loids. This was chromatographed on 150 g. of neutral alumina (activity II–III)[13] and from the 7:3 benzene–ether eluates was isolated 2.0 g. of pilocereine. Crystallization from ethyl acetate furnished 1.1 g. of pure pilocereine, the identity of which was confirmed by mixture melting point and infrared comparison.

L. gatesii.[14]—Fresh cactus (3.3 kg.) yielded 300 g. of dry powdered material which on extraction gave 39.6 g. of residue. This was partitioned and separated as previously described into 3 g. of phenolic and 5.4 g. of non-phenolic base. The non-phenolic base was chromatographed on 150 g. of alumina to yield 1.5 g. of pilocereine identified as before.

Isolation of Anhalonidine from *Lemaireocereus weberi*.[14]—By the usual procedure 9.27 kg. of cactus gave 48 g. of alcoholic residue which was extracted with ether until no more color was removed. The ether extract, weighing less than 2 g., did not contain alkaloids (Mayer's reagent) and only traces of oily material were obtained when this fraction was processed in the usual manner for triterpenes. The dark brown, ether-insoluble fraction (46 g.) was refluxed for 3 hr. with 1 l. of methanol and 200 cc. of concentrated hydrochloric acid. After cooling and dilution with water this was extracted with ether but evaporation left only traces of oily material. The aqueous acidic solution was neutralized with ammonium hydroxide and extracted with ether; evaporation yielded 1.73 g. of crude alkaloids which were chromatographed on 100 g. of activated alumina. Elution with chloroform–methanol (99:1) furnished a solid (0.65 g.) crystallizing as needles, m.p. 156–158° from acetone–hexane. The analytical sample after recrystallization from acetone showed m.p. 161–161.5°; reported[15] for anhalonidine, m.p. 160–161°.

Anal. Calcd. for $C_{12}H_{17}NO_3$: C, 64.55; H, 7.68; N, 6.27; $(OCH_3)_2$, 27.6; neut. equiv., 223. Found: C, 64.43; H, 7.80; N, 6.50; OCH_3, 26.9; neut. equiv., 215.

The picrate, prepared by adding a saturated solution of picric acid to a solution of the base gave needles, m.p. 200.5–201.5°, after recrystallization from ethanol; reported[15] m.p. 201–208°.

Anal. Calcd. for $C_{18}H_{20}N_4O_{10}$: C, 47.79; H, 4.46. Found: C, 48.03; H, 4.54.

(15) E. Spaeth, *Monatsh.*, **43**, 477 (1922).

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Some New 1-(Nitroxyalkyl)-3-nitroguanidines and their Cyclic Products[1]

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The cyclization of the N-(β-substituted ethyl)- and N-(β-nitroxypropyl)-N′-nitroguanidines to salts of 1-nitro-2-amino-Δ^2-1,3-diazacyclopentene and 1-nitro-2-amino-5-methyl-Δ^2-1,3-diazacyclopentene nitrate, respectively, was first reported by McKay.[2] A six-membered ring compound has also been formed by cyclizing N-(γ-nitroxybutyl)-N′-nitroguanidine to 1-nitro-2-amino-6-methyl-Δ^2-1,3-diazacyclohexene nitrate.[3]

It was of interest to this Laboratory to determine whether larger ring systems could be synthesized through cyclization of higher homologs of 1-(nitroxyalkyl)-3-nitroguanidines, the free bases of which are isomeric to those reported by McKay and Wright.[4] The cyclization of 1-(ω-nitroxypropyl)- and 1-(β-nitroxy-*t*-butyl)-3-nitroguanidine proceeded rapidly in boiling *n*-butanol to 1-nitro-amino-Δ^2-1,3-diazacyclohexene nitrate and 1-nitro-2-amino-4-dimethyl-Δ^2-1,3-diazacyclopentene nitrate, respectively. However, 1-(ω-nitroxybutyl)- and 1-(ω-nitroxyamyl)-3-nitroguanidine failed to cyclize to the respective seven- and eight-membered rings: *viz.*, 1-nitro-2-amino-Δ^2-1,3-diazacycloheptene and 1-nitro-2-amino-Δ^2-1,3-diazacycloöctene nitrate salts. Failure of the higher homologs to cyclize can be attributed to the greater strain in the seven- and eight-membered rings. In addition, attempts to prepare 1-nitro-2-amino-4-ethyl-Δ^2-1,3-diazocyclopentene nitrate by cyclizing 1-(α-nitroxy-β-butyl)-3-nitroguanidine were unsuccessful.

