22] or 139.5–140°[12]). A depression in melting point was not observed upon admixture with an authentic sample[12] of geronic acid, 2,4-dinitrophenylhydrazone.

(21) A. Bell, T. H. Stickland, and G. F. Wright, *J. Org. Chem.*, **16**, 1742 (1961); K. R. Bharucha, H. L. Cohen, and G. F. Wright, *ibid.*, **19**, 1097 (1954).

(22) H. H. Strain, *J. Am. Chem. Soc.*, **57**, 758 (1935).

Cyanoethylation. I. Weakly Basic Catalysts in the Reaction of Acrylonitrile with Active Methylene Compounds[1]

JOE A. ADAMCIK AND EDWARD J. MIKLASIEWICZ

Department of Chemistry, Texas Technological College, Lubbock, Texas

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Cyanoethylation of some active methylene compounds has been shown to proceed in the presence of triethylamine, often in high yields. With this catalyst at 25° the cyanoethylation of acetylacetone is greatly affected by the nature of the solvent. Little or no reaction occurs in tetrahydrofuran or dioxane, and the rate of the reaction varies with the nature of the solvent in this manner: *t*-butyl alcohol < isopropyl alcohol < 95% ethanol < "50% ethanol." The cyanoethylation of α-cyanoacetamide in the presence of triethylamine gave the expected product at 20°, but an isomer (VIII) at 65–70°. Studies on VIII have enabled us to formulate it as 3-cyano-3-(2′-cyanoethyl)-6-imino-2-piperidone.

Strong bases, such as benzyltrimethylammonium hydroxide and potassium hydroxide, are ordinarily used as catalysts in the cyanoethylation reaction.[2] However, the use of cyclohexylamine in the cyanoethylation of ethyl cyanoacetate has been reported.[3] Wakamatsu and Shimo have recently reported liquid ammonia-catalyzed Michael additions of nitroparaffins[4] and of derivatives of malonic and cyanoacetic acids[5,6] to acrylonitrile and other acceptors. Nevertheless, the use of such catalysts has not generally been exploited in synthesis. Since it might be expected to have the advantage of giving a more easily controllable reaction, the employment of triethylamine in the cyanoethylation of some active methylene compounds has been investigated.

The results obtained are reported in Table I. The yields can be quite high and the method is very convenient. It is necessary only to allow a solution of the active methylene compound, acrylonitrile, and triethylamine in a suitable solvent to stand at room temperature whereupon the product, if solid, separates from the reaction mixture.

In the course of the work, it was noted that the nature of the solvent had a great effect on the rate of the reaction and on the ultimate yields obtainable. In nonhydroxylic solvents such as dioxane and tetrahydrofuran the reaction took place extremely slowly if at all while it did proceed at a reasonable rate in alcohols.

This factor was therefore investigated more thoroughly by conducting the cyanoethylation of acetylacetone in various solvents at 25°. The ultimate yield of product was determined, and, as a rough indicator of the reaction rate, the time required to obtain one half of the ultimate yield. The results are shown in Table II.

That the reaction rate increases with the solvating ability of the solvent is shown by the order of reactivity in the solvents studied.

$$50\%\ C_2H_5OH\text{–}50\%\ H_2O > C_2H_5OH > (CH_3)_2CHOH > (CH_3)_3COH$$

The following explanation can be given for our results. The monocyanoethylation of acetylacetone in the presence of triethylamine proceeds as follows:

$$(CH_3CO)_2CH_2 + (C_2H_5)_3N \longrightarrow (CH_3CO)_2CH^- + (C_2H_5)_3NH^+$$

$$(CH_3CO)_2CH^- + CH_2{=}CHCN \longrightarrow (CH_3CO)_2CH{-}CH_2CH{-}CN$$

VI

where HA is an acidic species such as acetylacetone, triethylammonium ion, or possibly even solvent.[7] Since the reaction involves formation of the ionic species VI and triethylammonium from neutral molecules, the observed dependence of the rate on the solvent is expected.

(1) The support of this work by the Robert A. Welch Foundation is gratefully acknowledged.

(2) H. A. Bruson, *Org. Reactions*, **5**, 81 (1949).

