

added 1-ethyl-4-phosphorinanone¹² (27.5 g, 0.19 mole) in 80 ml of benzene-ether during a 30-min period, while the mixture stirred vigorously. The exothermic reaction required no temperature control. The mixture was refluxed for 1 hr and allowed to stand overnight. The flask was then placed in an ice bath, and 200 ml of glacial acetic acid was added. After stirring for 30 min, liquid was decanted and the residue was dissolved in 100 ml of 7 *N* hydrochloric acid. The combined acidic solutions were adjusted to pH 9 with concentrated aqueous ammonia and extracted with five 100-ml portions of benzene. Distillation of the residue from stripping the solvent on a rotary evaporator was attempted, using a 15-cm Vigreux column. A forerun of the unreacted ketone (6.8 g) was collected at 51–60° (0.3–0.6 mm), but decomposition commenced before the product could be distilled. The pot residue was extracted with ether, and the material left from stripping the solvent had the same infrared spectrum as that obtained previously² when the distillation had been successful. The yield was 19.6 g (44%).

4-(2-Hydroxyethyl)-1-ethyl-4-phosphorinanol.—To a suspension of 11.5 g (0.30 mole) of lithium aluminum hydride in 400 ml of dry ether was added during 1 hr an ethereal solution (200 ml) of the undistilled Reformatsky product (19.6 g, 0.084 mole). The flask was cooled in an ice bath during the addition. The mixture was refluxed for 1 hr, and then excess hydride was destroyed by careful addition of cold water to the chilled mixture. After stirring for 1 hr, a saturated sodium sulfate solution was added and the ether layer was separated. The aqueous layer was extracted with three 200-ml portions of ether. The ether was stripped and the residue was distilled to give a forerun of 1.03 g [bp 108–132° (0.3 mm)] and then 9.17 g (42.3% based on ketone consumed in the Reformatsky reaction) of product [bp 132–142° (0.3 mm); lit.² bp 128–130° (0.15–0.2 mm)].

Reaction of 1-Ethyl-4-(2-hydroxyethyl)-4-phosphorinanol (Ia) with 62% Hydrobromic Acid.—The reaction procedure, applied to 9.2 g (48.3 mmoles) of Ia, was the same as for the diol (Ib). The benzene reflux step produced 4.65 g of salt after 8 hr. Some color was removed from the salt by treatment in water with charcoal. The salt was recovered by evaporation of the water. The infrared spectrum showed a weak band at 2360, assigned to P–H, a weak band at 1660, assigned to C=C, and a strong, broad band at 810–820 cm^{-1} . The pmr spectrum run on a solution containing 0.2 g in 0.2 ml of D₂O, using an external TMS standard, showed vinyl proton (doublet, $J_{\text{PCH}} = 22$ cps) centered at 6.3 and CH₂CH₂OH protons (triplet, $J = 6.5$ cps) centered at 4.27 ppm, in the ratio 1:1. The combined area of the P-ethyl and ring methylene proton signals (poorly resolved) was about 16 with respect to the vinyl signal. A 0.070-g sample of the salt in 10 ml of water had pH 2.6; the titration curve with 0.05 *N* sodium hydroxide showed a break at 2.8 ml with pH 9.3. The equivalent weight was 500.

Registry No.—VII, 7781-76-2; VIII, 7781-77-3; Ib, 7781-78-4; 4-(carboethoxymethyl)-1-ethyl-4-phosphorinanol, 7781-79-5; Ia, 7781-80-8.

(12) R. P. Welcher, G. A. Johnson, and V. P. Wystrach, *J. Am. Chem. Soc.*, **82**, 4437 (1960).

Bimolecular Displacement Reactions. III. Reaction of Phenols with Triphenylphosphine and Bromine

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In 1959 Horner, Oediger, and Hoffmann¹ reported that the reaction of triphenylphosphine dihalides with alcohols produced alkyl halides and that the reaction was accompanied by a Walden inversion. In subsequent investigations the scope of this reaction

was more clearly defined^{2,3} and some mechanistic aspects of the reaction course have been elaborated.^{4,5}

Although bimolecular displacement reactions on aromatic rings are relatively uncommon, they are feasible when the substituent is activated by an electron-withdrawing group or when the leaving group is exceptionally stable (*e.g.*, N₂). Since the formation of triphenylphosphine oxide is an energetically favorable process, triphenylphosphine dihalides and similar reagents⁶ can be used to convert phenols to aryl halides. We have found that this reaction is general and is capable of producing aryl halides in high yields.

