obtained, b.p. 107° (25 mm.), b.p. 215° (763 mm.) (lit. b.p. 211–213°, $n^{25}\text{D}$ 1.5312).

Infrared spectrum showed bands at 9.81 (cyclopropyl), 3.27 (aromatic C–H), and 6.31 μ (vinyl). Other bands appeared at 12.80, 12.15, 11.98, 11.25, 10.68, 9.81, 9.55, 9.26, 7.96, 7.80, 7.25, 7.03, 6.98, 6.50, and 3.20 μ.

The n.m.r. spectrum showed a multiplet (relative area 5) at τ 2.39–2.92 (phenyl H); signals at 4.88 (relative area 1), and 5.08 (relative area 1) due to olefinic protons; and complex absorptions (relative area 1) at 8.20–8.68 (cyclopropyl methyne H) and (relative area 4) at 9.13–9.55 (cyclopropyl methylene H).

Anal. Calcd. for $C_{11}H_{12}$: C, 91.66; H, 8.33. Found: C, 91.74; H, 8.46.

The 1-*para*-substituted phenyl-1-cyclopropylethylenes were similarly prepared by the Wittig reaction from the corresponding ketones.

1-Cyclopropyl-1-(*p*-fluorophenyl)ethylene was obtained as a colorless liquid, yield 58%, b.p. 72° (40 mm.), and $n^{25}\text{D}$ 1.5292. Infrared bands appeared at 12.12 (para-substituted phenyl), 9.80 (cyclopropyl), and 6.24 μ (C=C stretch). Other bands were at 13.01, 12.43, 11.80, 11.08, 10.76, 9.75, 9.51, 9.27, 9.08, 8.68, 8.14, 8.00, 7.23, 7.01, 6.62, 3.32, and 3.22 μ. The n.m.r. spectrum showed multiplets (relative area 4) at τ 2.42–2.65 and 2.88–3.25 (phenyl H); and signals at 4.84 (relative area 1), 8.23–8.63 (cyclopropylmethyne H), and (relative area 4) 9.03–9.50 (cyclopropyl methylene H).

1-Cyclopropyl-1-(*p*-methoxyphenyl)ethylene was obtained as a colorless liquid, yield 46%, b.p. 116° (50 mm.), and $n^{25}\text{D}$ 1.5608. Infrared bands were at 12.01 (*para*-substituted phenyl), 9.75 (cyclopropyl), and 6.25 μ (C=C stretch). Other bands appeared at 13.17, 12.96, 11.10, 10.58, 9.20, 9.08, 8.92, 8.42, 8.00, 7.71, 7.20, 7.03, 6.90, 6.85, 6.62, 6.35, 3.53, 3.40, and 3.26 μ. The n.m.r. spectrum showed multiplets (relative area 4) at τ 2.52–2.66 and 3.17–3.33 (aromatic H); signals at 4.89 (relative area 1) and 5.27 due to olefinic protons; a singlet (relative area 3) at 6.27 (methoxy H); and complex absorptions (relative area 1) at 8.34–8.67 (cyclopropylmethyne H) and (relative area 4) 9.04–9.53 (cyclopropyl methylene H).

Anal. Calcd. for $C_{12}H_{14}$: C, 90.40; H, 9.59. Found: C, 91.35; H, 9.08.

1-Phenylcyclopentene.—A 5-g. sample of 1-cyclopropyl-1-phenylethylene was passed through a 50-cm. Vicor tube packed with glass wool and heated to 400°. The crude product was distilled through a 30-plate column. 1-Phenylcyclopentene (4.6 g.) was obtained as a colorless liquid, b.p. 122° (50 mm.) and $n^{25}\text{D}$ 1.5736 (lit. $n^{25}\text{D}$ 1.5734), having infrared bands at 6.25 (C=C stretch), 14.20, and 13.33 μ (monosubstituted benzene). Other bands were at 11.02, 10.98, 9.60, 9.31, 7.74, 7.52, 7.42, 6.90, 6.72, 5.52, 3.98, and 3.30 μ. The n.m.r. spectrum showed a multiplet (relative intensity 5) at τ 2.5–2.8 (phenyl H); a triplet (relative intensity 1) at 3.8 (olefinic H); a complex absorption (relative intensity 9) at 7.2–7.6 (methylene H at C-3 and C-5); and a complex absorption (relative intensity 2) at 7.8–8.2 (methylene H at C-4).