(3) G. Wiest and H. Glaser, U.S. Patent 2,396,626 (March 12, 1946).

(4) S. Wakamatsu and K. Shimo, *J. Org. Chem.*, **27**, 1609 (1962).

(5) S. Wakamatsu, *ibid.*, **27**, 1285 (1962).

(6) K. Shimo and S. Wakamatsu, *ibid.*, **26**, 3788 (1961).

(7) This mechanism is a modification of the one given for the hydroxide ion-catalyzed cyanoethylation of acetylacetone by Y. Ogata, M. Okano, Y. Furuya, and I. Tabushi, *J. Am. Chem. Soc.*, **78**, 5426 (1956). It is essentially the same as that given by Wakamatsu (ref. 5).

TABLE I

CYANOETHYLATIONS

Starting material	Solvent and catalyst		Time	Product	M.p., °C.	Lit. m.p., °C.	Yield, %	Lit. yield, %
Acetylacetone (0.1 mole)	*t*-BuOH	(45 ml.)	2 days	γ,γ-Diacetylpimelonitrile (I)	185–186	182–184[a]	77	76[a]
	H_2O	(15 ml.)						
	Et_3N	(10 ml.)						
Methyl acetoacetate (0.1 mole)	*i*-PrOH	(30 ml.)	1 day	γ-Acetyl-γ-carbomethoxypimelonitrile (II)	152–154	154[b]	88	50[b]
	H_2O	(30 ml.)						
	Et_3N	(10 ml.)						
Ethyl acetoacetate (0.1 mole)	*i*-PrOH	(30 ml.)	1 day	γ-Acetyl-γ-carbethoxypimelonitrile (III)	81–83	82[b]	77	80[c]
	H_2O	(30 ml.)						
	Et_3N	(10 ml.)						
Malononitrile (0.2 mole)	EtOH	(60 ml.)	2 hr.	γ,γ-Dicyanopimelonitrile (IV)	89–90	92[d]	87	95[d]
	Et_3N	(5 ml.)						
α-Cyanoacetamide	[e]		[e]	γ-Carbamyl-γ-cyanopimelonitrile (V)	117.0–118.5	118[f]	63	74[f]

[a] A. B. Boese, Jr., U. S. Patent, 2,438,961 (April 6, 1948). [b] H. A. Bruson and T. W. Riener, *J. Am. Chem. Soc.*, **64**, 2850 (1942). [c] G. R. Zellars and R Levine, *J. Org. Chem.*, **13**, 911 (1948). [d] Ref. 10. [e] When conducted at 20° by the procedure described in the Experimental. [f] Ref. 8.

TABLE II

CYANOETHYLATION OF ACETYLACETONE IN VARIOUS SOLVENTS AT 25°

Solvent	Ultimate yield, %	Time required to obtain half of ultimate yield, hr.
"50% Ethanol"[a]	50	2
95% Ethanol	57	23
Isopropyl alcohol	67	89
t-Butyl alcohol	54	106

[a] Equal volumes of 95% and water.

The triethylamine-catalyzed cyanoethylation of α-cyanoacetamide gave anomalous but interesting results. When the cyanoethylation was carried out at 20°, a 63% yield of γ-carbamyl-γ-cyanonitrile (VII) was obtained. Bruson and Riener[8] reported obtaining VII from the reaction of α-cyanoacetamide with acrylonitrile in the presence of benzyltrimethylammonium hydroxide at 35–40°. Also, Wakamatsu[5] prepared this compound by cyanoethylation of α-cyanoacetamide in liquid ammonia at −50°.

At 65-70° the sole product was VIII, an isomer of VII. A mixture of VII and VIII was obtained at intermediate temperatures; separation was effected by utilizing the insolubility of VIII in tetrahydrofuran. When VII was treated with triethylamine in aqueous alcohol solution at 60–70°, it was converted in good yield to VIII.

Hydrolysis of VIII in 6 *N* hydrochloric acid at 50–60° gave IX, formula $C_9H_9N_3O_2$. Hydrolysis of VII, VIII, or IX in refluxing concentrated hydrochloric acid gave X, formula $C_9H_{10}N_2O_4$.

