

technique and a standardized solution of methylsulfinyl carbanion.

Experimental

Methylenetriphenylphosphorane. General Procedure.—Sodium hydride (0.10 mole as a 55% dispersion in mineral oil) in a 300-ml. three-necked flask was washed with several portions of *n*-pentane to remove the mineral oil. The flask then was equipped with rubber stopples, a reflux condenser fitted with a three-way stopcock, and a magnetic stirrer. The system was alternately evacuated and filled with nitrogen; 50 ml. of dimethyl sulfoxide was introduced *via* syringe, and the mixture was heated at 75–80° for *ca.* 45 min., or until the evolution of hydrogen ceased. The resulting solution of methylsulfinyl carbanion² was cooled in an ice–water bath, and 35.7 g. (0.10 mole) of methyltriphenylphosphonium bromide³ in 100 ml. of warm dimethyl sulfoxide was added. The resulting dark red solution of the ylide was stirred at room temperature for 10 min. before use.

Methylenecyclohexane.—Freshly distilled cyclohexanone, 10.8 g. (0.11 mole), was added to 0.10 mole of methylenetriphenylphosphorane, and the reaction mixture was stirred at room temperature for 30 min. followed immediately by distillation under reduced pressure to give 8.10 g. (86.3%) of methylenecyclohexane, b.p. 42° (105 mm.) which was collected in a Dry Ice trap. [lit.,³ b.p. 99–101° (740 mm.).]

Methoxymethylenecyclohexane.—To a solution of 0.02 mole of methoxymethylenetriphenylphosphorane was added 1.96 g. (0.02 mole) of cyclohexanone, and the mixture was stirred for 1 hr. at room temperature. The resulting mixture was then distilled under reduced pressure; the fraction of b.p. 70–80° (30–35 mm.) was collected in a flask cooled at –20°, washed with aqueous potassium carbonate, extracted with *n*-pentane, and dried over anhydrous magnesium sulfate. Removal of the pentane and distillation of the residual oil gave 1.70 g. (67.6%) of methoxymethylenecyclohexane, b.p. 70–71° (37 mm.).⁴

The infrared spectrum showed bands at 5.90 and 11.10 μ .

2-Methylenebornane.—(+)-Camphor, 6.08 g. (0.04 mole), in 20 ml. of dimethyl sulfoxide was added to a solution of 0.05 mole of methylenetriphenylphosphorane, and the reaction mixture heated at 50° for 1 hr., at which time 5 ml. of *n*-pentane was introduced to wash down any sublimed camphor. Heating was continued for 16 hr. at a bath temperature of 56°; the solution was cooled and poured into 40 ml. of water. The aqueous phase (containing some precipitated triphenylphosphine oxide) was extracted three times with 100-, 75-, and 50-ml. portions of *n*-pentane, respectively. The triphenylphosphine oxide and dimethyl sulfoxide layer were further extracted with two 75-ml. portions of pentane. The pentane fractions were combined and washed with 100 ml. of a 1:1 water–dimethyl sulfoxide solution, and then with 200 ml. of a 50% saturated sodium chloride solution. The pentane layer was dried over anhydrous magnesium sulfate and passed through 25 g. of neutral alumina (activity 1). The alumina was eluted with pentane until a negative tetranitromethane test was obtained. All eluents were combined, and the pentane was distilled using a Vigreux column. The residual oil was sublimed to give 4.40 g. (73.4%) of 2-methylenebornane,⁵ m.p. 68–70°. The infrared spectrum was in agreement with expectations and with that given by Zeiss and Zwanzig⁵; the n.m.r. spectrum showed three sharp methyl peaks at 0.75, 0.90, and 0.92 p.p.m. downfield from tetramethylsilane, multiplets due to seven protons at 1.0 to 2.5 p.p.m. and two olefinic protons as a multiplet with center at *ca.* 4.6 p.p.m. downfield from tetramethylsilane.

3-Methylenecholestane.—A solution of 3-cholestanone, 0.357 g. (1.0 mmole), in 5 ml. of tetrahydrofuran (distilled from calcium hydride) was added to a solution of 1.5 mmoles of methylenetriphenylphosphorane, followed immediately by the addition of 20 ml. more of tetrahydrofuran to redissolve any precipitated cholestanone. The reaction mixture then was stirred at a bath temperature of 50° for 22 hr., poured into 150 ml. of water, and the aqueous solution was extracted with 75-, 50-, and 25-ml. portions of *n*-pentane. The pentane extracts were washed with 100 ml. of water, dried over anhydrous magnesium sulfate, and

passed through 5.0 g. of neutral alumina (activity I). Elution with pentane and evaporation and recrystallization from methanol gave 0.266 g. (69%) of 3-methylenecholestane,⁶ m.p. 64–65°.

