hydrogen ($\tau$ 3.1–3.2). The $H^1$ n.m.r. spectrum of I showed a sharp singlet for Si$CH_3$ ($\tau$ 10.03), doublets ($J$ = ~1.5 c.p.s.) for aliphatic hydrogen ($\tau$ 7.03) and olefinic hydrogen ($\tau$ 4.38), and a singlet for aromatic hydrogen ($\tau$ 3.13).

Stirring lithium wire, trimethylchlorosilane, and naphthalene in THF at 25° for 24 hr. gave approximately 50% conversion to I and II (2:3 ratio of I:II) by v.p.c. analyses.

**1,4-Bis(trimethylsilyl)naphthalene (III).**—A solution of 40 g. (0.14 mole) of 1,4-dibromonaphthalene and 30.2 g. (0.28 mole) of trimethylchlorosilane in 100 ml. of THF was added to 7.2 g. (0.3 g.-atom) of magnesium during 1 hr. at reflux temperature. After heating for 1 additional hr., the mixture was poured into ice–water. Fractional distillation of the organic phase and ether extracts of the aqueous phase gave 7 g. of crude III, b.p. 106–114° (0.5 mm.), m.p. 75–85°. Recrystallization from methanol gave 5.7 g. (20% yield) of III, m.p. 90–92°.

*Anal.* Calcd. for $C_{16}H_{24}Si_2$: C, 70.6; H, 8.9; Si, 20.6. Found: C, 70.9; H, 9.3; Si, 20.7.

**Aromatization of 1,2-Bis(trimethylsilyl)-1,2-dihydronaphthalene (II).**—Sulfur (5 g., 0.156 mole) and 40 g. (0.146 mole) of II were heated at 180–190° for 30 hr. Fractional distillation gave 3.6 g. of hexamethyldisilthian, b.p. 40–50° (10 mm.), infrared spectrum identical with reported spectrum,[8] and 23.5 g. of product, b.p. 123–124° (10 mm.), which was shown by comparison of n.m.r. and infrared spectra to be approximately 33% unchanged II, 60% 2-trimethylsilylnaphthalene (Si$CH_3$ at $\tau$ 9.65), and 7% 1-trimethylsilylnaphthalene (Si$CH_3$ at $\tau$ 9.57).

**Aromatization of 1,4-Bis(trimethylsilyl)-1,4-dihydronaphthalene (I).**—By the above procedure, 50 g. (0.18 mole) of I and 6 g. (0.19 mole) of sulfur gave 6.3 g. (17% yield) of 1-trimethylsilylnaphthalene, b.p. 89–92° (3 mm.), $n^{25}D$ 1.5810 (lit.[9] $n^{25}D$ 1.5810), infrared and n.m.r. identical with an authentic sample, and 37.5 g. (76.5% yield) of 1,4-bis(trimethylsilyl)naphthalene, b.p. 124–125° (3 mm.), m.p. 89–90.5°, infrared identical with that of an authentic sample.

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(8) H. Kriegsmann, *Z. Elektrochem.*, **61**, 1088 (1957).

(9) H. Gilman, R. A. Benkeser, and G. E. Dunn, *J. Am. Chem. Soc.*, **72**, 1689 (1950).

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# *gem*-Dinitro Esters. V. The Alcoholysis and Hydrolysis of 3,3-Dinitropropionitriles[1]

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*Received August 18, 1964*

Meisenheimer,[2] in his original work on the preparation of 3,3-dinitropropionitrile, briefly studied its hydrolysis and alcoholysis and reported some properties of crude 3,3-dinitropropionic acid and an unstable sample of the methyl ester. The present Note is concerned with a more detailed study of 3,3-dinitropropionitrile as a source of *gem*-dinitro esters and other derivatives.

