tene-1 and a mixture of two isomers in the ratio of 70/30 from pentene-2. The isomers are likely to be the 2-pentyl- and 3-pentyl-silanes.

EXPERIMENTAL

Addition of trichlorosilane to pentene-1. Burkhard and Krieble[3] added trichlorosilane to pentene-1 and reported the formation of *n*-pentyltrichlorosilane. *n*-Pentyltrichlorosilane has also been made from the *n*-pentylmagnesium bromide and tetrachlorosilane.[6] The reported properties were not sufficient to indicate with certainty that the pentyltrichlorosilane we obtained was *n*-pentyltrichlorosilane free of isomers. Therefore, the product obtained as described in the discussion was carefully distilled through a column 3 ft. long and 1 inch in diameter packed with $^1/_{16}$ inch "Helipak" packing. The product was *n*-pentyltrichlorosilane essentially free of isomers: b.p. 171.0° at 742 mm., n_D^{25} 1.4379, d_4^{25} 1.128; R_D 0.2327, Calc'd 0.2320.

Methylation with excess methylmagnesium bromide in ether gave an 80% yield of *n*-pentyltrimethylsilane: b.p. 139.3° at 743 mm., n_D^{25} 1.4069, d_4^{25} 0.7271; R_D 0.3385, Calc'd 0.3382.[7]

n-Pentyltrimethylsilane was prepared by adding a mixture of *n*-amyl chloride and trimethylchlorosilane to molten sodium in refluxing toluene, b.p. 138.9–139.1° at 740 mm., n_D^{25} 1.4069, d_4^{25} 0.7267; R_D 0.3387, Calc'd 0.3382.

The infrared absorption curves of the two samples were identical.

Addition of trichlorosilane to pentene-2. Under the same conditions pentene-2 yielded a pentyltrichlorosilane with properties quite easily distinguishable from those of *n*-pentyltrichlorosilane. From pentene-2 one might expect 2-pentyl- or 3-pentyl-trichlorosilane or a mixture of the two.

A gas-phase chromatographic analysis was performed on a 15 microliter sample on a six-foot Celite column impregnated with didecyl phthalate as the liquid substrate at 80°. Nitrogen was used as the carrier gas with an inlet pressure of 2 p.s.i. at a flow rate of 10 ml. per minute. Two peaks were obtained. The first had a retention time of 21.2 min. and amounted to 70% of the sample. The second at 23.1 min. contained about 30% of the sample. Because standard samples were not available it is impossible to ascertain the structures of the two components[8] at this time. The product had the properties: b.p. 165–167°, n_D^{25} 1.4455, d_4^{25} 1.145; R_D 0.2327, Calc'd 0.2320. An adduct prepared in this way has been reported[3] to boil at 164–168°.

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(6) F. C. Whitmore, *et al.*, *J. Am. Chem. Soc.*, **68**, 475 (1946).

(7) F. C. Whitmore, *et al.*[6] report b.p. 139° at 760 mm., n_D^{20} 1.4096, d_4^{20} 0.7313.

(8) This analysis was carried out in the Department of Research in Physical Chemistry at Mellon Institute.

Preparation of 6-Quinolyl- and 6-Quinolylmethyl-phosphonic Acids

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Received May 15, 1956

Although several phosphonic acids, in which the phosphono group is attached to a heterocyclic ring, have been prepared in recent years by various procedures, there is still a decided paucity of data about the phosphonic acids with the simple, more common nitrogen-bearing heterocyclic rings. In view of the fact that the classical Skraup reaction does not appear to have been applied to the readily available aminoarylphosphonic acids, it was felt that this application of the Skraup reaction should be examined. In order to avoid the separation of isomeric phosphonic acids the present synthesis was confined to amino derivatives which can give only one compound by the Skraup reaction.

EXPERIMENTAL

6-Quinolylphosphonic acid. *p*-Nitrophenylphosphonic acid was prepared according to Doak and Freedman[1] and was hydrogenated to *p*-aminophenylphosphonic acid over a palladium-charcoal catalyst in aqueous solution at room temperature and atmospheric pressure. The amino acid (3.0 g.), 13 ml. of 70% sulfuric acid, 4.0 g. of dry glycerol, and 3.5 g. of nitrobenzene were mechanically stirred and refluxed gently for 1.5 hours. The dark mixture was diluted with 20 ml. of water, steam-distilled, cooled, and filtered from tarry material. The filtrate was adjusted to the Congo Red end-point with 20% sodium hydroxide and the crude product which precipitated was collected. The precipitate was dissolved in 15% hydrochloric acid and re-precipitated by the addition of sodium hydroxide solution. It was finally dissolved in 10% sodium hydroxide solution and precipitated by the addition of 15% hydrochloric acid. At each step of the purification the solution was treated with charcoal. There was obtained 2.0 g. (56%) of 6-quinolylphosphonic acid, in the form of colorless, stubby flat needles which melted to a bright red liquid at 303–304°. Titration of the material with 0.1 *N* sodium hydroxide yielded a curve with inflections near *p*H 5 and 10.5, the latter inflection being the more clearly defined of the two.

Anal. Calc'd for $C_9H_8NO_3P$: P, 14.85; Equiv. wt. 209. Found: P, 14.7, 14.8; Equiv. wt. 210.

6-Quinolylmethylphosphonic acid. The procedure described above was followed, with 6.0 g. of *p*-aminobenzylphosphonic acid,[2] 26 ml. of 70% sulfuric acid, 8.0 g. of glycerol, and 7.0 g. of nitrobenzene. There was obtained, after three acid-base re-precipitations, 3.9 g. (54%) of 6-quinolylmethylphosphonic acid, in the form of light-tan colored, fine plates which decomposed to a red liquid at 328–329°.

Anal. Calc'd for $C_{10}H_{10}NO_3P$: P, 13.9; Equiv. wt., 223. Found: P, 13.8, 13.75; Equiv. wt., 219, 220 (inflection points on the titration curve occurred at approximately *p*H 5.8 and 11).

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(1) G. O. Doak and L. D. Freedman, *J. Am. Chem. Soc.*, **73**, 5658 (1951).

(2) G. M. Kosolapoff, *J. Am. Chem. Soc.*, **69**, 2112 (1947).

The Geminal Alkyl Effect on the Rates of Ring Closure of Bromobutylamines

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Received May 16, 1956

In view of the temporary interruption of an investigation[1] of the profound effect which geminal

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(1) R. F. Brown and N. van Gulick, *J. Am. Chem. Soc* **77**, 1079, 1083, 1089 (1955).