When a solution of triphenylphosphine in acetonitrile is treated with bromine at 0°, triphenylphosphine dibromide (1) is formed rapidly and quantitatively. Addition of an equimolar quantity of a phenol results in the formation of a complex which is readily decomposed on heating to the aryl halide, triphenylphosphine oxide, and hydrogen bromide. Utilizing this procedure, β -bromonaphthalene was obtained in yields of 82–86% from β -naphthol. The reaction is suitable for large-scale preparations and is currently the best method for preparing this compound, which is normally tedious to synthesize. Using similar conditions, α -naphthol was converted to α -bromonaphthalene in 72% yield.

The reaction is also applicable to heterocyclic systems. Treatment of 3-hydroxypyridine with 1 gave 3-bromopyridine in 76% yield. Similarly, 2-bromopyridine could be isolated in 61% yield from 2-hydroxypyridine, and 8-hydroxyquinoline was converted to the corresponding bromide in 48% yield.

Although many simple aryl halides are readily available through direct halogenation of the aromatic nucleus, cases frequently arise when isomer formation makes this route impractical. In these cases and those in which heterocycles are normally inert to direct halogenation, reaction of the appropriate phenols with 1 presents a practical alternative. For example, from *o*-cresol, *o*-bromotoluene was isolated in 72% yield.

Experimental Section

The following procedure is typical of those used. When the product was a liquid, distillation was used to purify the halide.

2-Bromonaphthalene.—A 500-ml three-necked, round-bottom flask was equipped with a Trubore stirrer, a pressure-compensating dropping funnel, and a reflux condenser with drying tube. The flask was charged with 144 g of triphenylphosphine (0.55 mole) and 125 ml of acetonitrile. With stirring, the solution was cooled in an ice bath and 88 g (0.55 mole) of bromine was added dropwise over a period of 20–30 min. After the addition of the bromine, the ice bath was removed, 72 g (0.50 mole) of β -naphthol in 100 ml of acetonitrile was added in one portion, and the reaction mixture was heated to 60–70° for at least 30 min. The flask was then fitted for a simple distillation and the acetonitrile was distilled under water aspirator pressure until the oil bath temperature reached 110°. After all the acetonitrile had been removed, the condenser was replaced with a short, large-diameter glass tube connected to a 500-ml flask half-filled with water and the oil bath was replaced with a Wood's metal bath. The bath temperature was raised to 200–220° and kept at this temperature

(2) G. A. Wiley, R. L. Hershkowitz, B. M. Rein, and B. C. Chung, *J. Am. Chem. Soc.*, **86**, 964 (1964).

(3) G. A. Wiley, B. M. Rein, R. L. Hershkowitz, and W. R. Stine, Abstracts of the 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April, 1964, p 37N.

(4) J. P. Schaefer and D. S. Weinberg, *J. Org. Chem.*, **30**, 2635 (1965).

(5) J. P. Schaefer and D. S. Weinberg, *ibid.*, **30**, 2639 (1965).

(6) D. G. Coe, H. N. Rydon, and B. L. Tonge, *J. Chem. Soc.*, 323 (1957).

(1) L. Horner, H. Oediger, and H. Hoffmann, *Ann.*, **626**, 26 (1959).

until all the solid had melted. Stirring was continued and the bath temperature was raised to 340° and held there until evolution of hydrogen bromide had ceased (approximately 20–30 min). The Wood's metal bath was removed; the reaction mixture was cooled to approximately 100°, poured into an 800-ml beaker, and cooled to room temperature. Pentane (300 ml) was added; the solid was broken into fine pieces, filtered off by suction, and washed thoroughly twice with 300-ml portions of pentane. The pentane filtrates were combined, washed with 200 ml of 20% sodium hydroxide, and dried over anhydrous magnesium sulfate. The pentane extract was then passed through a 25-mm diameter column filled to 35 cm in depth with alumina. Distillation of the pentane solution gave 87 g (82–86%) of 2-bromonaphthalene; no impurities were detectable by vapor phase chromatography or nuclear magnetic resonance analysis.

Registry No.—Triphenylphosphine, 603-35-0; 2-bromonaphthalene, 580-13-2.