3,3-Dinitropropionitrile is readily and conveniently obtained as its potassium salt by the reaction of potassium cyanide on 1,1,1-trinitroethane.[2] Methanol, in the presence of hydrogen chloride, reacts with this salt to give a nitrile adduct, which, upon further reaction with water, produces a mixture of methyl esters composed principally of the 3,3-dinitropropionate and the 3-chloro-3-nitropropionate. This unusual replacement of a nitro group by a chlorine to form the latter compound does not appear to be influenced by substituting 3,3-dinitropropionitrile for its potassium salt as starting material, but is, however, favored by higher temperatures. Under the most favorable conditions studied for the preparation of the dinitro ester, the two esters are produced in approximately equal amounts. The mixture of esters is not readily separated into the individual components but samples of each over 90% pure are obtained by repeated fractional distillation.

Treatment of samples estimated to be over 90% pure methyl 3-chloro-3-nitropropionate with methanolic potassium nitrite produces the potassium salt of methyl 3,3-dinitropropionate in over 70% yield by the ter Meer[3] reaction. Potassium nitrite also precipitates the dinitro ester as its potassium nitronate salt from an alcoholic solution. Thus pure methyl 3,3-dinitropropionate is obtained from the original crude mixture of esters by treatment with methanolic potassium nitrite and acidification of the resulting salt.

The alcoholysis reaction with 3-chloro- and 3-bromo-3,3-dinitropropionitrile, available by direct halogenation of the potassium salt of the dinitronitrile, similarly leads to mixtures of products, generally with reduced nitro content. The reaction with the bromo derivative is particularly interesting in that copious amounts of free bromine are liberated during the reaction and a yellow crystalline solid, tentatively believed to be 3-chloro-4-nitroso-5-aminoisoxazole 2-oxide, accompanies the crude product.

The hydration of 3,3-dinitropropionitrile and its chloro and bromo derivatives is readily accomplished to the corresponding amides by using 85% sulfuric acid as the hydrolytic medium. Further hydrolysis to the corresponding acids, however, is complicated by side reactions similar to those encountered in the alcoholysis experiments. Concentrated hydrochloric acid, at or below room temperature, converts 3-bromo-3,3-dinitropropionitrile to a mixture from which the corresponding amide and dichloroglyoxime may be isolated. The same reagent converts the chlorodinitronitrile to the amide but in lower yield than when 85% sulfuric acid is employed.

## Experimental[4]

**Potassium 3,3-Dinitropropionitrile.**—The crude salt, containing some potassium cyanide and nitrite, was obtained in 95% yield by the method of Meisenheimer.[2] Crystallization from aqueous ethanol resulted in 85–95% recoveries of purified salt. The dry salt is stable at room temperature and may be stored for several months without any apparent deterioration. When tested in an impact device its sensitivity appeared to be approximately like that of pentaerythritol tetranitrate (PETN). *Caution* must therefore be exercised when the dry salt is handled. The moist salt, though less sensitive to impact, slowly decomposes at room temperature with the evolution of oxides of nitrogen. A freshly prepared aqueous solution of potassium 3,3-dinitropropionitrile shows the typical ultraviolet absorption for 1,1-dinitroalkane anions,[5] $\lambda_{max}$ 363 m$\mu$ ($\epsilon$ 1.9 × $10^4$). Its infrared spectrum in potassium bromide disks was characterized by the following prominent bands: $\lambda$ [$^-C(NO_2)_2$] 6.77, 7.76, 8.1–8.5 $\mu$; $\lambda$ (CN) 4.46 $\mu$; $\lambda$ (other) 7.38, 9.00, 10.72, 13.18, 13.51, and 14.61 $\mu$.

*Anal.* Calcd. for $C_3H_2KN_3O_4$: K, 21.34; N, 22.94. Found: K, 21.13; N, 22.73.

**3,3-Dinitropropionitrile.**—Twenty grams (0.11 mole) of potassium 3,3-dinitropropionitrile, suspended in dry dichloromethane,

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(1) This work was performed under the auspices of the U. S. Atomic Energy Commission. Paper IV: *J. Org. Chem.*, **28**, 2491 (1963).

(2) J. Meisenheimer and M. Schwarz, *Ber.*, **39**, 2543 (1906).

(3) E. ter Meer, *Ann.*, **181**, 4 (1876).

(4) All temperatures are uncorrected. Microanalyses were by M. J. Naranjo.