Titration of IX with aqueous sodium hydroxide showed it to be a weak acid with pK_a' of roughly 8.6. Titration of X showed that it is a somewhat weaker acid than IX, although it was not possible to obtain a definite value.

Reduction of IX with lithium aluminum hydride gave a diamine, XI, formula $C_9H_{18}N_2$.

A consideration of these facts, the infrared spectra of the compounds involved, and the nuclear magnetic resonance spectrum of XI enabled us to formulate these transformations as shown in Figure 1.

The spiro-diimide (X) has been previously reported

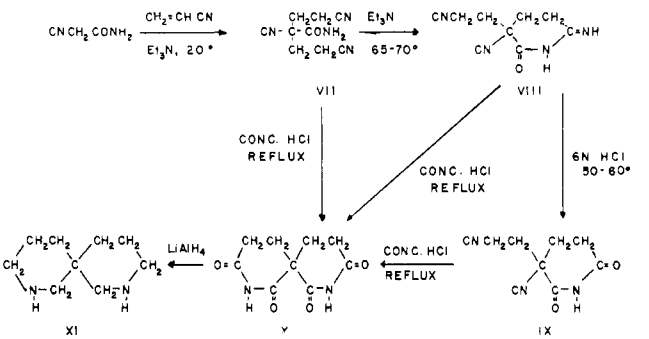
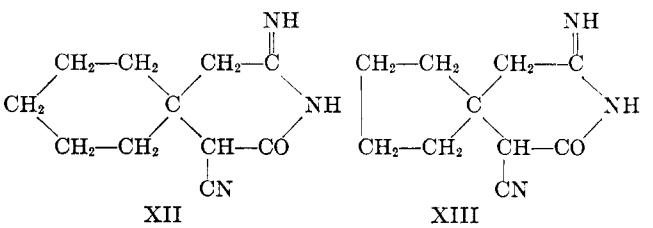


Figure 1

by Sury and Hoffmann[9] and by Mariella, Clutter, and Ebner.[10] The first-mentioned workers obtained it by cyclization of diethyl γ,γ-dicyanopimelate with sulfuric and acetic acids; the latter by cyclization of γ,γ-dicyanopimelonitrile, γ-carbamyl-γ-cyanopimelonitrile or γ,γ-dicarbamylpimelonitrile with concentrated hydrochloric acid. The melting points reported by these two groups disagree significantly; our value agrees closely with that of Mariella, Clutter, and Ebner.

The spiro-diamine (XI) has been obtained by Sury and Hoffmann[9] from lithium aluminum hydride reduction of X, as well as from reduction of related starting materials. The decomposition point of the picrate which we observed differed significantly from their value.[11] However, the nuclear magnetic resonance spectrum and the other data reported here leave little doubt as to the structure of XI.

The interesting cyclization of VII to VIII is not without precedent. Birch and Kon[12] reported the synthesis of XII and XIII from the reaction of Δ¹-cy-



XII XIII

(8) H. A. Bruson and T. W. Riener, *J. Am. Chem. Soc.*, **65**, 23 (1943).

(9) E. Sury and K. Hoffmann, *Helv. Chim. Acta*, **36**, 1815 (1953).

(10) R. P. Mariella, R. Clutter, and H. G. Ebner, *J. Org. Chem.*, **20**, 1702 (1955).

(11) Sury and Hoffmann did not correct their melting points.

(12) S. F. Birch and G. A. R. Kon, *J. Chem. Soc.*, **123**, 2440 (1923).

clohexenylacetonitrile and Δ^1-cyclopentenylacetonitrile, respectively, with cyanoacetamide. Kandiah and Linstead[13] showed that these products resulted from the isomeric α,β-unsaturated nitrile formed by isomerization in the alkaline medium.

Experimental

All melting points are corrected. Microanalyses were performed by Schwarzkopf Microanalytical Laboratories and Geller Microanalytical Laboratories. Infrared spectra were obtained with a Perkin-Elmer Infracord, Model 137. Nuclear magnetic resonance spectra were recorded with a Varian Associates Model A-60 spectrometer.

