

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 $C_8H_{11}N_5O_5$: 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- Δ^2 -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 $C_8H_{13}N_5O_5$: 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- Δ^2 -1,3-diazacyclooctene 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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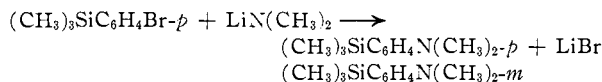
The Reaction of Trimethyl-(*p*-bromophenyl)-silane with Lithium Dimethylamide

BY HENRY GILMAN, H. W. MELVIN AND JACK J. GOODMAN
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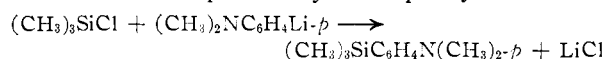
The reaction of certain *o*- and *p*-halophenyl compounds with metal amides in liquid ammonia and with lithium dialkylamides in ether has been found to result in the formation of *m*-amino derivatives. For example, *o*-halophenyl methyl sulfides and *o*-bromophenyl methyl sulfone react with metal amides 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}

(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).

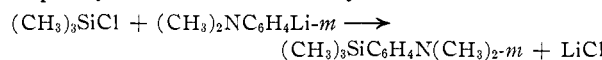
We now wish to report that when the amination reaction was extended to include organosilicon compounds, trimethyl-(*p*-bromophenyl)-silane was observed to react with lithium dimethylamide in ether and in a benzene-ether mixture to form the expected trimethyl-(*m*-dimethylaminophenyl)-silane and some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



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)-silane³ which was prepared from trimethylchlorosilane and *p*-dimethylaminophenyllithium.



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.



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*-butyllithium⁶ at the rate of 5 ml. per minute. Color Test II-A⁷ 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-

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

(4) L. Ruzicka and L. Ehmman, *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.

silane had been added, the low-temperature bath was removed and the suspension was stirred for 2.5 hours prior to being heated at the reflux temperature for one hour. The reaction mixture was worked up in the usual way and the product was distilled. The yield of trimethyl-(*p*-bromophenyl)-silane, distilling at 53–56° at 0.2 mm., was 32.6 g. (79%). The constants observed were n_D^{20} 1.5285, d_4^{20} 1.2206.

Anal. Calcd. for C_6H_9BrSi : Br, 34.9; Si, 12.2; MR_D , 57.63.⁹ Found: Br, 34.7; Si, 12.1; MR_D , 57.53.

In subsequent preparations, the yields were between 75 and 83%, the quantities of trimethylchlorosilane used being 0.12 to 0.40 mole. Burkhard,¹⁰ who prepared this compound from trimethylchlorosilane and *p*-bromophenylmagnesium bromide, lists the constants as n_D^{20} 1.5302, d_4^{20} 1.2197.

Trimethyl-(*p*-bromophenyl)-silane and Lithium Dimethylamide.—Ten grams (0.0436 mole) of trimethyl-(*p*-bromophenyl)-silane in ether was added to lithium dimethylamide (prepared in ether from 0.057 mole of *n*-butyllithium and dimethylamine).¹¹ The mixture was heated at its reflux temperature with stirring for 48 hours. After hydrolysis, the ether layer was extracted with five 10-ml. portions of hydrochloric acid. From the ether layer was obtained 2.0 g. (20% recovery) of trimethyl-(*p*-bromophenyl)-silane. The aqueous portion was made basic with 20% sodium hydroxide, and the yield of what was believed to be trimethyl-(*p*-dimethylaminophenyl)-silane, distilling at 73–76° at 1 mm., was 4.7 g. (56%), n_D^{20} 1.5211, d_4^{20} 0.9103. On the basis of the quantity of trimethyl-(*p*-bromophenyl)-silane reacting, the yield of the amine was 82.4%.

Anal. Calcd. for $C_{11}H_{19}NSi$: N, 7.25; Si, 14.51; MR_D , 64.80.⁹ Found: N, 7.22; Si, 14.35; MR_D , 64.45.

The picrate melted at 154–156° (recrystallized from ethanol).

In a second experiment, 16.0 g. (0.070 mole) of trimethyl-(*p*-bromophenyl)-silane in ether was added to an ether suspension of lithium dimethylamide (from 0.082 mole of *n*-butyllithium and dimethylamine).¹¹ Most of the ether was removed by distillation and replaced with 65 ml. of pure benzene. The suspension was then refluxed for 108 hours. The yield of the supposed trimethyl-(*p*-dimethylaminophenyl)-silane obtained was 8.3 g. (62.2%), and 3.0 g. (19%) of the starting silane was recovered. The melting point of the picrate of the amination product was 153–155° (after recrystallization from 95% ethanol). The melting point of a mixture of this picrate and that of the previous run was not depressed. When adjustment was made to include only the quantity of trimethyl-(*p*-bromophenyl)-silane reacting, the yield of amine was 90.2%, n_D^{20} 1.5280, d_4^{20} 0.9194. In another experiment, 45.8 g. (0.200 mole) of trimethyl-(*p*-bromophenyl)-silane in 150 ml. of anhydrous ether was added to lithium dimethylamide (prepared as above) at a rate to maintain gentle reflux. The gray color of the reaction mixture became orange on refluxing for 48 hours. After subsequent treatments as described above, there was recovered 1.5 g. (3.3%) of trimethyl-(*p*-bromophenyl)-silane. There was also obtained 9.6 g. (24.9% yield) of trimethyl-(*m*-dimethylaminophenyl)-silane distilling at 60–61° at 0.4 mm., n_D^{20} 1.5324, d_4^{20} 0.9500. On the basis of the quantity of the trimethyl-(*p*-bromophenyl)-silane reacting, the yield of the amine was 25.8%. A lower boiling fraction distilling at 34–36° at 0.55 mm., and weighing 4.5 g. gave a negative qualitative test for silicon.¹² A considerable quantity of a highly viscous residue could not be distilled under our conditions. In a check experiment, essentially the same results were obtained as in the experiment just described, and the yield of trimethyl-(*m*-dimethylaminophenyl)-silane was 25.3%.