(5) M. J. Kamlet and D. J. Glover, *J. Org. Chem.*, **27**, 537 (1962).

was acidified with dry hydrogen chloride at 0–5°. The precipitated potassium chloride was removed by filtration and the solvent was evaporated from the filtrate under reduced pressure. 3,3-Dinitropropionitrile remained as a pale yellow oil, $n^{25}\text{D}$ 1.4728, 13.5 g. (85%). A nearly colorless sample resulted by distillation of small quantities from a Hickman molecular still at 65–70° (0.005 mm.): $n^{25}\text{D}$ 1.4725; λ ($NO_2$) 6.33 and 7.59 μ (strong) in chloroform solution, and λ (CN) 4.45 μ (weak) in liquid films. In hexane its ultraviolet absorption is approximately normal for a terminal *gem*-dinitro compound.[6] In 95% ethanol, however, a second band, characteristic of the anion or the *aci* form, is also present ($\lambda_{\max}$ 360 mμ). 3,3-Dinitropropionitrile is a strong organic acid with a $K_a$-value of 4.3 × $10^{-3}$ in aqueous solution.[7] By comparison 1,1-dinitroethane has a reported[8] $K_a$-value of 5.2 × $10^{-6}$.

*Anal.* Calcd. for $C_3H_3N_3O_4$: C, 24.83; H, 2.08; N, 28.97; neut. equiv., 145. Found: C, 24.97; H, 2.21; N, 28.93; neut. equiv., 144.3.

**Ammonium 3,3-Dinitropropionitrile.**—Dry ammonia was added to a 2–4% solution of purified 3,3-dinitropropionitrile in ether at 0–5° until no more salt precipitated. The resulting finely crystalline orange precipitate was filtered, washed with ether, and air dried, m.p. 90° dec. The most prominent absorptions in the infrared resembled those of the potassium salt with additional moderate to strong absorption at 3.20 and 7.2–7.3 μ due to the ammonium ion.

*Anal.* Calcd. for $C_3H_6N_4O_4$: C, 22.23; H, 3.73; N, 34.56. Found: C, 21.69; H, 4.42; N, 34.43.

Dry samples appeared insensitive to impact and showed no signs of decomposition on exposure to the atmosphere.

**Piperidinium 3,3-dinitropropionitrile**, prepared in the same way as the ammonium salt, was less stable and could not be stored without extensive decomposition resulting. A freshly prepared sample was insensitive to impact and its infrared spectrum grossly resembled that of the ammonium salt.

*Anal.* Calcd. for $C_8H_{14}N_4O_4$: C, 41.74; H, 6.09; N, 24.34. Found: C, 41.91; H, 5.82; N, 24.11.

**Methyl 3,3-Dinitropropionate and Methyl 3-Chloro-3-nitropropionate.**—A suspension of 5 g. (0.027 mole) of crude dry potassium 3,3-dinitropropionitrile in 25 ml. of methanol was chilled to −10° in a flask protected from moisture with a calcium chloride filled drying tube while a slow stream of dry hydrogen chloride was added with stirring. The introduction of hydrogen chloride was stopped when the methanol was saturated and the reaction mixture was allowed to come to room temperature in the slowly melting ice bath. After a total of 18 hr. of stirring, the suspension was poured into 100 ml. of water and ice and the product was extracted with four 50-ml. portions of dichloromethane. Drying and removal of the solvent by distillation gave 3.3–3.7 g. (68–76%) of residue, $n^{25}\text{D}$ 1.4532–1.4635, composed of a mixture of methyl 3,3-dinitropropionate and methyl 3-chloro-3-nitropropionate.