Anal. Calcd. for $C_{11}H_{12}$: C, 91.66; H, 8.33. Found: C, 91.46; H, 8.27.

1-*para*-Substituted phenylcyclopentenes were prepared by similar pyrolyses of the corresponding 1-*para*-substituted phenyl-1-cyclopropylethylenes.

1-(*p*-Fluorophenyl)cyclopentene was obtained as a colorless liquid, b.p. 232° (760 mm.), $n^{25}\text{D}$ 1.5578, having infrared bands at 6.24 (C=C stretch) and at 12.2 μ (*para*-substituted phenyl). Other bands appeared at 12.48, 10.43, 9.83, 9.60, 9.09, 8.17, 7.68, 7.51, 5.97, 3.52, 3.40, and 3.29 μ. The n.m.r. spectrum showed a multiplet (relative intensity 4) in the region τ 2.7–3.2 (aromatic H); a multiplet (relative intensity 1) centered at 3.95 (olefinic H); and a complex absorption (relative intensity 6) at 7.10–8.25 (methylene H).

Anal. Calcd. for $C_{11}H_{11}F$: C, 81.49; H, 6.77; F, 11.73. Found: C, 81.69; H, 6.90; F, 11.59.

1-(*p*-Methoxyphenyl)cyclopentene was obtained as colorless crystals, m.p. 81°, having infrared bands at 6.23 (C=C stretch) and 12.25 μ (*para*-substituted phenyl). Other bands were at 11.96, 10.45, 10.12, 9.67, 9.00, 8.51, 8.17, 8.03, 7.28, 4.00, 6.62, and 3.48 μ. The n.m.r. spectrum showed doublets (relative intensity 4) at τ 2.62 and 3.18 (phenyl H); a triplet at 3.95 (olefinic H); a singlet at 6.22 (methoxy H); a complex absorption at 7.30–7.65 (methylene H at C-3 and C-5); and a complex absorption at 7.75–8.20 (methylene H at C-4).

Anal. Calcd. for $C_{12}H_{19}O$: C, 82.76; H, 8.05; O, 9.20. Found: C, 82.47; H, 8.14; O, 9.68.

1-(*p*-Methylphenyl)cyclopentene was obtained as colorless crystals, m.p. 53°, having infrared bands at 6.1 (C=C stretch) and 12.30 μ (*para*-substituted phenyl). Other bands were at 11.11, 10.12, 9.62, 8.92, 8.83, 8.43, 8.07, 7.63, 7.44, 7.28, 6.89, 6.57, 6.38, and 3.48 μ. The n.m.r. spectrum showed a quartet (relative intensity 4) in the region τ 2.6–3.2 (aromatic H); a multiplet (relative intensity 1) centered at 4.0 (olefinic H); a complex absorption (relative intensity 6) at 7.0–8.9 (methylene H); and a singlet (relative intensity 3) at 7.68 (methyl H).

Anal. Calcd. for $C_{12}H_{14}$: C, 90.40; H, 9.59. Found: C, 90.81; H, 8.89.

