establishment of phenyl-nitrogen, -oxygen and -sulfur bonds. In an extension of studies involving amines as nucleophiles, Wittig and Benz[3] have shown that triarylphosphines react with benzyne; thus, phenyl biphenylene phosphine can be isolated in low yield from the reaction of benzyne with triphenyl phosphine. We now report the phenylation of the organophosphorous nucleophiles, sodium dialkylphosphonates, and trialkyl phosphites, via a benzyne intermediate; the reaction leads to the formation of phenyl phosphonates and constitutes a new synthetic method for this class of compounds.

Sodium diethylphosphonate (0.05 mole) and *o*-fluorobromobenzene (0.05 mole) were treated with magnesium (0.062 mole) in anhydrous tetrahydrofuran. After the spontaneous reaction had ceased, the mixture was refluxed for 1 hr. and hydrolyzed by established procedures.[3,4] The organic residue was distilled to yield diethyl phenylphosphonate (I) (41%), b.p. 103–104° (0.5 mm.) [lit.[5] b.p. 104–105° (0.5 mm.)]. The infrared spectrum of the product was identical in all respects with that of an authentic sample. Triphenylene (*ca.* 5%), a normal byproduct of benzyne reactions,[4] was isolated from a lower boiling fraction. In a similar experiment, sodium dimethylphosphonate was phenylated to yield dimethyl phosphonate (II) (37%), b.p. 103–104° (4 mm.), 243–245° (760 mm.), (lit.[6] b.p. 247°).

Triethyl phosphite (0.30 mole), *o*-fluorobromobenzene (0.06 mole) and magnesium (0.06 mole) in anhydrous tetrahydrofuran reacted vigorously with the evolution of a gaseous product which was identified as uncontaminated ethyl bromide by its infrared spectrum. From the reaction mixture, the sole isolable product was I (21%); variation in reactant ratios gave no appreciable increase in yield.[7] When triethyl phosphite was employed as solvent, initiation of the reaction was difficult and a lower yield of I was obtained.[8] The ester (I) was identified by a comparison of its infrared spectrum with that of an authentic sample and, in one experiment, by acidic hydrolysis to the known acid, phenylphosphonic acid. Trimethyl phosphite was similarly phenylated to form II in low yield. Benzyne phenylation is not restricted to phosphites but may be extended to other trivalent esters, *e.g.* ethyl diphenylphosphinite was phenylated to yield triphenyl phosphine oxide in 17% yield.

While the phenylation of sodium dialkylphosphonates probably follows the conventional course for reaction of benzyne with anions,[2] the phenylation of the trivalent esters differs mechanistically from previously demonstrated courses.[3,8] Further studies directed toward an elucidation of the mechanism of the latter reactions and a determination of the scope of the synthetic method are in progress.

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Hydration of Steroidal 1,2-Disubstituted Ethylenes

Sir:

The hydration of certain steroidal trisubstituted ethylenes to the corresponding secondary alcohols through successive hydroboration and hydrogen peroxide oxidation has recently been described,[1] the hydroboration being carried out by means of lithium aluminum hydride and boron trifluoride in ether (method a)[1b,2] or by passing diborane into a solution of the steroid in an ether (method b).[3]

We have found that steroidal 1,2-disubstituted ethylenes on similar hydration give rise to comparable amounts of both possible positionally isomeric alcohols. Thus Δ^1-cholestene (I) by method a[4] followed by chromatography on alumina yielded 35%[5] of cholestan-1α-ol (II) (m.p. 103–104°, $[\alpha]_D$ +36°[6]; ketone: m.p. 86–88°, $[\alpha]_D$ +114°) and 40% of cholestan-2α-ol (III) (m.p. 181–182°, $[\alpha]_D$ +28°; acetate: m.p. 89–91°, $[\alpha]_D$ 0°; ketone: m.p. 129–130°, $[\alpha]_D$ +50°). Δ^2-Cholestene (IV) either by method a[4] or by method b (in tetrahydrofuran solu-

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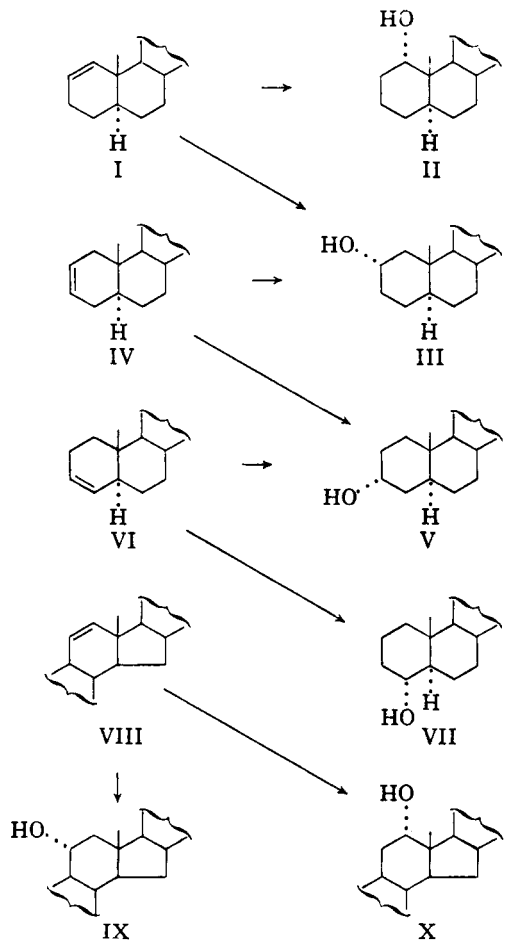
(4) Experimental details as for cholesterol,[1b] except that the peroxide oxidation was carried out as described in the experimental example given below.
(5) Yields are given to the nearest 5%.
(6) All rotations in chloroform unless otherwise stated.