The crude mixture (5 g., 0.028 mole) was added to 150 ml. of methanol saturated with potassium nitrite (4.5 g., 0.052 mole) with stirring during 5 min. After 0.5 hr. of stirring, the pale yellow potassium salt of methyl 3,3-dinitropropionate was filtered: 3.7 g. (61%); m.p. 153–156° dec.; λ (CO) 5.75, and λ [$^-C(NO_2)_2$] 6.69 and 7.55 μ. The dry salt was suspended in 100 ml. of dichloromethane and dry hydrogen chloride was added with stirring during 0.5 hr. while the pale yellow salt was replaced by the white, formed potassium chloride. The suspension was filtered and the solvent was removed under reduced pressure to give 2.9 g. (96%) of methyl 3,3-dinitropropionate, $n^{25}\text{D}$ 1.4504. Distillation from a modified Hickman still at 45–48° pot temperature and 0.2 mm. gave 2.6 g. of ester: $n^{25}\text{D}$ 1.4486; λ (CO) 5.74, and λ ($NO_2$) 6.31, 7.52, 11.30, and 11.55 μ.

*Anal.* Calcd. for $C_4H_6N_2O_6$: C, 26.97; H, 3.40; N, 15.73. Found: C, 26.91; H, 3.65; N, 15.97.

The crude ester prior to the potassium nitrite treatment always contained from 9–12% chlorine and was difficult to distil without some decomposition. A forefraction from two distillations from a 5-in. Vigreux column, b.p. 41–42° (0.1 mm.), $n^{25}\text{D}$ 1.4512, λ (CO) 5.72 μ and λ ($NO_2$) 6.32 μ, was obtained containing nearly the theoretical analytical composition for methyl 3-chloro-3-nitropropionate.

*Anal.* Calcd. for $C_4H_6ClNO_4$: C, 28.67; H, 3.61; Cl, 21.16; N, 8.36. Found: C, 28.40; H, 3.51; Cl, 20.46; N, 8.21.

A dichloromethane solution of this methyl 3-chloro-3-nitropropionate was stirred with an aqueous solution of sodium acetate at room temperature for 2 hr. with no change in the infrared spectrum. In contrast, similar treatment of a sample of methyl 2-chloro-3-nitropropionate,[9] λ (CO) 5.71 and λ ($NO_2$) 6.38 μ, shifted the *as*-nitro band to 6.46 μ as methyl 3-nitroacrylate was formed.

Another sample of this 3-chloro ester (0.15 g., 0.001 mole) was added to a stirred solution of 10 ml. of methanol saturated with potassium nitrite at room temperature. After 1 hr. the pale yellow salt was filtered and dried giving 0.15 g. of the potassium salt of methyl 3,3-dinitropropionate: m.p. 152–154° dec.; λ (CO) 5.75, and λ [$^-C(NO_2)_2$] 6.69 and 7.56 μ.

*Anal.* Calcd. for $C_4H_5KN_2O_6$: K, 18.08; N, 12.96. Found: K, 18.21; N, 12.91.

**3-Bromo-3,3-dinitropropionitrile.**—Five grams (0.028 mole) of crude potassium 3,3-dinitropropionitrile was suspended in 75 ml. of carbon tetrachloride at 0–5° and 4.8 g. (0.03 mole) of bromine was added dropwise with stirring. The separated potassium bromide was filtered and washed with carbon tetrachloride. The solvent was removed from the combined carbon tetrachloride solutions and the residue was distilled from a Hickman molecular still at 80° (0.1 mm.) giving 5.9 g. (95%) of nearly colorless material which solidified in the refrigerator. Recrystallization from a mixture of chloroform and carbon tetrachloride gave colorless plates: m.p. 55–56°; λ ($NO_2$) 6.29 and 7.73 μ; λ (other) 7.11, 7.45, 9.00, 10.09, 11.79, and 12.39 μ in chloroform; and λ (CN) 4.38 μ (weak) in a liquid film.

*Anal.* Calcd. for $C_3H_2BrN_3O_4$: C, 16.08; H, 0.90; Br, 35.68; N, 18.76. Found: C, 16.67; H, 0.86; Br, 35.01; N, 18.64.

**3-Chloro-3,3-dinitropropionitrile.**—By a similar procedure potassium 3,3-dinitropropionitrile was chlorinated in 62% yield. After recrystallization from carbon tetrachloride, 3-chloro-3,3-dinitropropionitrile was obtained as white needles: m.p. 36°; λ ($NO_2$) 6.31 and 7.73 μ; and λ (other) 7.15, 7.51, 8.92, 10.00, and 11.82 μ in carbon tetrachloride.