Experimental[5]

1-(ω-Hydroxypropyl)-3-guanidinium Nitrate.—Seventy-five grams (1.0 mole) of 3-amino-1-propanol (obtained from American Cyanamid; b.p. 85° (10 mm.)) was added, slowly with stirring, to 139.2 g. (0.5 mole) of 2-methyl-2-thiopseudouronium sulfate in a 1-liter beaker. Thirty cc. of water was then added to the mixture. Considerable foaming and evolution of methyl mercaptan occurred immediately. The reaction mixture was allowed to stand overnight at room temperature. The product, a clear, viscous oil, was treated with an equivalent weight of hot aqueous barium nitrate solution. The barium sulfate precipitate was removed by filtration, and the filtrate evaporated yielding 108 g. (60.0% yield) of crude product which melted at 85–88°. One crystallization from 95% ethanol raised the m.p. to 91–92°.

Anal. Calcd. for $C_4H_{12}N_4O_4$: C, 26.6; H, 6.7; N, 31.1. Found: C, 26.7; H, 6.9; N, 31.0.

The picrate salt, crystallized from ethanol, melted at 127–128°.

Anal. Calcd. for $C_{10}H_{14}N_6O_8$: C, 34.9; H, 4.1; N, 24.4. Found: C, 34.8; H, 4.3; N, 24.3.

1-(ω-Hydroxypropyl)-3-nitroguanidine.—1-(ω-Hydroxypropyl)-3-nitroguanidine was prepared in 90% yield by the procedure of Fishbein and Gallaghan[6] utilizing 2-methyl-1(or 3)nitro-2-thiopseudourea and 3-amino-1-propanol. The crude m.p. of 123–126° was raised to 128–129° by one crystallization from 95% ethanol.

Anal. Calcd. for $C_4H_{10}N_4O_3$: C, 29.6; H, 6.2; N, 34.6. Found: C, 29.4; H, 6.1; N, 34.3.

1-(ω-Nitroxypropyl)-3-nitroguanidine. 1. From 1-(ω-Hydroxypropyl)-3-guanidinium Nitrate.—Forty-three grams (0.23 mole) of 1-(ω-hydroxypropyl)-3-guanidinium nitrate was added portionwise to a nitrating mixture composed of 88.0 g. of 95% sulfuric acid and 30 g. of 98% nitric acid. The nitration was performed at 0–5°. After stirring for five minutes the mass was poured into 500 g. of ice; the contents were stirred for an additional five minutes and filtered. Forty-four grams (93.1% yield) of white crystals was obtained, which on crystallization from 95% ethanol (350 cc.) gave 33 g. of crystals melting at 121–122°.

Anal. Calcd. for $C_4H_9N_5O_5$: C, 23.2; H, 4.3; N, 33.8. Found: C, 23.0; H, 4.5; N, 33.8.

2. From 1-(ω-Hydroxypropyl)-3-nitroguanidine.—1-(ω-Hydroxypropyl)-3-nitroguanidine was nitrated according to the procedure of McKay and Milks.[2a] An 85% yield of product was obtained melting at 121–122°. A mixed m.p. with an authentic sample was not depressed.

1-Nitro-2-amino-Δ^2-1,3-diazacyclohexene Nitrate.—Ten grams (0.05 mole) of 1-(ω-nitroxypropyl)-3-nitroguanidine was dissolved in 25 cc. of boiling *n*-butanol. After five minutes of refluxing, a crystalline precipitate formed. The

(1) Publication approved by the Bureau of Ordnance, Navy Department.

