the mescaline had Rf 0.48, and gave a single well-rounded spot, the residual material gave both a mescaline spot and a faint tail suggestive of presence of another alkaloid. This was not identified.

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Isolation of Evolitrine from *Cusparia macrocarpa*

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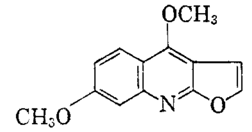
Received May 9, 1960

Cusparia macrocarpa is a rutaceous plant indigenous to Brazil where the leaves and stems are used in folk medicine. As part of an investigation of Brazilian flora, we have examined this plant for alkaloids.

The residue from an alcoholic extract of the leaves and stems[2] was distributed between an aqueous phase, at various *p*H's, and ether, essentially following the general scheme used with *Balfourodendron riedelianum*.[3] Further purification of the crude fractions was effected by chromatography on alumina.

Crystalline material resulted only from that fraction obtained by continuous extraction of the aqueous phase at *p*H 2. This very weakly basic compound had the composition $C_{13}H_{11}O_3N$. Its ultraviolet absorption (λ_{max} 246, 308, 319, 333 mμ) was practically identical with that reported for evolitrine[4] (I), and it formed a picrate with the same melting point as reported[4] for evolitrine picrate (201–202°). Direct comparison[5] by ultraviolet and infrared absorption, and mixed melting point clearly established the identity of this alkaloid as evolitrine.



A paper chromatographic examination of the various fractions showed the absence of any other alkaloidal material. However, evidence was obtained for the presence of a polar, non-extractable form of evolitrine which was converted to evolitrine by the action of alkali. This evidence was the fact that the ether extract of the *p*H 7 aqueous phase showed the complete absence of evolitrine, but when this extraction was continued at *p*H 10, evolitrine was found in the ether phase. Efforts to isolate this polar form by addition of chloride ion and extraction with butanol failed.

EXPERIMENTAL

The *isolation scheme* was the same as that used previously.[3] From 2.3 kg. of plant material (leaves and stems) were isolated ether extracts from the aqueous phase at *p*H 2, 4, 7, and 10. These fractions were chromatographed on alumina using benzene, benzene-chloroform, and chloroform for elution. Recombination on the basis of ultraviolet absorption and crystallization from benzene-hexane led to 600 mg. of evolitrine from the *p*H 2 extract. This material, after sublimation, melted at 113–114° (reported[4] m.p. 114–115°). It formed a picrate with alcoholic picric acid, m.p. 201–202° (reported[4] 201–202°).

Paper chromatography of the various fractions and subfractions was carried out by the ascending method with 1-butanol-5% acetic acid as solvent and Dragendorff's reagent for detection.

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[2] We are indebted to Dr. Glenn E. Ullyot of Smith Kline and French Laboratories, Philadelphia, and Dr. Oscar Ribeiro of Instituto de Quimica Agricola, Rio de Janeiro, for their assistance in procuring this material.

[3] H. Rapoport and K. G. Holden, *J. Am. Chem. Soc.*, **81**, 3738 (1959).

[4] R. G. Cooke and H. F. Haynes, *Austral. J. Chem.*, **7**, 273 (1954); **11**, 225 (1958).

[5] We are grateful to Dr. R. G. Cooke, University of Melbourne, for this sample.

Some Reactions of Triphenylethoxysilane

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Received March 7, 1960

In connection with studies on the comparison of organosilicon compounds with their carbon analogs,[1] some reactions of triphenylethoxysilane have been examined.

Alkoxytriphenylsilanes resemble alkoxytriphenylmethanes in one respect; they react with potassium metal to give triphenylsilylpotassium[2] and triphenylmethylpotassium,[3] respectively. However, the reaction of triphenylethoxysilane with sodium does not give the silylsodium compound or hexaphenyldisilane. Under similar conditions, triphenylchlorosilane reacts with sodium to give high yields of hexaphenyldisilane.[4]

When triphenylmethyl ethyl ether is treated with phenyllithium or with *n*-butyllithium, 9-phenylfluorene is formed on hydrolysis.[5] How-

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[1] H. Gilman and G. E. Dunn, *Chem. Revs.*, **52**, 77 (1953).