*Anal.* Calcd. for $C_3H_2ClN_3O_4$: C, 20.07; H, 1.12; Cl, 19.75; N, 23.41. Found: C, 20.31; H, 1.50; Cl, 20.09; N, 22.85.

**3,3-Dinitropropionamide.**—A suspension of 5.7 g. (0.039 mole) of 3,3-dinitropropionitrile in 17.7 ml. of 85% sulfuric acid was slowly stirred at room temperature for 24 hr. After pouring the solution on ice, the crude amide was extracted from the solution with ether. Removal of the ether by evaporation and crystallization of the residue from benzene or chloroform gave 3.55 g. (56%) of 3,3-dinitropropionamide: m.p. 54.5–55°; λ (NH) 2.90 and 2.99 μ; λ (CO) 5.88 μ; λ ($NO_2$) 6.33 and 7.52 μ; and λ (other) 8.31, 8.43, and 11.58 μ in acetonitrile.

*Anal.* Calcd. for $C_3H_5N_3O_5$: C, 22.09; H, 3.09; N, 25.77. Found: C, 22.32; H, 3.10; N, 25.61.

**3-Bromo-3,3-dinitropropionamide** was prepared in 88–92% yields by a similar hydrolysis of 3-bromo-3,3-dinitropropionitrile. After recrystallization from benzene it melted at 106–107°; λ (NH) 2.96 and 3.01 μ; λ (CO) 5.86 μ; λ ($NO_2$) 6.29 and 7.67 μ; and λ (other) 7.45, 10.03, 10.85, 11.68, and 12.39 μ.

*Anal.* Calcd. for $C_3H_4BrN_3O_5$: C, 14.89; H, 1.67; Br, 33.02; N, 17.37; mol. wt., 242. Found: C, 15.10; H, 1.98; Br, 33.35; N, 17.50; mol. wt. (freezing point depression in nitrobenzene), 245.

**3-Chloro-3,3-dinitropropionamide** was obtained from 3-chloro-3,3-dinitropropionitrile in 78–84% yields by a similar hydrolysis with 85% sulfuric acid. After recrystallization from water or benzene, it melted at 112–113°; λ (NH) 2.92 and 3.01 μ; λ (CO) 5.87 μ; λ ($NO_2$) 6.29 and 7.66 μ; and λ (other) 7.24, 7.47, 10.02, 12.29, and 12.75 μ in acetonitrile.

*Anal.* Calcd. for $C_3H_4ClN_3O_5$: C, 18.24; H, 2.04; Cl, 17.95; N, 20.73; mol. wt., 197.5. Found: C, 18.47; H, 1.83; Cl, 18.03; N, 20.70; mol. wt. (freezing point depression in nitrobenzene), 196.

**Hydrolysis of 3-Bromo-3,3-dinitropropionitrile.**—A suspension of 5 g. (0.022 mole) of 3-bromo-3,3-dinitropropionitrile in 25 ml. of 37% hydrochloric acid was allowed to stand at room temperature for 30 hr. and was then diluted with 50 ml. of ice–water and refrigerated overnight. The aqueous solution, deeply colored by this time with free bromine, was extracted with dichlorometh-

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(6) H. E. Ungnade and L. W. Kissinger, *J. Org. Chem.*, **22**, 1088 (1957).

(7) Determined by R. N. Rogers from equilibrium pH of a solution in conductivity water and by titration of the compound in aqueous solution.

(8) J. S. Belew and L. G. Hepler, *J. Am. Chem. Soc.*, **78**, 4005 (1956).

(9) Prepared by the addition of nitryl chloride to methyl acrylate as described by H. Shechter, F. Conrad, A. L. Daulton, and R. B. Kaplan [*ibid.*, **74**, 3054 (1952)].

ane, then with ether, and the dried extracts (magnesium sulfate) were worked up separately.

Removal of the dichloromethane from the first extract by evaporation was accompanied by free bromine and gave 1.7 g. of a crude oily residue which showed carbonyl and nitrile absorption in the infrared. After decolorizing a benzene solution of the mixture, 0.92 g. (17%) of 3-bromo-3,3-dinitropropionamide, m.p. 105–107°, was obtained with the same infrared spectrum as the analytical sample prepared in 85% sulfuric acid described above.