(2) (a) A. F. McKay and J. E. Milks, THIS JOURNAL, **72**, 1616 (1950); (b) A. F. McKay, *Chem. Revs.*, **51**, 340 (1952); (c) R. H. Hall, A. F. McKay and G. F Wright, THIS JOURNAL, **73**, 2205 (1951); (d) A. F. McKay, *J. Org. Chem.*, **16**, 1395 (1951); (e) A. F. McKay and R. O. Brawn, *ibid.*, **16**, 1829 (1951).

(3) A. F. McKay and H. P. Thomas, *Can. J. Chem.*, **29**, 391 (1951).

(4) A. F. McKay and G. F Wright, THIS JOURNAL, **70**, 430 (1948).

(5) All melting points are uncorrected.

(6) L. Fishbein and J. A. Gallaghan, THIS JOURNAL, **76**, 1877 (1954).

crystals, removed by filtration, were crystallized from 95% ethanol yielding 7 g. of cyclic product melting at 172–173°.

Anal. Calcd. for $C_4H_9N_5O_5$: C, 23.1; H, 4.4; N, 33.8. Found: C, 23.0; H, 4.5; N, 33.8.

1-Nitro-2-amino-Δ^2-1,3-diazacyclohexene nitrate (0.35 g., 0.001 mole) was dissolved in 5 cc. of water and treated with a saturated picric acid solution. A crystalline picrate (m.p. 205–207°) separated immediately. One crystallization from 95% ethanol raised the m.p. to 207–208° dec.

Anal. Calcd. for $C_{10}H_{11}N_7O_9$: C, 32.2; H, 3.0; N, 26.3. Found: C, 32.4; H, 3.1; N, 25.9.

1-Nitro-2-amino-Δ^2-1,3-diazacyclohexene.—Two cc. of concentrated ammonium hydroxide was added to a solution of 0.5 g. (0.003 mole) of 1-nitro-2-amino-Δ^2-1,3-diazacyclohexene nitrate in 4 cc. of water. A white crystalline product separated immediately. This product was removed by filtration and washed with 5 cc. of cold water. A yield of 0.25 g. (68%) was obtained. The m.p. of 81–82° was raised to 83–84° after one crystallization from ethanol.

Anal. Calcd. for $C_4H_8N_4O_2$: C, 33.3; H, 5.5; N, 38.8. Found: C, 32.9; H, 5.3; N, 38.4.

1,3-Dinitraminopropane from 1-(ω-Nitroxypropyl)-3-nitroguanidine.—Two grams (0.01 mole) of 1-(ω-nitroxypropyl)-3-nitroguanidine was added portionwise at 10° to a nitrating mix consisting of 3 cc. of 95% sulfuric acid and 1.5 cc. of 98% nitric acid. The contents were kept at 0° overnight, allowed to warm slowly to 40°, and then added to 10 g. of ice. The product, 1.0 g. (77% yield) melted at 64–66°. One crystallization from ethanol raised the m.p. to 66–67°.[7] It was identified by a mixed melting point of an authentic sample obtained by the hydrolysis of 1,3-dinitro-1,3-diazacyclohexanone-2.

1,3-Dinitro-1,3-diazacyclohexanone-2 from 1-Nitro-2-amino-Δ^2-1,3-diazacyclohexene Nitrate.—1-Nitro-2-amino-Δ^2-1,3-diazacyclohexene nitrate was converted to 1,3-dinitro-1,3-diazacyclohexanone-2 in 75% yield by the procedure of McKay and Wright.[8] The product melted at 121–122°. It was identified by a mixed m.p. determination and hydrolysis to 1,3-dinitraminopropane (m.p. 66–67°).

1-(ω-Nitroxypropyl)-1-nitroso-3-nitroguanidine.—1-(ω-Nitroxypropyl)-3-nitroguanidine was nitrosated according to the procedure of McKay and Milks.[2a] A 60% yield of product was obtained, melting at 113–116°. One crystallization from 95% ethanol gave a crystalline product melting at 116–118°.