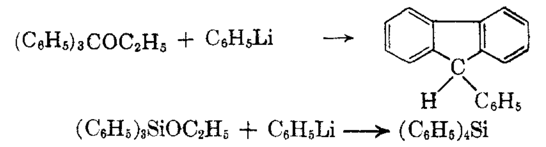
[2] H. Gilman and T. C. Wu, *J. Am. Chem. Soc.*, **73**, 4031 (1951).

[3] K. Ziegler and B. Schnell, *Ann.*, **437**, 227 (1924).

[4] H. Gilman and G. E. Dunn, *J. Am. Chem. Soc.*, **73**, 5077 (1951).

[5] H. Gilman, W. J. Meikle, and J. W. Morton, Jr., *J. Am. Chem. Soc.*, **74**, 6282 (1952).

ever, only tetraphenylsilane has been isolated when triphenylethoxysilane is allowed to react with



$$(C_6H_5)_3SiOC_2H_5 + C_6H_5Li \longrightarrow (C_6H_5)_4Si$$

either phenyllithium or with phenylmagnesium bromide. Similarly, treatment of triphenylethoxysilane with triphenylsilylpotassium gives hexadisilane. Thus, it should be noted, that triphenylethoxysilane resembles the triphenylhalosilanes in many reactions, although there are also significant differences.

EXPERIMENTAL[6]

Triphenylethoxysilane. Polis obtained triphenylethoxysilane by dissolving triphenylchlorosilane in absolute ethanol but did not report the yield.[7] In this laboratory, triphenylethoxysilane has been prepared by the reaction of ethyl orthosilicate with phenyllithium,[8] by the reaction of triphenylsilane with ethanol in the presence of piperidine,[9] and by the reaction of triphenylchlorosilane with sodium ethoxide. Following is the procedure used for the last reaction.

Triphenylchlorosilane, 29.5 g. (0.1 mole), was added in portions to an ethanolic solution of sodium ethoxide prepared by treating 2.3 g. (0.1 g.-atom) of sodium with 100 ml. of absolute ethanol. The reaction mixture was refluxed for 14 hr. and filtered rapidly while it was still hot. The filtrate was cooled in a refrigerator and the crystals thus formed were separated by filtration. There was obtained 18.6 g. (62%) of triphenylethoxysilane (identified by mixed melting point) melting at 65–67°. One recrystallization from petroleum ether (b.p. 60–70°) raised the melting point to 67–68°.

The insoluble solids from the original reaction mixture (7.3 g.) were treated with water to extract the sodium chloride formed, leaving 2.9 g. of bright, colorless crystals of hexaphenyldisiloxane (identified by mixed melting point) melting at 227–229°. In addition, another 2.5 g. of the same compound was recovered from the mother liquor from which the 18.6 g. of triphenylethoxysilane had been separated. The total yield of hexaphenyldisiloxane was 5.4 g. (0.01 mole, 20% yield based on the triphenylchlorosilane used).

Reaction of triphenylethoxysilane with phenyllithium. An ethereal solution containing 0.07 mole of freshly prepared phenyllithium was added to 10.5 g. (0.035 mole) of triphenylethoxysilane dissolved in 50 ml. of ether. Some heat was evolved and a large amount of white precipitate was formed. The ether was removed by distillation and 100 ml. of dry toluene was added to the pasty residue. The resulting toluene suspension was refluxed for 24 hr. The deep brown suspension at this stage gave a positive Color Test I.[10] Water was added to the reaction mixture after it had been cooled to room temperature. There was obtained 10.2 g. of white solid residue melting at 233–235°. A mixed melting point determination with an authentic specimen of tetraphenylsilane showed no depression. Distillation of the toluene solution yielded a solid residue. This was recrystallized twice from benzene to give an additional 1.2 g. of tetraphenylsilane (identified by mixed melting point) melting at 233–235°. The combined yield of pure product was 11.4 g. (97%).