The ether extract was decolorized with charcoal and the solvent was removed by evaporation leaving 2.74 g. of a semisolid residue. Trituration with 10 ml. of dichloromethane gave 0.57 g. of colorless needles as a residue, m.p. 199–201°. Recrystallization from 1,2-dichloroethane or toluene gave an analytical sample of unchanged melting behavior. The infrared spectrum in potassium bromide disks showed bands of nearly equal medium intensity at 3.10, 7.10, 10.02, and 11.72 and weak bands at 3.56–3.60, 6.06, and 6.17 $\mu$. By comparison of this infrared spectrum with that of an authentic sample of dichloroglyoxime,[10] and the following analytical data, the sample was identified as dichloroglyoxime. It was obtained in 16% yield.

*Anal.* Calcd. for $C_2H_2Cl_2N_2O_2$: C, 15.30; H, 1.28; Cl, 45.18; N, 17.85. Found: C, 15.81; H, 1.56; Cl, 44.58; N, 17.86.

The dichloromethane solution from which the dichloroglyoxime had been filtered showed an infrared spectrum devoid of nitro content and was not further investigated.

Hydrolysis of 3-chloro-3,3-dinitropropionitrile, under similar conditions, gave 3-chloro-3,3-dinitropropionamide in 48% yield and some recovered nitrile.

**Attempted Preparation of Methyl 3-Bromo-3,3-dinitropropionate.**—A solution of 5 g. (0.022 mole) of 3-bromo-3,3-dinitropropionitrile in 25 ml. of methanol was saturated with dry hydrogen chloride at −10° and stirred at the slowly melting ice bath and then room temperature for a total of 24 hr. after which it was poured into 50 ml. of water and ice. The liquid phase, containing liberated bromine, was separated from a yellow crystalline solid by filtration and was then extracted with dichloromethane. Removal of the solvent from the dried dichloromethane solution gave a liquid residue (2.3–2.6 g.) containing 4–6% nitrogen (methyl 3-bromo-3,3-dinitropropionate requires 10.90% N). Infrared analyses indicated that the crude product was composed of at least two esters; these could not be separated by molecular distillation and they decomposed on attempted distillation through a column under reduced pressure.

The yellow crystalline solid which had been separated from the reaction mixture above, m.p. 172–176°, was obtained in 1.73–2.21-g. quantities. Crystallization from 70% ethanol, water, or benzene gave 80–95% recoveries of a bright yellow crystalline product, m.p. 185–187° with decomposition. It sublimed unchanged at 70–80° (0.02 mm.). Its ultraviolet absorption spectrum was characterized by a broad band, $\lambda_{max}$ 360 m$\mu$ (log $\epsilon$ 3.06), and a narrower band, $\lambda_{max}$ 235 m$\mu$ (log $\epsilon$ 4.10), in 95% ethanol. In the infrared, in a potassium bromide pressing, the following prominent bands were observed: strong bands at 6.02–6.06 (doublet), 6.61, 7.57, 12.01; medium intensity bands at 2.94, 3.08, 3.13, 6.44; and weak bands at 7.36, 8.62, 9.68, and 10.60 $\mu$. In an acetone solution, n.m.r. examination showed the presence of a substantial amount of water even after the sample was sublimed.[11]

*Anal.* Calcd. for $C_3H_2ClN_3O_3 \cdot 0.5H_2O$: C, 20.88; H, 1.75; Cl, 20.55; N, 24.36. Found: C, 21.91; H, 1.75; Cl, 20.16; N, 24.44.

A pale yellow acetyl derivative, m.p. 121–122°, was obtained by heating a solution of the yellow solid with acetic anhydride for 2 hr. In the infrared it showed strong bands at 5.89, 6.11, 6.42, 6.75, 7.43, 8.10, and 11.98 $\mu$; medium bands at 5.89, 7.75, and 9.00 $\mu$; and weak absorption at 7.30, 6.62, 10.00, and 10.22 $\mu$ in a potassium bromide pressing.