Cyanoethylations.—The general procedure for cyanoethylations involved allowing a solution of the active hydrogen compound and an equivalent quantity of acrylonitrile in a suitable solvent–catalyst mixture to stand in a water bath at 25°. Reaction of malononitrile was so vigorous that ice-bath cooling was utilized initially. The product was then removed by filtration, washed thoroughly with ethanol, and dried.

Cyanoethylation of α-Cyanoacetamide.—A solution of 8.41 g. (0.10 mole) of α-cyanoacetamide, 20 ml. of triethylamine, and 10.6 g. (0.2 mole) of acrylonitrile in 30 ml. of 95% ethanol and 30 ml. of water was placed in a water bath maintained at the desired temperature for the time indicated. The product was isolated by filtration and washed with ethanol.

When the water-bath temperature was maintained between 65 and 70°, the reaction time was 3 hr. and 14.75 g. or 77% of 3-cyano-3-(2′-cyanoethyl)-6-imino-2-piperidone (VIII), m.p. 221–222°, was obtained. After recrystallization from ethanol–water, the product melted at 223–224°.

Anal. Calcd. for $C_9H_{10}N_4O$: C, 56.83; H, 5.30; N, 29.46. Found: C, 57.09; H, 5.42; N, 29.68.

When the water-bath temperature was 20°, the reaction time was 8 hr. and the yield of γ-carbamyl-γ-cyanopimelonitrile (VII) was 11.9 g. (63%), m.p. 117.0–118.5°; lit.,[8] 118°. The product was completely soluble in tetrahydrofuran.

When the water-bath temperature was maintained between 40 and 50°, the reaction time was 2.5 hr. and the yield of product was 12.10 g. (64%). When the product was treated with tetrahydrofuran, 9.55 g. (50%) of VIII remained undissolved. The tetrahydrofuran was removed from the filtrate by distillation, whereupon 2.5 g. (13%) of VII remained as a residue.

The infrared spectrum of VII (KBr disk) showed the following significant bands: 3450 cm.$^{-1}$ (s), 3200 cm.$^{-1}$ (s), 2260 cm.$^{-1}$ (m), 1700 cm.$^{-1}$ (s), 1630 cm.$^{-1}$ (m). That of VIII (KBr disk) showed: 3400 cm.$^{-1}$ (s), 2270 cm.$^{-1}$ (m), 1680 cm.$^{-1}$ (m-shoulder), 1650 cm.$^{-1}$ (s).

Transformation of VII to VIII.—A mixture of 20 g. of VII, 135 ml. of 95% ethanol, and 45 ml. of water was prepared and placed in a water bath held between 60 and 70° for 5 min. Then 40 ml. of triethylamine was added and heating was continued for 1.25 hr. The mixture was filtered and the product (VIII) washed with ethanol; m.p. 221–222°. The yield was 15.45 g. (77%).

Hydrolysis of VIII in 6 *N* Hydrochloric Acid.—Ten grams (0.053 mole) of VIII in 150 ml. of 6 *N* hydrochloric acid was heated in a water bath held between 50 and 60° for 45 min. The mixture was placed in a refrigerator overnight, filtered, and the product, 3-cyano-3-(2′-cyanoethyl)-2,6-piperidinedione (IX), washed with cold water. The yield was 5.65 g. (56%); m.p. 134–135°. The analytical sample was obtained by recrystallization from ethanol–water; m.p. 134–135°.

Anal. Calcd. for $C_9H_9N_3O_2$: C, 56.54; H, 4.74; N, 21.98. Found: C, 56.53; H, 4.72; N, 21.88.

Significant band in the infrared spectrum of IX (KBr disk) were: 3400 cm.$^{-1}$ (w), 3200 cm.$^{-1}$ (s), 3100 cm.$^{-1}$ (m), 2260 cm.$^{-1}$ (m), 1720 cm.$^{-1}$ (s).