Methyl 4-(*p*-Anisyl)-4-pentenoate.—To a solution of 0.013 mole of methylenetriphenylphosphorane was added 2.22 g. (0.10 mole) of methyl 3-*p*-anisoylpropionate. After keeping at room temperature for 23 hr., the solution was poured into 250 ml. of water and the product was extracted with pentane. The greenish yellow pentane extracts were combined, washed with 100 ml. of a 1:1 water–dimethyl sulfoxide solution and then with 200 ml. of water, dried, and filtered through 5 g. of neutral alumina (activity 3). The product was eluted with 300 ml. of pentane, the colorless eluents combined, and the pentane removed on a steam bath. The semisolid remaining was crystallized from methanol–water at low temperatures. The yield of crude product was 1.77 g. (80.5%), m.p. 26–28°. The infrared spectrum was entirely free from the ketone absorption at 5.93 μ , and showed the characteristic methylene bands at 3.12 μ , 6.12 μ (both appeared as shoulders), and 11.12 μ . An analytical sample was prepared by evaporative distillation at 0.10 mm., bath temperature, *ca.* 135°.

Anal. Calcd. for C₁₃H₁₆O₂: C, 70.89; H, 7.32. Found: C, 70.70; H, 7.28.

Spiro(cyclopropane-1,9-fluorene).—To a solution of 0.04 mole of methylenetriphenylphosphorane was added 1.80 g. (0.01 mole) of 9-fluorenone in 20 ml. of dimethyl sulfoxide. The reaction mixture was stirred at a bath temperature of 55° for 3 days and the resulting deep greenish blue solution was poured into 100 ml. of water followed by extraction with 75-, 50-, and 25-ml. portions of *n*-pentane. The yellow pentane extracts were combined, and the total volume reduced to *ca.* one-fourth the original. An excess of a 30% hydrogen peroxide solution was added to the pentane and the heterogeneous mixture stirred for 3 hr. to ensure the oxidation of all triphenylphosphine present. The pentane layer was separated, washed with water, dried, and passed through 15 g. of neutral alumina (activity 1). Elution with pentane was continued until no further solid was obtained on evaporation of the eluent. Recrystallization from methanol gave 0.565 g. (29.4%) of spiro(cyclopropane-1,9-fluorene), m.p. 69–70° (lit.,⁷ m.p. 70–71°).

1,1-Diphenylpropen-1.—A solution of sodium methylsulfinyl carbanion was prepared under nitrogen from 0.03 mole of sodium hydride and 20 ml. of dimethyl sulfoxide. The solution was cooled in a cold water bath and stirred during the addition of 11.1 g. (0.03 mole) of ethyl triphenylphosphonium bromide in 60 ml. of dimethyl sulfoxide, whereupon the deep red color of the ethylidene phosphorane was produced. After stirring at room temperature for 15 min., 4.55 g. (0.025 mole) of benzophenone in 10 ml. of dimethyl sulfoxide was added and stirring continued for 3 hr. at room temperature and 1.5 hr. at 60°. The reaction mixture was cooled and poured into 200 ml. of cold water in a round-bottomed flask. The mixture of solid and liquid was shaken with five 100-ml. portions of pentane which were decanted, combined and washed once with water, dried over anhydrous sodium sulfate, evaporated to a volume of 50 ml., and filtered through 50 g. of Merck alumina, using 1 l. of pentane to elute the product. Evaporation of the pentane left 4.73 g. (97.5%) of the product as a white crystalline solid, m.p. 46–49°. Recrystallization from 95% ethanol gave colorless plates, m.p. 49° (lit.,⁸ m.p. 52°; 46–48°).

(6) F. Sondheimer and R. Mechoulam, *ibid.*, **79**, 5029 (1957).

(7) E. Mechoulam and F. Sondheimer, *ibid.*, **80**, 4386 (1958).

(8) L. Horner, H. Hoffmann, and H. G. Wippel, *Ber.*, **91**, 61 (1958).

Synthesis of Trichloromethylmercury Derivatives

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Two groups of Russian workers recently have reported that dichlorocarbene undergoes an insertion

(4) S. G. Levine, *J. Am. Chem. Soc.*, **80**, 6150 (1958), reports isolation, in 40% yield, of the 2,4-dinitrophenylhydrazones of cyclohexane carboxaldehyde from this reaction.

(5) H. H. Zeiss and F. R. Zwanzig, *ibid.*, **79**, 1733 (1957), report the preparation of 2-methylenebornane, m.p. 62.5–64°, by a different route.