Reaction of triphenylethoxysilane with phenylmagnesium bromide. To 0.04 mole of phenylmagnesium bromide was added, over a period of 2 min., 6.1 g. (0.02 mole) of triphenylethoxysilane dissolved in ether. Very little heat was evolved during the addition. The solvent was then removed by distillation, and the residue was refluxed in 100 ml. of dry toluene for 24 hr. Color Test I of the turbid white mixture was strongly positive. The reaction mixture was cooled and hydrolyzed with dilute hydrochloric acid. There was obtained by filtration 4.9 g. of colorless needles melting at 231–233°. The melting point was not depressed by admixture with tetraphenylsilane. The residue obtained by the evaporation of the toluene solution was recrystallized twice from benzene to give 0.6 g. of pure tetraphenylsilane. The total yield of tetraphenylsilane was 5.5 g. (82%).

Reaction of triphenylethoxysilane with triphenylsilylpotassium. A triphenylsilylpotassium suspension was prepared by cleaving 0.01 mole of hexaphenyldisilane with sodium-potassium alloy in accordance with a described procedure.[11] The excess alloy was removed from the triphenylsilylpotassium suspension by the amalgamation method.[11] A solution containing 6.1 g. (0.02 mole) of triphenylethoxysilane in 50 ml. of ether was added rapidly to the triphenylsilylpotassium suspension. There was no apparent change during the period of addition. Upon stirring at room temperature the reaction mixture gradually became dark brown. After 48 hr. of stirring the reaction mixture still gave a positive Color Test I. Water was added to effect hydrolysis, and the mixture was stirred and filtered to separate 7.4 g. (71%) of white solid melting at 368°. A mixed melting point determination with hexaphenyldisilane showed no depression. From the ethereal solution there was obtained 2.7 g. of colorless crystals melting at 130–145°. Two recrystallizations from petroleum ether (b.p. 60–70°) yielded 2.1 g. of triphenylsilanol (identified by mixed melting point) melting at 150–151°. The yield was 19% calculated on the basis of total silicon content, *i.e.*, assuming both triphenylsilylpotassium and triphenylethoxysilane would give triphenylsilanol on hydrolysis.

Reaction of triphenylethoxysilane with sodium. A mixture of 6.1 g. (0.02 mole) of triphenylethoxysilane, 0.5 g. of sodium, and 25 ml. of xylene was stirred at the refluxing temperature for 72 hr. There was very little change in the reaction mixture except for a small amount of cloudy precipitate formed gradually upon prolonged refluxing. The unused sodium was first amalgamated and then destroyed by adding water dropwise. The hydrolyzed mixture was filtered to remove 0.12 g. of light gray powder. This was recrystallized from a small amount of benzene-ethanol to give 70 mg. of colorless needles melting at 232–234°. A mixed melting point determination with an authentic specimen of tetraphenylsilane showed no depression. The xylene solution was distilled to give 5.5 g. of gummy residue, from which only triphenylsilanol and some impure triphenylethoxysilane were obtained. There was no hexaphenyldisilane formed in this reaction.

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(6) All melting points are uncorrected.

(7) A. Polis, *Ber.*, **19**, 1012 (1886).

(8) H. Gilman and L. S. Miller, *J. Am. Chem. Soc.*, **73**, 968 (1951).

(9) H. Gilman, G. E. Dunn, H. A. Hartzfeld, and A. G. Smith, *J. Am. Chem. Soc.*, **77**, 1287 (1955).

(10) H. Gilman and F. Schulze, *J. Am. Chem. Soc.*, **47**, 2002 (1925).

(11) H. Gilman and T. C. Wu, *J. Org. Chem.*, **18**, 753 (1953).