1-(*p*-Isopropylphenyl) cyclopentene was obtained as a colorless liquid, b.p. 120° (4.0 mm.), having infrared bands at 6.22 (C=C stretch) and 12.32 μ (*para*-substituted phenyl). Other bands were at 11.98, 10.40, 9.79, 9.62, 9.45, 7.68, 7.30, 7.21, 7.04, 6.86, 6.60, and 3.48 μ. The n.m.r. spectrum showed a multiplet (relative intensity 4) at τ 2.61–3.02 (phenyl H); a triplet (relative intensity 1) at 3.95 (olefinic H); complex absorptions (relative intensity 7) at 7.15–8.21 (methylene and methyne protons); and a sharp doublet (relative intensity 6) at 8.73 (methyl H).

Anal. Calcd. for $C_{14}H_{18}$: C, 90.32; H, 9.68. Found: C, 90.34; H, 9.90.

***p*-Methylphenylcyclopentane**—A 1.75-g. portion of the crude product from the pyrolysis of 1-cyclopropyl-1-(*p*-methylphenyl)-ethylene was hydrogenated with sodium borohydride in a Brown[2] apparatus.[5] The catalyst was filtered off and the ethanol solvent was removed by distillation. *p*-Methylphenylcyclopentane (88% yield) was obtained as a colorless liquid after purification by preparative v.p.c. on a silicone oil column at 162°. The n.m.r. spectrum showed a singlet (relative intensity 4) centered at τ 2.82 (aromatic H); a broad absorption (relative intensity 1) centered at 7.12 (aliphatic H on carbon adjacent to phenyl); a singlet (relative intensity 3) centered at 7.67 (methyl H); and broad absorptions at 7.6–9.1 (relative intensity 8) assignable to methylene protons.

Anal. Calcd. for $C_{11}H_{14}$: C, 90.41; H, 9.59. Found: C, 90.50; H, 9.48.

Rate Studies.—Samples (0.1 ml.) were sealed under vacuum in 10 × 2 cm. glass tubes. The tubes were placed in a muffle furnace equipped with an electronic controller which kept the temperature (350°) within ±0.5°. After equilibration for 10 min., tubes were rapidly removed at noted times and quenched in a stream of compressed air. Five microliters from each tube was analyzed using an F and M gas chromatograph with an integrating recorder. First-order rate constants were computed from the areas of the peaks corresponding to initial and residual starting materials.

Acknowledgment.—The authors are indebted to Mr. L. Fisher and Mr. D. Clancy for technical assistance.

(5) H. C. Brown and C. A. Barton, *J. Am. Chem. Soc.*, **84**, 2829 (1962).

Disilyldihydronaphthalenes from Alkali Metal Naphthalenides and Chlorosilanes

DONALD R. WEYENBERG AND LOUIS H. TOPORCER

Organic Research Laboratories,
Dow Corning Corporation, Midland, Michigan

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Although the reaction of chlorosilanes and alkali metal naphthalenides is known to give disilyldihydronaphthalenes,[1,2] the previous data do not rigorously establish the positions of the silyl groups in these struc-

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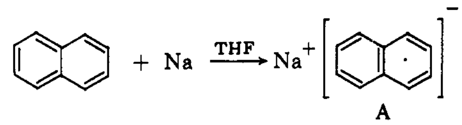
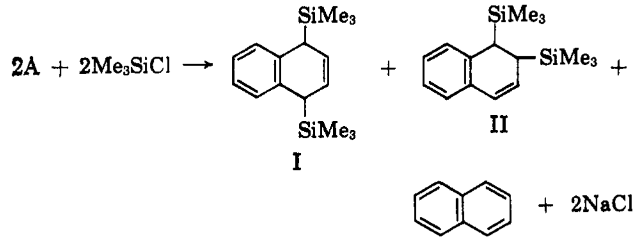
(1) A. D. Petrov and T. I. Chernysheva, *Dokl. Akad. Nauk SSSR*, **89**, 73 (1953); *Chem. Abstr.*, **48**, 3917*a* (1954).

(2) J. F. Brown, Jr., U. S. Patent 2,967,160 (1961); *Chem. Abstr.* **55**, 6456*b* (1961).