Trimethyl-(*m*-dimethylaminophenyl)-silane.—To 0.442 g. (0.0636 g. atom) of lithium wire (cut into pieces of less than 1 cm. in length) in 25 ml. of anhydrous ether was added 5.80 g. (0.0289 mole) of *m*-bromodimethylaniline (kindly provided by S. D. Rosenberg and F. J. Marshall) in 20 ml. of anhy-

drous ether at a rate to maintain gentle reflux. After completion of addition, the solution was stirred for 2 hours at reflux temperature. The excess lithium was filtered off and there was added to the solution 3.12 g. (0.0289 mole) of trimethylchlorosilane in 35 ml. of anhydrous ether. A white precipitate formed during this addition. Hydrolysis of the reaction mixture was carried out after refluxing overnight. The ether layer was extracted several times with 20 ml. portions of 1:1 concd. HCl. The acid layer was separated, made basic with 20% KOH, and ether-extracted several times. This ether extract was dried over anhydrous Na_2SO_4 , the solvent distilled, and the remaining liquid vacuum distilled. There was obtained 2.6 g. (46.4% yield) of material distilling at 59–60° at 0.4 mm., n_D^{20} 1.5312, d_4^{20} 0.9484.

Anal. Calcd. for $C_{11}H_{19}NSi$: Si, 14.51; MR_D , 64.80.⁹ Found: Si, 14.41, 14.36; MR_D , 63.9.

Trimethyl-(*p*-dimethylaminophenyl)-silane.—This compound was prepared³ in 78.6% yield from 8.20 g. (0.075 mole) of trimethylchlorosilane and 0.079 mole of *p*-dimethylaminophenyllithium. The constants observed were n_D^{20} 1.5362, and d_4^{20} 0.9254. The constants previously reported were n_D^{20} 1.5338, d_4^{20} 0.9249.³ The picrate melted at 154–156°, and the melting point of a mixture of this picrate with that of each amination product from the first two experiments described was 154–155°.

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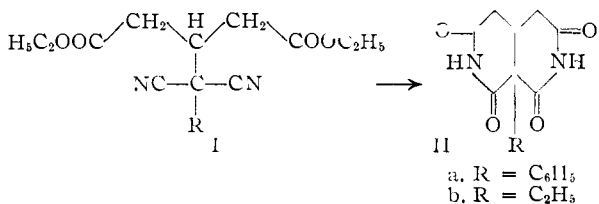
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A New Synthesis of 2,7-Naphthyridine Derivatives¹

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Gabriel and Colman² described the preparation of 1,4-dihydroxy-2,7-naphthyridine starting from pyridine-3,4-dicarboxylic acid (cinchomeronic acid). There exists, to our knowledge, no other report in the literature on the synthesis of this ring system. In continuation of our earlier studies on the intramolecular cyclization of ω -cyanocarboxylic acids³ we condensed monosubstituted malonitriles with ethyl β -bromoglutarate to give the diester I which, on treatment with sulfuric acid in glacial acetic acid, yielded the perhydro-2,7-naphthyridine derivatives II.



When ethyl was the substituent in position 9 (IIb) the oxo groups were eliminated by reduction with lithium aluminum hydride to give perhydro-9-ethyl-2,7-naphthyridine as the main product. A minor fraction consisted of a compound which still contained one oxygen function. Re-

(9) Molar refractions were calculated from the values of R. O. Sauer, *THIS JOURNAL*, **68**, 954 (1946); E. L. Warrick, *ibid.*, **68**, 2455 (1946).

(10) C. E. Burkhard, *ibid.*, **68**, 2103 (1946).

(11) H. Gilman, N. N. Crouse, S. P. Massie, R. A. Benkeser and S. M. Spatz, *ibid.*, **67**, 2106 (1945).

(12) H. Gilman, R. K. Ingham and R. D. Gorsich, *ibid.*, **76**, 918 (1954).

(1) Number 7 on Alkyleneimides. For No. 6 see E. Tagmann, R. Sury and K. Hoffmann, *Helv. Chim. Acta*, **37**, 185 (1954).

(2) S. Gabriel and J. Colman, *Ber.*, **35**, 1358 (1902).

(3) E. Tagmann, R. Sury and K. Hoffmann, *Helv. Chim. Acta*, **35**, 1235 (1952).