The Pyrolysis of 2-Acetylcyclodecanone

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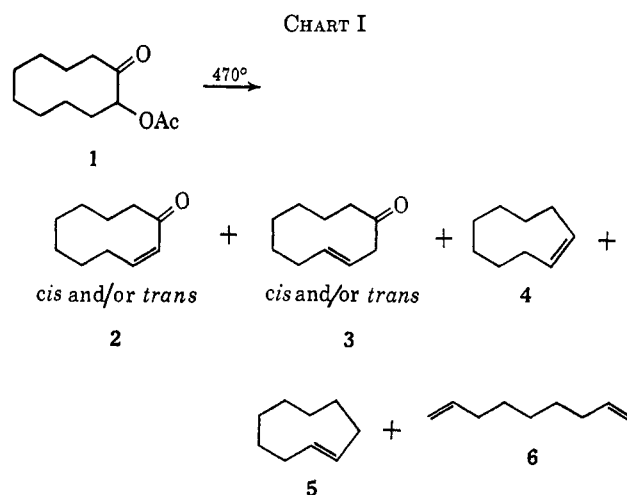
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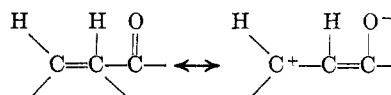
In connection with another study we required a convenient route to 2-cyclodecenone (2). The only reported preparation of this compound involved the pyrolytic dehydration of 2-hydroxycyclodecanone over alumina at 330–350°.¹ The spectral and chemical properties reported for 2 by Leonard and Owens¹ and the recent studies of Heap and Whitham² on 2-cyclononone led us to suspect that the product obtained by the dehydration of 2-hydroxycyclodecanone was a mixture of conjugated and nonconjugated cyclodecenones. We therefore attempted the preparation of 2 by pyrolysis of 2-acetylcyclodecanone (1).

Pyrolysis of 1 by passing the ester down a tube packed with glass beads and maintained at 470° produced a mixture of products which consisted chiefly of nine-carbon olefins along with a smaller amount of a mixture of cyclodecenones (Chart I). The nine-carbon olefins were separated by a combination of fractional distillation and preparative vapor phase chromatography (vpc) and identified as *cis*-cyclononene (4), *trans*-cyclononene (5), and 1,8-nonadiene (6). The cyclodecenone fraction consisted of a mixture of conjugated and nonconjugated isomers as discussed below. A small-scale run in which the relative amounts of products were determined by vpc before fractionation gave the following percentages of products: 30% cyclononenes, which contained the *cis* and *trans* isomers in a ratio of 7:1; 6% 1,8-nonadiene; and 23% the mixture of cyclodecenones and 8% unreacted 1. In various runs the ratio of *cis*- to *trans*-cyclononene varied from 7:1 to 3.5:1. In addition to the products characterized there were several unidentified products present in minor amounts.

The cyclodecenone obtained by this procedure exhibited an ultraviolet maximum at 225 m μ (ϵ 3180) in ethanol, considerably higher than the extinction coefficient reported by Leonard.¹ Catalytic hydro-



genation afforded cyclodecanone in quantitative yield. Other evidence, however, clearly indicated that the cyclodecenone was a mixture of at least two isomers. The nmr spectrum showed a doublet at δ 3.0 ($J = 7$ cps) with some fine splitting consistent with the presence of a methylene group between a double bond and carbonyl group³ and indicated the presence of 3. Integration of the nmr spectrum indicated that 2 and 3 were present in a ratio of *ca.* 2:1. The olefinic region of the nmr spectrum is of interest. The absorption at lowest field consists of a doublet at δ 6.2 ($J = 12.0$ cps) and corresponds (by integration) to one proton of the major component, the α,β -unsaturated ketone 2. Generally in α,β -unsaturated ketones the β hydrogen appears at lowest field, presumably owing to deshielding by contribution from resonance structures of the type shown below.⁴ If the β hydrogen



of 2 were at lowest field, however, a more complex pattern than a doublet should result from coupling with the γ hydrogens. It thus appears that for 2 the α hydrogen appears at lower field than the β hydrogen and indicates that in the ground state the more stable conformation does not involve coplanarity of the double bond and the carbonyl group. A similar nmr spectrum has been reported by Eaton⁵ for *trans*-2-cyclooctenone. No conclusive evidence as to the stereochemistry of the double bonds in 2 and 3 is available. The infrared spectrum of the mixture shows absorption corresponding to both *cis* and *trans* double bonds and the coupling constants of the olefinic protons in the nmr spectrum ($J = ca.$ 11–12 cps) can be interpreted in terms of either *cis* or *trans* double bonds. Thus far all attempts to separate the mixture of cyclodecenones have been unsuccessful.

The formation of olefins containing one carbon less than the expected product appears to be a general

(3) In 3-cycloheptenone the C-2 methylene appears as a doublet at δ 3.1.³

(4) N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry. Illustrations from the Steroid Field," Holden-Day, Inc., San Francisco, Calif., 1964, p 90.

(5) P. E. Eaton and K. Lin, *J. Am. Chem. Soc.*, **86**, 2087 (1964).

(1) N. J. Leonard and F. H. Owens, *J. Am. Chem. Soc.*, **80**, 6039 (1958).

(2) N. Heap and G. H. Whitham, *J. Chem. Soc. (B)*, 164 (1966).