Anal. Calcd. for $C_4H_8N_6O_6$: C, 20.3; H, 3.4; N, 35.6. Found: C, 20.2; H, 3.6; N, 35.0

1-(ω-Nitroxypropyl)-1,3-dinitroguanidine.—1-(ω-Nitroxypropyl)-1,3-dinitroguanidine was prepared in 31.7% yield from 1-(ω-nitroxypropyl)-3-nitroguanidine by the procedure of McKay and Milks.[2a] The m.p. of 60–63° was raised to 64–66° by one crystallization from methanol.

Anal. Calcd. for $C_4H_8N_6O_7$: C, 19.0; H, 3.2; N, 33.3. Found: C, 18.8; H, 3.0; N, 33.2.

1-(ω-Hydroxybutyl)-3-guanidinium Sulfate.—Four grams (0.05 mole) of 4-amino-1-butanol (prepared by the procedure of Tietze[9]) was added to 5.6 g. (0.02 mole) of 2-methyl-2-thiopseudouronium sulfate suspended in 10 cc. of water. The contents were allowed to stand at room temperature for three hours. The resultant clear solution was evaporated almost to dryness; 100 cc. of absolute ethanol was then added. The crystalline product which separated was removed by filtration and washed with 20 cc. of absolute ethanol. A 46.3% yield (3.3 g.) of 1-(ω-hydroxybutyl)-3-guanidinium sulfate melting at 164–166° was obtained. Two crystallizations from 95% ethanol raised the m.p. to 168–169°.

Anal. Calcd. for $C_{10}H_{28}N_6O_6S$: C, 33.3; H, 7.8; N, 23.4. Found: C, 33.5; H, 7.8; N, 23.5.

1-(ω-Hydroxybutyl)-3-guanidinium nitrate was obtained in an analogous manner described for the preparation of 1-(ω-hydroxypropyl)-3-guanidinium nitrate. A 92% yield of product melting at 115–116° was obtained. One crystallization from 95% ethanol raised the m.p. to 116–117°.

Anal. Calcd. for $C_5H_{14}N_4O_4$: C, 30.9; H, 7.2; N, 28.3. Found: C, 30.5; H, 7.0; N, 28.5.

The picrate salt, crystallized from ethanol, melted at 153–155°.

Anal. Calcd. for $C_{11}H_{16}N_6O_8$: C, 36.6; H, 4.5; N, 23.3. Found: C, 36.4; H, 4.3; N, 22.8.

1-(ω-Nitroxybutyl)-3-nitroguanidine.—1-(ω-Nitroxybutyl)-3-nitroguanidine was prepared in 70% yield by an analogous procedure for the preparation of 1-(ω-nitroxypropyl)-3-nitroguanidine. The m.p. 103.5–105.5° was raised to 105–106° by two crystallizations from ethanol.

Anal. Calcd. for $C_5H_{11}N_5O_5$: C, 27.1; H, 5.0; N, 31.7. Found: C, 27.1; H, 5.0; N, 31.5.

1-(ω-Nitroxybutyl)-3-nitroguanidine (1.0 g., 0.004 mole) was refluxed with 8 cc. of *n*-butanol for one hour. After removal of the solvent, 0.9 g. of the original compound was recovered unchanged. No cyclic product could be obtained when the reflux period was extended to four hours. A mixed m.p. of the recovered substance with an authentic sample was not depressed.

1-(ω-Nitroxybutyl)-1,3-dinitroguanidine was prepared in 34.8% yield according to the procedure of McKay and Milks.[2a] The compound, crystallized from ethanol, melted at 92–93°.

Anal. Calcd. for $C_5H_{10}N_6O_7$: C, 22.5; H, 3.7; N, 31.6. Found: C, 22.4; H, 3.6; N, 31.5.

1-(ω-Nitroxybutyl)-1-nitroso-3-nitroguanidine was prepared in 50% yield according to the procedure of McKay and Milks.[2a] The yellow crystalline product, crystallized from ethanol, melted at 99–101°.