Hydrolysis of VII in Concentrated Hydrochloric Acid.—A mixture of 24 g. (0.126 mole) of VII and 150 ml. of concentrated hydrochloric acid was refluxed until a white solid precipitated and for a few minutes thereafter. The mixture was cooled to room temperature, filtered, and the product, 2,8-diazaspiro[5.5]-undecane-1,3,7,9-tetrone (X), washed with ethanol. It weighed 10.0 g. (38%). On repeated recrystallization from water, it melted at 283–284°.

Sury and Hoffmann[9] reported m.p. 268–270°, Mariella, Clatter, and Ebner[10] reported m.p. 283°.

Anal. Calcd. for $C_9H_{10}N_2O_4$: C, 51.42; H, 4.80; N, 13.33. Found: C, 51.47, 51.63; H, 5.09, 4.95; N, 13.30, 13.54.

The infrared spectrum of X (KBr disk) showed the following significant bands: 3250 cm.$^{-1}$ (s), 1720 cm.$^{-1}$ (s), 1680 cm.$^{-1}$ (s). There was no band near 2260 cm.$^{-1}$.

Hydrolysis of VIII in Concentrated Hydrochloric Acid.—The hydrolysis of 20 g. (0.105 mole) of VIII in 100 ml. of concentrated hydrochloric acid was carried out in a similar manner to the hydrolysis of VII. The product (X) weighed 11.0 g. (42%). After repeated recrystallization from water it melted at 283.0–284.5°.

Anal. Calcd. for $C_9H_{10}N_2O_4$: C, 51.42; H, 4.80; N, 13.33. Found: C, 51.23; H, 4.73; N, 13.54.

The identity of the product obtained from VIII with that obtained from VII was further shown by the identity of the X-ray patterns[14,15] and infrared spectra.

Hydrolysis of IX in Concentrated Hydrochloric Acid.—The hydrolysis of 6.3 g. (0.033 mole) of IX in 50 ml. of concentrated hydrochloric acid was carried out in a similar manner to the hydrolysis of VII. The product (X) weighed 3.0 g. (43%) and melted at 283–284°. The infrared spectrum (KBr disk) was identical to that of the products obtained from VII and VIII.

Potentiometric Titrations.—A Beckman Model H pH meter with glass and calomel electrodes was used for the titration with approximately tenth normal sodium hydroxide. The pK_a' (pH at half-neutralized point) of IX was 8.6. Titration of X showed that it was an acid weaker than IX, but it was not possible to obtain a definite value due, probably, both to the weakness of X as an acid and to the fact that it is diprotic.

Reduction of X with Lithium Aluminum Hydride.—To a 2000-ml. three-necked flask fitted with a mechanical stirrer was attached a Soxhlet extractor containing a glass thimble with sintered glass bottom. In the flask were placed 15.2 g. (0.4 mole) of lithium aluminum hydride and 1200 ml. of tetrahydrofuran (dried over sodium hydride and distilled). The thimble contained 21.0 g. (0.1 mole) of X. The mixture was refluxed, with constant stirring, for 26 hr. This period of time was more than sufficient for complete extraction of X from the thimble. The reaction mixture was then cooled in an ice bath and 100 ml. of water was added slowly. Stirring was continued for 20 min. after addition of the water. The mixture was filtered, the solid washed with tetrahydrofuran, and the combined filtrate and washings acidified to congo red with concentrated hydrochloric acid. The lower (aqueous) layer was separated and evaporated to dryness at reduced pressure. The residue was dissolved in 25 ml. of water and basified with solid potassium hydroxide. Extraction with four portions of chloroform followed by removal of the chloroform at reduced pressure yielded a residue which was distilled twice *in vacuo* through a 350 × 14 mm. Vigreux column to give 2,8-diazaspiro[5.5]undecane(XI). The fraction boiling at 73.5–74.5°/0.8 mm. weighed 4.60 g. (30%); lit.,[9] b.p. 117–119°/11 mm.

Anal. Calcd. for $C_{90}H_{18}N_2$: C, 70.07; H, 11.77; N, 18.16. Found: C, 69.98; H, 11.82; N, 18.00.

The picrate was formed in methanol and recrystallized from water. It decomposed at 251°. Sury and Hoffmann[9] reported decomposition at 233–234°.