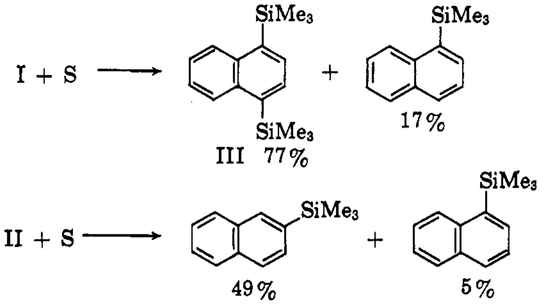
tures. For example, no attempt was made by Petrov and Chernysheva to differentiate between 1,2- and 1,4-substitution in their assignment of the 1,4-disilyl-1,4-dihydronaphthalene structure to their products from chlorosilanes and lithium naphthalenide in ether.[1]

During our studies of the disilylation reaction,[3] which involves the coupling of chlorosilanes and anion radicals, we found that sodium naphthalenide reacts rapidly with trimethylchlorosilane in tetrahydrofuran (THF) to give both 1,4-bis(trimethylsilyl)-1,4-dihydronaphthalene (I) and 1,2-bis(trimethylsilyl)-1,2-dihydronaphthalene (II). These two isomers were separated by careful fractional distillation. Products I and II are

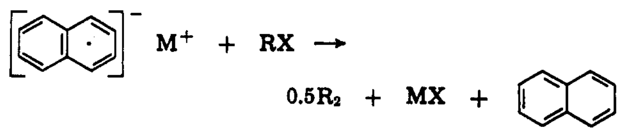




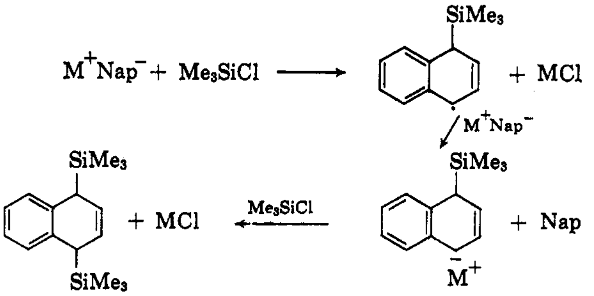
also obtained from lithium, naphthalene, and trimethylchlorosilane in THF, undoubtedly by the same sequence of reactions. The H^1 n.m.r. spectra show one and two CH_3Si absorptions for I and II, respectively, and suggest that each structure is a single geometric isomer. The spectra, however, do not permit an assignment of *cis* or *trans* configuration. Further confirmation of these structural assignments was provided by conversion to known derivatives on aromatization by heating with sulfur. Whereas I is readily dehydrogenated by sulfur, II undergoes aromatization *via* loss of a hydrogen and trimethylsilyl group. Hexamethyldisilthian, from the condensation of trimethylmercaptosilane, was isolated from this latter reaction. The thermal aromatization of disilyldihydronaphthalenes is known[2] to involve loss of a hydrogen and silyl group to give silanes and monosilylnaphthalenes.



The 1,2- and 1,4-addition of silyl groups is analogous to the 1,2- and 1,4-addition of hydrogen or carboxylate by treatment of alkali metal naphthalenides with protic reagents[4] or with carbon dioxide.[5] The naphthalenide is reacting as a typical organometallic reagent with the chlorosilane to give substitution of the organo group for the halogen on the silicon rather than by electron (and metal) transfer to give a silyl radical or anion. This latter type of reaction is often encountered in the reaction of naphthalenides with alkyl halides.[4]



The path of this substitution reaction is presumably the same as that proposed for the disilylation of benzene[3a] and the carbonation of naphthalenides,[6] and is shown below for the production of the 1,4-derivative.



The 1,2-addition would result from reaction at the 2-position in the first or last step of this reaction. This scheme is analogous to the currently accepted path for the chemical reduction of aromatic compounds.[7]

Experimental

All experiments were carried out under dry nitrogen in flasks fitted with reflux condensers and stirrers. Boiling points and melting points are uncorrected. Vapor phase chromatograms were obtained on an 8-ft. dimethylpolysiloxane gum column.