Anal. Calcd. for $C_5H_{10}N_6O_6$: C, 24.0; H, 4.0; N, 33.6. Found: C, 23.9; H, 3.9; N, 33.2.

1-(α-Hydroxy-β-butyl)-3-guanidinium Sulfate.—2-Amino-1-butanol (Commercial Solvents; 17.8 g., 0.2 mole) was added to 27.8 g. (0.1 mole) of 2-methyl-2-thiopseudouronium sulfate in 20 cc. of water. The reaction was extremely sluggish in contrast to the preparation of 1-(ω-hydroxybutyl)-3-guanidinium sulfate. The contents was allowed to stand at room temperature for one week, after which the clear solution was evaporated almost to dryness. The addition of 200 cc. of absolute ethanol caused the crystalline 1-(α-hydroxy-β-butyl)-3-guanidinium sulfate (m.p. 173–176°, 40% yield) to separate. One crystallization from a 1:1 ether–ethanol mixture raised the m.p. to 175–177°. The compound contained one molecule of water of crystallization.

Anal. Calcd. for $C_{10}H_{30}O_7N_6S$: C, 31.7; H, 7.9; N, 22.2. Found: C, 31.3; H, 7.9; N, 22.1.

The picrate salt, crystallized from ethanol, melted at 153–155°.

Anal. Calcd. for $C_{11}H_{16}N_6O_8$: C, 36.6; H, 4.5; N, 23.3. Found: C, 36.4; H, 4.4; N, 23.0.

1-(α-Nitroxy-β-butyl)-3-nitroguanidine.—1-(α-Nitroxy-β-butyl)-3-nitroguanidine was obtained under conditions described for the preparation of 1-(ω-nitroxypropyl)-3-nitroguanidine. A 90% yield of product melting at 99–100° was obtained. One crystallization from 95% ethanol raised the m.p. to 100–102°.

Anal. Calcd. for $C_5H_{11}N_5O_5$: C, 27.1; H, 5.0; N, 31.7. Found: C, 27.2; H, 4.8; N, 31.7.

Attempts to cyclize 1-(α-nitroxy-β-butyl)-3-nitroguanidine to 1-nitro-2-amino-4-ethyl-Δ^2-1,3-diazacyclopentene-nitrate salt were unsuccessful. The compound was refluxed in *n*-butanol for periods ranging from one to five hours without change.

1-(β-Hydroxy-*t*-butyl)-3-guanidinium Sulfate.—2-Amino-2-methyl-1-propanol (Eastman Kodak; 8.9 g., 0.1 mole) was mixed together with 13.9 g. (0.05 mole) of 2-methyl-2-thiopseudouronium sulfate and 20 cc. of water. The contents was allowed to stand at room temperature for ten days. The clear solution was then evaporated almost to dryness; 200 cc. of absolute ethanol was added causing the immediate precipitation of a white crystalline compound (m.p. 182–185°). One crystallization from 95% ethanol raised the m.p. to 185–187°. The compound contained one molecule of water of crystallization.

Anal. Calcd. for $C_{10}H_{30}N_6O_7S$: C, 31.7; H, 7.9; N, 22.2. Found: C, 31.8; H, 7.7; N, 22.5.

(7) (a) A. P. N. Franchimont and E. A. Klobbie, *Rec. trav. chim.*, **7**, 349 (1888); (b) A. F. McKay and D. F. Manchester, THIS JOURNAL, **71**, 1973 (1949).

(8) A. F. McKay and G. F Wright, *ibid.*, **70**, 3990 (1948).

(9) E. Tietze, German Patent 730,237 (1943).

The picrate salt, crystallized from ethanol, melted at 195–196°.

Anal. Calcd. for $C_{11}H_{16}N_6O_8$: C, 36.6; H, 4.5; N, 23.3. Found: C, 36.2; H, 4.3; N, 23.1.

1-(β-Nitroxy-*t*-butyl)-3-nitroguanidine.—1-(β-Nitroxy-*t*-butyl)-3-nitroguanidine was prepared in 91% yield (m.p. 113–115°) by the method described for the preparation of 1-(ω-nitroxypropyl)-3-nitroguanidine. One crystallization from 95% ethanol yielded crystals melting at 112–114°, resolidifying and remelting at 175–177°.