Anal. Calcd. for $C_{21}H_{24}N_8O_{14}$: C, 41.18; H, 3.95; N, 18.30. Found: C, 41.22; H, 4.21; N, 18.00.

The infrared spectrum (liquid film) showed maxima at 3350 cm.$^{-1}$ and 1650 cm.$^{-1}$ (w).

The nuclear magnetic resonance spectrum (102 mg./ml. in carbon tetrachloride) showed chemical shifts (p.p.m. downfield from tetramethylsilane as internal standard) of 2.64 (α-protons), 1.39 (β- and γ-protons), and 1.14 (N-protons); intensity ratios 4:4:1. For comparison, the spectrum of redistilled piperidine was determined at a similar concentration; the chemical shifts

(13) A. Kandiah and R. P. Linstead, *J. Chem. Soc.*, 2139 (1929).

(14) The X-ray patterns were kindly obtained by Dr. Arthur L. Draper and Mr. Richard L. Garner using a Phillips X-ray diffraction unit with Cr $K\alpha$ radiation. We desire to express our gratitude for these determinations.

(15) There was some difficulty connected with this. Most commonly, the infrared spectrum of the product showed a strong band at 795 cm.$^{-1}$ (α-form). Occasionally, a product lacking this band, and having a different X-ray pattern, was obtained (β-form). These were shown to be crystal modifications by the fact upon seeding a supersaturated solution of the α-form (maintained at 40°) with the β-form, the latter form crystallized.

were 2.72, 1.48, and 1.18; intensity ratios 4:6:1. The chemical shift of the N-proton was very dependent on concentration; at about 400 mg./ml. it was superimposed on the β- and γ-proton resonances in the spectra of both compounds.

Effect of Solvent on the Cyanoethylation of Acetylacetone.—A mixture of 9.8 g. (0.1 mole) of acetylacetone, 10.7 g. (0.2 mole) of acrylonitrile, and 60 ml. of the solvent was placed in a water bath thermostatted at 25.0 ± 0.1°. After thermal equilibrium had been reached, 10 ml. of triethylamine was added. The mixture was filtered shortly before and shortly after the estimated time required for half-completion of the reaction (as determined by preliminary experiments). The product (I) from each filtration was washed with ethanol, dried, and weighed. The filtrate was maintained at 25° until the reaction was essentially complete and the product removed by filtration, washed, dried, and weighed to obtain the ultimate yield. A graphical interpolation was then used to determine the time required to obtain half of the ultimate yield.

Michael-type Reactions with $\alpha,\alpha,\omega,\omega$-Tetranitroalkanes[1]

HENRY FEUER, GERD LESTON,[2] ROBERT MILLER,[2] AND ARNOLD T. NIELSEN

Department of Chemistry, Purdue University, Lafayette, Indiana

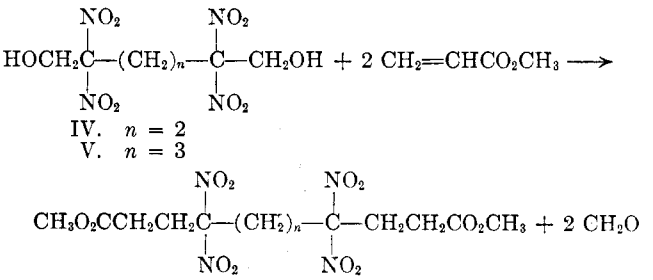
Received September 17, 1962

Michael-type reactions of 1,1,4,4-tetranitrobutane (I), 1,1,5,5-tetranitropentane (II), and 1,1,6,6-tetranitrohexane (III) with a molar excess of acceptor, such as acrylic acid, methyl acrylate, acrylonitrile, acrolein, methyl vinyl ketone, methyl vinyl sulfone, and nitroethylene, afford α,ω-bisadducts in each case. Either the free $\alpha,\alpha,\omega,\omega$-tetranitroalkanes or their α,ω-bismethylol derivatives can be employed, the latter being demethylolated *in situ*. The reaction of the disodium salt of III with 2-bromo-2,2-dinitroethyl acetate and with 2-nitrobutyl acetate leads respectively to 1,1,3,3,8,8,10,10-octanitrodecane (XX) and 3,5,5,10,10,12-hexanitrotetradecane (XXII). The dibasic acids 4,4,7,7-tetranitrodecanedioic acid (XI) and 4,4,8,8-tetranitroundecanedioic acid (XV) are converted, consecutively into their respective acid chloride, diazide, diisocyanate, methyl carbamate, diamine, and diacetamido derivatives.

