to be stable toward hydrolysis. Therefore, a typical representative of this group, N,N-diethylbenzamidine, was subjected to the action of an excess of lithium aluminum hydride, and its reduction was found to be analogous to that of N,N-diethylbenzamide, the former yielding benzylamine, the latter, benzyl alcohol.[2]

Experimental[4]

Benzylamine.—N,N-Diethylbenzamidine (13.5 g., 0.0767 mole) in 50 ml. of absolute ether reacted with lithium aluminum hydride (3.8 g., 0.1 mole) in 200 ml. of absolute ether in the usual way.[2] After the completion of the addition, reflux was continued on the steam-bath for 20 hours. Hydrolysis of the organometallic complex was carried out with 200 ml. of 5% sodium hydroxide. Rectification afforded 1.1 g. (15.4%) of benzylamine, b.p. 60° (7 mm.), and 9.8 g. (72.5%) of N,N-diethylbenzamidine, b.p. 114° (7 mm.).

Phenylthioureide.—The reaction of benzylamine with phenyl isothiocyanate[5] gave the phenylthioureide. The product was recrystallized from 95% ethanol to yield white crystals, m.p. 153–154°, as recorded in the literature.[6]

Anal. Calcd. for $C_{14}H_{14}N_2S$: N, 11.56. Found: N, 11.40.

Picrate.—When benzylamine was treated with picric acid in 95% ethanol, a yellow precipitate was obtained on standing overnight. Washing with 95% ethanol afforded a product of m.p.[7] 194–195°.

Anal. Calcd. for $C_{13}H_{12}N_4O_7$: N, 16.66. Found: N, 16.65.

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[4] All m.ps. and b.ps. are uncorrected.

[5] R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," 3rd edition, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 206.

[6] K. N. Campbell, B. K. Campbell and S. J. Patelski, *Proc. Ind. Acad. Sci.*, **53**, 119 (1943).

[7] R. Boudet, *Bull. soc. chim.*, [5] **15**, 390 (1948), reported 195–196°.

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Cleavage of Tetraphenylsilane and Benzyltriphenylsilane by Potassium Amide[1]

BY CHARLES R. HANCE AND CHARLES R. HAUSER

It was shown recently[2] that the benzyl-, diphenylmethyl- and triphenylmethyltrimethylsilanes are cleaved by potassium amide in liquid ammonia to form toluene, diphenylmethane and triphenylmethane, respectively. It has now been found that even tetraphenylsilane is cleaved readily by this base, benzene being isolated in 62% yield. The reaction may be represented by equation 1. As with other tetrasubstituted silanes,[2] the mechanism involves presumably the displacement of the hydrocarbon anion from silicon accompanied by the acquisition of a proton from the medium to form the hydrocarbon.

$$(C_6H_5)_3Si{-}C_6H_5 \xrightarrow[NH_3]{K^+NH_2^-} C_6H_6 + \text{silicate} \quad (1)$$

Similarly, benzyltriphenylsilane was cleaved by potassium amide in liquid ammonia, both benzene and toluene apparently being formed. This tetrasubstituted hydrocarbon silane was synthesized in 51% yield from triphenylchlorosilane and benzylmagnesium chloride.

Experimental

Triphenylchlorosilane (practical grade), obtained from Anderson Laboratories, Inc., was purified by distillation at 2 mm. followed by several recrystallizations from benzene and petroleum ether (b.p. 30–60°); the product then melted at 88–90°. Tetraphenylsilane, also obtained from Anderson Laboratories, was recrystallized once from benzene; the product then melted at 231–233°.

Benzyltriphenylsilane.—To a stirred solution of benzylmagnesium chloride (prepared from 0.31 mole of benzyl chloride and 0.29 mole of magnesium) in 500 ml. of anhydrous ether was added 29.4 g. (0.1 mole) of triphenylchlorosilane in 100 ml. of ether. The mixture was refluxed 13 hours and allowed to stand 40 hours. The ether was removed and the residue heated on the steam-bath 11 hours. After adding ether again, the mixture was decomposed with 200 ml. of 25% (by volume) hydrochloric acid. The ether phase was washed several times with water and 10% sodium bicarbonate, dried over anhydrous sodium sulfate, and the solvent removed. The residue was taken up in petroleum ether (b.p. 30–60°) and the solution washed successively with concentrated sulfuric acid, water and 10% sodium bicarbonate. After drying over sodium sulfate, the solution was concentrated to one-fourth its volume to precipitate 17.7 g. (51%) of benzyltriphenylsilane (m.p. 96–98°). Recrystallization from 95% ethanol gave the pure compound melting at 98–99.5°.

Anal.[3] Calcd. for $C_{25}H_{22}Si$: C, 85.68; H, 6.33. Found: C, 85.55; H, 6.40.

Cleavages by Potassium Amide.—Tetraphenylsilane (9.4 g., 0.028 mole) was stirred one hour with 0.0665 mole of potassium amide in 200 ml. of liquid ammonia. After neutralizing the muddy brown mixture with excess (10 g.) ammonium chloride, ether (100 ml.) was added and the ammonia allowed to evaporate. The mixture was filtered and the insoluble salts washed with ether. The filtrate and washings were fractionated through a 30-cm. glass helices-packed column to give 5.4 g. (62%) of benzene boiling at 78–80°, $n^{24}D$ 1.4890; *m*-dinitro derivative, m.p. and mixed m.p. 88–89°. The solid salts were treated with water leaving undissolved a granular material (1.9 g.) which appeared to be an inorganic silicate.

Similarly, benzyltriphenylsilane (3.90 g., 0.0111 mole) was stirred one hour with 0.048 mole of potassium amide in 200 ml. of liquid ammonia. The orange-red mixture was decomposed with ammonium chloride, the liquid ammonia replaced by ether and the mixture filtered. Fractionation of the filtrate gave 0.6 g. of material, b.p. 89–100°, having the characteristics of a mixture of benzene and toluene. None of the original silane was recovered. There was obtained from the solid a granular material (0.5 g.) which appeared to be an inorganic silicate.

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[1] This work was supported by a grant from the Duke University Research Council.

[2] C. R. Hauser and C. R. Hance, THIS JOURNAL, **73**, 5846 (1951).

[3] Analysis by Clark Microanalytical Laboratory, Urbana, Ill.

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The Synthesis of Doubly Labeled Parathion

BY R. E. HEIN AND R. H. MCFARLAND

As an aid in studying the mode of action and metabolism of O,O-diethyl O-*p*-nitrophenyl thiophosphate (parathion), the synthesis of a labeled compound was undertaken. The synthesis of parathion starting with either thiophosphoric trichloride[1] ($PSCl_3$) or phosphorus pentasulfide[2] (P_2S_5) has been described previously. Phosphorus trichloride may also be utilized as a starting material. The direct

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[1] J. H. Fletcher, J. C. Hamilton, I. Hechenbleikner, E. I. Hoegberg, B. J. Sertl and J. T. Cassaday, THIS JOURNAL, **72**, 2461 (1950).

[2] J. H. Fletcher, J. C. Hamilton, I. Hechenbleikner, E. I. Hoegberg, B. J. Sertl and J. T. Cassaday, *ibid.*, **70**, 3943 (1948).