Anal. Calcd. for $C_5H_{11}N_5O_5$: C, 27.1; H, 5.0; N, 31.7. Found: C, 27.3; H, 5.0; N, 32.1.

1-Nitro-2-amino-4-dimethyl-Δ²-1,3-diazacyclopentene Nitrate.—1-(β-Nitroxy-*t*-butyl)-3-nitroguanidine (0.3 g., 0.001 mole) was refluxed with 6 cc. of *n*-butanol for one-half hour. The solution was evaporated to 1 cc. and 10 cc. of absolute ethanol then added; the cyclic product, 0.2 g., separated out. The m.p. of 175–177° was raised to 179–181° by one crystallization from absolute ethanol.

Anal. Calcd. for $C_5H_{11}N_5O_5$: C, 27.1; H, 5.0; N, 31.7. Found: C, 27.3; H, 5.2; N, 32.0.

1-(ω-Hydroxyamyl)-3-guanidinium Nitrate.—1-(ω-Hydroxyamyl)-3-guanidinium nitrate was prepared in 50% yield (m.p. 108–110°) by the procedure described for the preparation of 1-(ω-hydroxypropyl)-3-guanidinium nitrate. One crystallization from 95% ethanol raised the m.p. to 110–111°.

Anal. Calcd. for $C_6H_{16}N_4O_4$: C, 34.7; H, 7.7; N, 27.0. Found: C, 34.7; H, 8.0; N, 26.6.

1-(ω-Nitroxyamyl)-3-nitroguanidine.—1-(ω-Nitroxyamyl)-3-nitroguanidine was prepared in 94.3% yield (m.p. 102–103°) by the procedure described for the preparation of 1-(ω-nitroxypropyl)-3-nitroguanidine. One crystallization from ethanol raised the m.p. to 103–104°.

Anal. Calcd. for $C_6H_{13}N_5O_5$: C, 30.7; H, 5.5; N, 29.8. Found: C, 30.7; H, 5.7; N, 30.3.

Attempts to cyclize 1-(ω-nitroxyamyl)-3-nitroguanidine to 1-nitro-2-amino-Δ²-1,3-diazacycloöctene by analogous conditions described for the cyclization of 1-(ω-nitroxypropyl)-3-nitroguanidine were unsuccessful. A mixed m.p. of the recovered product with an authentic sample was not depressed.

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The Reaction of Trimethyl-(*p*-bromophenyl)-silane with Lithium Dimethylamide

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The reaction of certain *o*- and *p*-halophenyl compounds with metal amides in liquid ammonia and with lithium dialkylamides in ether has been found to result in the formation of *m*-amino derivatives. For example, *o*-halophenyl methyl sulfides and *o*-bromophenyl methyl sulfone react with metal amides in liquid ammonia to yield the respective *m*-amino compounds,[1] and *m*-dialkylaminoanisoles are formed when *o*- and *p*-haloanisoles are treated with lithium dialkylamides in ether.[2a] Similarly, *o*-chlorotrifluoromethylbenzene reacts with sodium amide in liquid ammonia to give *m*-aminotrifluoromethylbenzene.[2b]

We now wish to report that when the amination reaction was extended to include organosilicon compounds, trimethyl-(*p*-bromophenyl)-silane was observed to react with lithium dimethylamide in ether and in a benzene–ether mixture to form the expected trimethyl-(*m*-dimethylaminophenyl)-silane and some trimethyl-(*p*-dimethylaminophenyl)-silane.

$$(CH_3)_3SiC_6H_4Br\text{-}p + LiN(CH_3)_2 \longrightarrow (CH_3)_3SiC_6H_4N(CH_3)_2\text{-}p + LiBr$$
$$(CH_3)_3SiC_6H_4N(CH_3)_2\text{-}m$$