1,4-Bis(trimethylsilyl)-1,4-dihydronaphthalene (I) and 1,2-Bis(trimethylsilyl)-1,2-dihydronaphthalene (II).—A solution of 64 g. (0.5 mole) of naphthalene in 100 ml. of THF was added during 30 min. to 28 g. (1.2 equiv.) of sodium (approximately 1-cm.^{3} pieces) and 250 ml. of THF. To this green solution was added 108.5 g. (1.0 mole) of trimethylchlorosilane at a rate such that sodium naphthalenide (green color) was present throughout the addition of the silane. The temperature was maintained at 20–25° during the 2-hr. addition. Filtration and fractional distillation after the addition of 10 g. of trimethylchlorosilane gave 80 g. (58% yield) of bis(trimethylsilyl)dihydronaphthalene, b.p. 123–33° (5 mm.), $n^{25}\text{D}$ 1.5282, approximately 1:2 ratio of I:II by H^1 n.m.r. spectrum. Fractional distillation through a 6-ft. Podbielniak distillation column of the products from a duplication of the above experiment on a larger scale gave pure II, b.p. 134–136° (11.5 mm.), $n^{25}\text{D}$ 1.5273–1.5278, single component by v.p.c.

Anal. Calcd. for $C_{16}H_{36}Si_2$: Si, 20.5. Found: Si, 20.6, 20.7.

I was the other product of this distillation, b.p. 141–142° (11.5 mm.), $n^{25}\text{D}$ 1.5320–1.5322, some decomposition on v.p.c. column.

Anal. Found: Si, 20.7, 20.7.

The H^1 n.m.r. spectrum of II showed equal intensity singlets for SiCH_3 (τ 9.97 and 10.10) and multiplets for aliphatic hydrogen (τ 7.7–8.1), olefinic hydrogen (τ 4.1–4.4), and aromatic

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[3] (a) D. R. Weyenberg and L. H. Toporcer, *J. Am. Chem. Soc.*, **84**, 2843 (1962); (b) D. R. Weyenberg, L. H. Toporcer, and M. J. Napoli, Abstracts, 140th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1961, p. 31Q.

[4] N. D. Scott, J. F. Walker, and V. L. Hansley, *J. Am. Chem. Soc.*, **58**, 2442 (1936).

[5] J. F. Walker and N. D. Scott, *ibid.*, **60**, 951 (1938).

[6] D. E. Paul, D. Lipkin, and S. I. Weissman, *ibid.*, **78**, 116 (1956).

[7] For an excellent recent review of this topic, see H. Smith, "Organic Reactions in Liquid Ammonia," Vol. 1, part 2, Interscience Publishers, Inc., New York, N. Y., 1963, pp. 212–279.

hydrogen (τ 3.1–3.2). The H^1 n.m.r. spectrum of I showed a sharp singlet for $\mathrm{Si}CH_3$ (τ 10.03), doublets ($J = \sim 1.5$ c.p.s.) for aliphatic hydrogen (τ 7.03) and olefinic hydrogen (τ 4.38), and a singlet for aromatic hydrogen (τ 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 ($\mathrm{Si}CH_3$ at τ 9.65), and 7% 1-trimethylsilylnaphthalene ($\mathrm{Si}CH_3$ at τ 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]

ANN MULFORD AND L. W. KISSINGER

University of California, Los Alamos Scientific Laboratory, Los Alamos, New Mexico

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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 mμ (ϵ 1.9×10^4). Its infrared spectrum in potassium bromide disks was characterized by the following prominent bands: λ $[^-C(NO_2)_2]$ 6.77, 7.76, 8.1–8.5 μ; λ (CN) 4.46 μ; λ (other) 7.38, 9.00, 10.72, 13.18, 13.51, and 14.61 μ.

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).