tion) afforded 35% of cholestan-2α-ol (III) (m.p. 180–182°, identified with the above-described compound) and 45% of cholestan-3α-ol (V) (m.p. 187–188°, $[\alpha]_D$ +24°; acetate: m.p. 97–98°, $[\alpha]_D$ +28°; ketone: m.p. 127–128°, $[\alpha]_D$ +40°, identified with an authentic sample). Δ^3-Cholestene (VI) by method a[4] yielded 40% of cholestan-3α-ol (V) (m.p. 187–188°, identified with the compound obtained above) and 45% of cholestan-4α-ol (VII) (m.p. 188–189°, $[\alpha]_D$ +3°; acetate: m.p. 110–112°, $[\alpha]_D$ +15°; ketone: m.p. 99–100°, $[\alpha]_D$ +30°). 5α-25D-Δ^{11}-Spirosten-3β-ol acetate (VIII) by method b (in tetrahydrofuran solution) followed by saponification gave 40% of 5α-25D-spirostane-3β,11α-diol (IX) (m.p. 216–218°, $[\alpha]_D$ −68°, identified with an authentic sample; diacetate: m.p. 175–177°) and 40% of 5α-25D-spirostane-3β,12α-diol (X) (m.p. 214–217°, $[\alpha]_D$ −30°[7]; diacetate: m.p. 153–155°, $[\alpha]_D$ −12°[7])



Very recently Brown and Zweifel[8] have shown that hydroboration of acyclic olefins with the sterically hindered bis-3-methyl-2-butylborane results in greater steric control than if diborane is employed. Consequently we have investigated the hydration of several steroidal 1,2-disubstituted ethylenes by use of this reagent and subsequent oxidation. Reaction of Δ^1-cholestene (I) with bis-3-methyl-2-butylborane (prepared by hydroboration of 2-methyl-2-butene either with lithium aluminum hydride and boron trifluoride in ether[1b,2] or with sodium borohydride and boron trifluoride in diglyme[8]) followed by oxidation with hydrogen peroxide indeed yielded 75% of cholestan-2α-ol (III), the less hindered isomer, and no detectable amount of cholestan-1α-ol (II). On the other hand no very significant change from the previous results were observed when Δ^2-cholestene (IV) and Δ^3-cholestene (VI) were allowed to react with bis-3-methyl-2-butylborane, the former giving 35% of cholestan-2α-ol (III) and 45% of cholestan-3α-ol (V), while the latter gave 45% of cholestan-3α-ol (V) and 35% of cholestan-4α-ol (VII).

A typical experimental procedure for carrying out the reaction of Δ^1-cholestene (I) with bis-3-methyl-2-butylborane follows.

A solution of 0.50 g. (13.2 mmoles) of lithium aluminum hydride in 30 cc. of dry ether was added dropwise during 20 min. to a stirred solution containing 2.47 g. (35.3 mmoles) of 2-methyl-2-butene and 2.50 g. (17.6 mmoles) of boron trifluoride etherate in 40 cc. of ether, with ice-cooling under nitrogen. After an additional 1 hr. at 0°, a solution of 0.50 g. (1.35 mmoles) of Δ^1-cholestene (I) (m.p. 69–70°, $[\alpha]_D$ +14°) in 30 cc. of ether was added during 5 min. and the mixture was allowed to stand for 4 hr. without further cooling. It was then treated with a saturated sodium sulfate solution and solid sodium sulfate, and was filtered and evaporated. The residue dissolved in 20 cc. of tetrahydrofuran was oxidized with 10 cc. of 30% hydrogen peroxide and 15 cc. of 10% aqueous sodium hydroxide for 1 hr. at 0°. Isolation with ether followed by chromatography on alumina and crystallization from methanol yielded 0.39 g. (74%) of cholestan-2α-ol (III), m.p. 178–180°, $[\alpha]_D$ +27°. Almost identical results were obtained when the hydroboration of 2-methyl-2-butene was carried out with sodium borohydride and boron trifluoride in diethyleneglycol dimethyl ether.[8]

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(7) In acetone.

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Protonolysis and Deuterolysis of Tri-2-norbornylborane—Evidence for the Retention of Configuration in the Protonolysis of Organoboranes

Sir:

The hydroboration of olefins, followed by protonolysis with carboxylic acids, provides a convenient