In the initial experiments, the only product believed isolated was the unrearranged or *para* isomer. Identification of the structure of the amination product was made by comparing its picrate with that of authentic trimethyl-(*p*-dimethylaminophenyl)-silane[3] which was prepared from trimethylchlorosilane and *p*-dimethylaminophenyllithium.

$$(CH_3)_3SiCl + (CH_3)_2NC_6H_4Li\text{-}p \longrightarrow (CH_3)_3SiC_6H_4N(CH_3)_2\text{-}p + LiCl$$

Since there exists reasonable doubt as to the reliability of identification by the mixed melting points of picrates,[4] further work was carried out. The subsequent experiments showed that the rearranged or *meta* isomer was the predominant product. The structure of this material was confirmed by comparing its infrared spectrum with that of the product obtained from the reaction of *m*-dimethylaminophenyllithium and trimethylchlorosilane.

$$(CH_3)_3SiCl + (CH_3)_2NC_6H_4Li\text{-}m \longrightarrow (CH_3)_3SiC_6H_4N(CH_3)_2\text{-}m + LiCl$$

These results are in general agreement with the one noted earlier in which the reaction of triphenyl-(*p*-bromophenyl)-silane with lithium dimethylamide under corresponding conditions yielded largely triphenyl-(*m*-dimethylaminophenyl)-silane.[5] In each instance, some unreacted starting material was recovered. Furthermore, it is probable that the unresolved reaction mixture may have contained other products formed in what appears to be a complex reaction.

Experimental

Trimethyl-(*p*-bromophenyl)-silane.—In a typical preparation of this compound, 47.2 g. (0.20 mole) of *p*-dibromobenzene was dissolved in sufficient ether to ensure complete solution at −15° in a reaction flask submerged in a Dry Ice–acetone-bath. To this solution was added 0.194 mole of *n*-butyllithium[6] at the rate of 5 ml. per minute. Color Test II-A[7] became negative after 20 minutes. Then, 19.5 g. (0.18 mole) of trimethylchlorosilane in ether was added at such a rate that the temperature of the reaction mixture did not rise above −10°.[8] After all the trimethylchloro-

(1) H. Gilman and G. A. Martin, THIS JOURNAL, **74**, 5317 (1952).

(2) (a) See H. Gilman and R. H. Kyle, *ibid.*, **74**, 3027 (1952), for general references to rearrangement aminations by alkali amides in liquid ammonia, and by lithium dialkylamides in ether; (b) R. A. Benkeser and R. G. Severson, *ibid.*, **71**, 3838 (1949); (c) H. Gilman and S. Avakian, *ibid.*, **67**, 349 (1945). For two very recent references see: R. A. Benkeser and G. Schroll, *ibid.*, **75**, 3196 (1953), and J. D. Roberts, H. E. Simmons, Jr., L. A. Carlsmith and C. W. Vaughan, *ibid.*, **75**, 3290 (1953).

(3) H. Gilman and F. J. Marshall, *ibid.*, **71**, 2066 (1949).

(4) L. Ruzicka and L. Ehmann, *Helv. Chim. Acta*, **15**, 140 (1932).

(5) H. Gilman and H. W. Melvin, THIS JOURNAL, **72**, 995 (1950).

(6) *n*-Butyllithium was prepared by the directions of H. Gilman, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn and L. S. Miller, *ibid.*, **71**, 1499 (1949). The titer was determined by the double titration method of H. Gilman and A. H. Haubein, *ibid.*, **66**, 1515 (1944).

(7) H. Gilman and J. Swiss, *ibid.*, **62**, 1847 (1940).

(8) In the preparation of trimethyl-(*p*-bromophenyl)-silane, it was found that better yields are obtained if the halogen–metal interconversion reaction and the subsequent addition of trimethylchlorosilane are carried out at −15 to −10°. If these precautions are not observed, lower yields of the desired product result, and a high-boiling fraction also forms. See H. Gilman, W. Langham and F. W. Moore, *ibid.*, **62**, 2327 (1940), for the effects of temperature on side reactions in halogen–metal interconversion reactions.