*Anal.* Calcd. for $C_5H_4ClN_3O_4$: C, 29.21; H, 1.96; Cl, 17.25; N, 20.44. Found: C, 29.35; H, 2.04; Cl, 17.08; N, 19.50.

On the basis of these data and its mass spectral fragmentation pattern,[11] the yellow crystalline by-product is believed to be 3-chloro-4-nitroso-5-aminoisoxazole 2-oxide,[12] although other isomeric structures have not been completely excluded. The acetyl derivative is believed to be the corresponding 5-acetylaminoisoxazole oxide.

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[10] G. Ponzio and F. Baldracco, *Gazz. chim. ital.*, **60**, 415 (1930).

[11] The n.m.r. and mass spectral analyses were made by E. M. Roberts and E. D. Loughran, respectively, of this laboratory.

[12] This structure requires a $\beta$-nitro group, in its *aci* form, or an oximino group to add to the nitrile group to give the 5-iminooxazole ring. Nitrosation on the $\alpha$-carbon atom and replacement of a $\beta$-nitro group by chlorine, also required for this structure, have been observed in the hydrolysis of the bromodinitronitrile and in the methanolysis of the parent 3,3-dinitropropionitrile, respectively.

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# Phosphonitrilic Compounds. IV. Preparation and Polymerization of Allylaminophosphonitrile Compounds[1,2]

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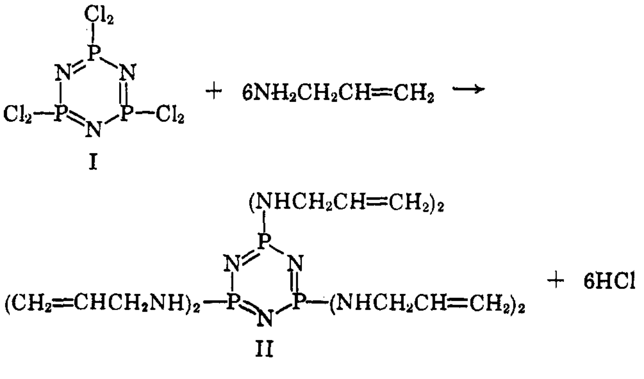
*Received October 5, 1964*

Although the reactions of halophosphonitriles with amines have been widely reported,[3] the reactions with allylamine have not been described in detail.[4] The preparation of allylaminophosphonitrile compounds was of particular interest, however, since the allyl groups would provide a valuable means for the incorporation of phosphonitrile units into polymeric systems. We now report the synthesis of three representative compounds in this series together with preliminary polymerization data.

Hexachlorocyclotriphosphonitrile (I) was treated with 6 equiv. of allylamine in benzene or tetrahydrofuran, to yield hexa(allylamino)cyclotriphosphonitrile (II). Excess allylamine or triethylamine were used as hydrohalide acceptors. These reactions afforded II in yields of up to 30%. The remaining reaction product in each case was a resinous conglomerate which resisted purification and which appeared to contain



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[1] Part III: H. R. Allcock and L. A. Siegel, *J. Am. Chem. Soc.*, **86**, 5140 (1964).

[2] Good reasons have been put forward (see ref. 3a) for adapting an alternative "phosphazene" nomenclature for compounds which contain the –P=N– unit. The *Chemical Abstracts* notation considers these compounds as "hydro azaphosphorine" derivatives. In the present paper, the more familiar "phosphonitrile" terminology is retained but the alternative names based on the *Chemical Abstracts* classification are also given in the Experimental.

[3] For reviews of this topic see (a) R. A. Shaw, B. W. Fitzsimmons, and B. C. Smith, *Chem. Rev.*, **62**, 247 (1962); (b) C. D. Schmulbach, *Progr. Inorg. Chem.*, **4**, 275 (1962).

[4] During the course of this work, E. T. McBee and S. E. French [*Dissertation Abstr.*, **24**, 4993 (1964)] reported the synthesis of the monohydrochloride of hexaallylaminophosphonitrile trimer.