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 $C_{18}H_{12}N_4O_7$: N, 16.66. Found: N, 16.65.

(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°.

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.

$$(C_6H_5)_3Si\!-\!C_6H_5 \xrightarrow[\text{NH}_3]{\text{K}^+\text{NH}_2^-} C_6H_6 + \text{silicate} \quad (1)$$
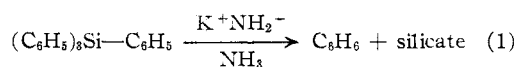
Similarly, benzyltriphenylsilane was cleaved by potassium amide in liquid ammonia, both benzene and toluene apparently being formed. This tetrasubstituted hydrocarbon silane was synthesized in

(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).

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.

(3) Analysis by Clark Microanalytical Laboratory, Urbana, Ill.
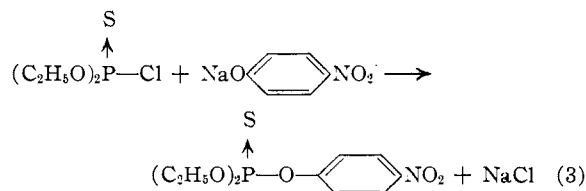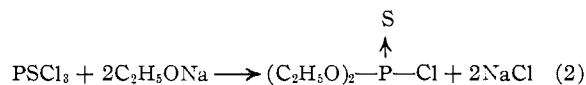
The Synthesis of Doubly Labeled Parathion

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

(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).

combination of sulfur and phosphorus trichloride in the presence of anhydrous aluminum chloride produces thiophosphoric trichloride[3] in 97% yield. The steps in the synthesis of parathion are

$$PCl_3 + S \xrightarrow{AlCl_3} PSCl_3 \quad (1)$$

$$PSCl_3 + 2C_2H_5ONa \longrightarrow (C_2H_5O)_2\overset{\text{S}}{\overset{\|}{P}}\text{—}Cl + 2NaCl \quad (2)$$

$$(C_2H_5O)_2\overset{\text{S}}{\overset{\|}{P}}\text{—}Cl + NaO\text{—}\langle\ \rangle\text{—}NO_2 \longrightarrow$$

$$(C_2H_5O)_2\overset{\text{S}}{\overset{\|}{P}}\text{—}O\text{—}\langle\ \rangle\text{—}NO_2 + NaCl \quad (3)$$

While the insecticide may be tagged with C^{14}, P^{32} or S^{35}, from the radiation detection standpoint, cost and waste disposal, it seemed advisable in this preliminary experimentation to label with P^{32}. Although not previously reported in the literature, if labeled phosphorus trichloride could be produced by neutron bombardment of phosphorus trichloride, the starting material could be obtained in this manner. Complicating factors in this procedure are the production of S^{35} by a (n,p) reaction on Cl^{35} isotopes in the phosphorus trichloride molecule and the subsequent recoil energies given to the molecule both by this reaction and the (n,γ) reaction producing P^{32}. As the recoil energies are sufficient to break the phosphorus–chlorine bonds, the production of labeled phosphorus trichloride depends on the recombination of fragments. Experimentally, one gram of phosphorus trichloride irradiated in the Oak Ridge reactor for three weeks did contain labeled phosphorus trichloride. Further, either the chemical form of S^{35} was such as to be incorporated in the thiophosphoric trichloride in step I or trace amounts of labeled thiophosphoric trichloride were synthesized by the recombination of fragments during bombardment. In any event, the insecticide was labeled with both P^{32} and S^{35}.

Since the preparation of labeled parathion was to be carried out on a semi-micro basis (1 g. PCl₃ starting weight), several syntheses were performed with inactive materials on this scale. When consistent, although low yields, for the individual steps and over-all process (25% based on starting weight of PCl₃) had been attained and the purity of the product established by the standard colorimetric method,[4] radioactive parathion was synthesized from the irradiated PCl₃. An over-all yield of 26% was obtained with a specific activity of 2 microcuries/mg. of parathion.

The chemical purity of the active parathion was established by the method of Averell and Norris[4] and found to be 94% parathion. The radiochemical purity of the insecticide was established by absorption of the emitted radiations in aluminum. Analysis of this information indicated that only P^{32} and S^{35} were present in the final product.

As a result of the covalent bonding of the phosphorus atom in parathion, it is unlikely that ex-

(3) F. Knotz, Osterr. Chem. Z., 50, 128 (1949).

(4) P. R. Averell and M. V. Norris, Anal. Chem., 20, 753 (1948).

change would take place between that atom and other phosphorus atoms. However, this possibility was tested by shaking mixtures of inactive parathion and P^{32}-labeled phosphate ion in the presence of various radiation sources for periods of several hours. No exchange took place. In similar tests with the radioactive parathion, no exchange of the labeled phosphorus or sulfur atoms with the substrate occurred.

Experimental

Thiophosphoric Trichloride.—Anhydrous aluminum chloride (0.1–0.2 g.) was added to 1 g. of phosphorus trichloride and 0.24 g. of powdered sulfur. On heating in a water-bath to the b.p. of phosphorus trichloride (74°) the reaction proceeded rapidly (30 sec.) particularly with 0.2 g. of aluminum chloride. After the solution was cooled, the aluminum chloride was extracted in 0.3 ml. of water and the thiophosphoric trichloride layer dried with calcium chloride. The thiophosphoric trichloride was then distilled (at 124–126°) into the second reaction vessel. The average yield for three runs with inactive materials for this step was 78%. The yield with active phosphorus trichloride was 61%.

O,O-Diethyl Chlorothiophosphate.—The method of synthesis for the trial runs and active compound was very similar to that described by Fletcher and colleagues.[1] Because of the semi-micro scale the organic layer was transferred by capillaries rather than filtering. The average yield on this step for two inactive runs was 42.5%. Because of better stirring techniques the yield with active thiophosphoric trichloride was 69%.

Parathion.—The general procedure for p-nitrophenyl thiophosphates as reported by Fletcher, et al.,[2] was followed in this step with the exception again that the transferring of the active compound was done by capillaries. The average yield for two inactive runs was 51% and for the active material a 69% yield was obtained.

Cholesteryl Laurate[1]

BY DAVID KRITCHEVSKY AND MARGARET E. ANDERSON

Several isomorphic modifications of cholesteryl laurate have been reported. Page and Rudy[2] prepared the ester, m.p. 91°, $[\alpha]D$ $-27.6°$, by heating cholesterol and lauric acid in a current of carbon dioxide; Jaeger[3] used the same method to obtain an ester m.p. 100°; Cataline and co-workers[4] heated the sterol and acid in benzene in the presence of benzene sulfonic acid to obtain this compound m.p. 92° and Abderhalden and Kautzsch[5] heated a chloroform solution of cholesterol and lauroyl chloride to obtain a product sintering at 78°, m.p. 110°; $[\alpha]D$ $-31.3°$. In our hands, heating a pyridine solution of the sterol and acid chloride[6] yielded an

(1) This work was sponsored by the U. S. Atomic Energy Commission.

(2) I. H. Page and H. Rudy, Biochem. Z., 220, 304 (1930).

(3) F. M. Jaeger, Rec. trav. chim., 25, 334 (1906), quoted by Page and Rudy.

(4) E. L. Cataline, L. Worrell, S. F. Jeffries and S. A. Aronson, J. Am. Pharm. Assoc., 33, 107 (1944).

(5) E. Abderhalden and K. Kautzsch, Z. physiol. Chem., 65, 69 (1910).

(6) D. Kritchevsky, THIS JOURNAL, 65, 480 (1943).