Michael addition reactions of mononitroalkanes have been studied extensively and numerous examples are known.[3] Fewer examples of additions of 1,1-dinitroalkanes have been reported,[4-9] but the scope of this reaction appears potentially equal to that employing mononitroalkanes. The addition of methyl acrylate to dipotassium 1,1,3,3-tetranitropropane[9] appears to be the only reported example of the Michael-type reaction with an $\alpha,\alpha,\omega,\omega$-tetranitroalkane. In this instance, only monoaddition took place and methyl 3,3,5,5-tetranitropentanoate was obtained.

In continuation of our study of the Michael-type addition with nitroalkanes,[10-13] we are now reporting our findings with $\alpha,\alpha,\omega,\omega$-tetranitroalkanes[14] such as 1,1,4,4-tetranitrobutane (I), 1,1,5,5-tetranitropentane (II), and 1,1,6,6-tetranitrohexane (III), leading to α,ω-disubstituted products. Two procedures were used with such Michael acceptors as methyl acrylate, acrylic acid, acrylonitrile, acrolein, methyl vinyl ketone, methyl vinyl sulfone, and nitroethylene.

Procedure A.—The α,ω-bismethylol-$\alpha,\alpha,\omega,\omega$-tetranitroalkanes[14] were employed, the tetranitroalkanes being generated *in situ* by demethylolation in the presence of catalytic amounts of sodium hydroxide. In the equation below, Procedure A is illustrated by the reactions of 2,2,5,5-tetranitro-1,6-hexanediol (IV) and 2,2,6,6-tetranitro-1,7-heptanediol (V) with methyl acrylate to yield dimethyl 4,4,7,7-tetranitrodecanedioate (VI) and dimethyl 4,4,8,8-tetranitroundecanedioate (VII), respectively.

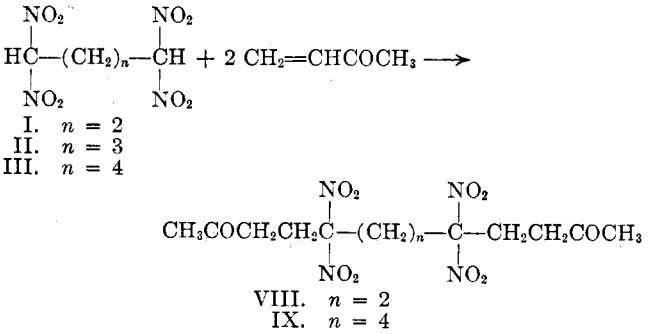


IV. $n = 2$
V. $n = 3$

VI. $n = 2$
VII. $n = 3$
XIV. $n = 4$

Procedure A

Procedure B, which was very effective with more reactive or base sensitive acceptors such as methyl vinyl ketone, nitroethylene, or acrolein, employed the free $\alpha,\alpha,\omega,\omega$-tetranitroalkanes with a trace of basic catalyst. Procedure B is illustrated by reactions of 1,1,4,4-tetranitrobutane (I) and 1,1,6,6-tetranitrohex-



I. $n = 2$
II. $n = 3$
III. $n = 4$

VIII. $n = 2$
IX. $n = 4$

Procedure B

(1) Presented before the Division of Organic Chemistry at the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., September, 1962.

(2) Taken, in part, from the Ph.D. theses of Gerd Leston (1952) and Robert Miller (1958), Purdue University.

(3) For a thorough survey of the literature, reference is made to E. D. Bergman, D. Ginsburg, and R. Pappo, *Org. Reactions*, **10**, 179 (1959).

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(6) H. Shechter and L. Zeldin, *J. Am. Chem. Soc.*, **73**, 1276 (1951).

(7) M. B. Frankel, *J. Org. Chem.*, **23**, 813 (1958).

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