on a boiling water bath for 2 hr. After cooling, 50 ml. of water was added and extracted with ether. The ethereal solution was washed with dilute hydrochloric acid and successively extracted three times with 50-ml. portions of 5% aqueous sodium hydroxide. Acidification of the aqueous alkaline solution with dilute hydrochloric acid followed by extraction with ether furnished an oily material which solidified on cooling in Dry Ice–methanol bath. Recrystallizations from a mixture of *n*-hexane and ethyl ether gave 7.2 g. (40%) of colorless crystals, m.p. 66–67.5°.

Anal. Calcd. for $C_{11}H_{20}O_3$: C, 65.97; H, 10.07. Found: C, 65.88; H, 10.04.

The infrared spectrum (Nujol) showed absorption maxima at 3390, 1690, 1685, and 975 cm.$^{-1}$. Reported absorption maxima for natural Royal Jelly acid[27] (Nujol) are at 3390, 1710, 1658, and 976 cm.$^{-1}$ and for the synthetic one[1a] (Nujol), at 2.92, 5.89, and 6.05 μ.

In an analogous way 8-hydroxyoctanal [2,4-dinitrophenylhydrazone, m.p. 64 and 87–96° (double melting points) reported[10] m.p. 91–93°], and 10-hydroxy-*trans*-2-decenoic acid were obtained from *dl*-1,2,9-trihydroxynonane as well as 1,8,9-trihydroxydecane, and 10-hydroxydecanal (2,4-dinitrophenylhydrazone, m.p. 100°; reported[10] m.p. 101–103°) and 12-hydroxy-*trans*-2-dodecenoic acid[1a] were obtained from 1,2,11-trihydroxyundecane.

Migration of the Double Bond in Nonenoic Acid During the Preparation from 2-Allylcyclohexane-1,3-dione.—2-Allylcyclohexane-1,3-dione was treated exactly according to the published procedure[7] and the acid obtained was purified by esterification followed by saponification, b.p. 110–114° (2.5 mm.), iodine value (Wijs) found, 156; calcd. for nonenoic acid, 162.

Oxidation of 5 g. (0.032 mole) of this acid with a solution of 23.5 g. of potassium permanganate in 500 ml. of water under slightly alkaline conditions gave 3.5 g. of a mixture of dibasic acids, m.p. 83–93°. Neutralization value found, 696; calcd. for pimeric acid, 701; for suberic acid, 644. This mixture was fractionally recrystallized from water into suberic acid, m.p. 139–141°, and pimelic acid, m.p. 95–97°; both were identified by mixed melting points with authentic specimens as well as by analyses for carbon and hydrogen.

9-Hydroxy-*trans*-2-nonenoic Acid from Alueritic Acid.—Aleuritic acid, m.p. 99.8–100.1° (reported[28] m.p. 100–101°), was obtained from commercial wax-free shellac resin according to the published procedure.[19] To a solution of 4 g. of potassium periodate in 200 ml. of 1 *N* sulfuric acid was added a solution of 5 g. of aleuritic acid in 400 ml. of ethanol and the mixture was kept at 35–40° for 20 min. with vigorous agitation. The reaction mixture was diluted with 500 ml. of water and extracted repeatedly with ether. The ethereal solution was washed with aqueous sodium bicarbonate and water and dried ($MgSO_4$). Evaporation of ether afforded crude hydroxy aldehyde, the 2,4-dinitrophenylhydrazone of which melted at 82.5–85° and gave correct analyses for carbon and hydrogen (reported[20] m.p. 99.5°). A mixture of the crude hydroxyaldehyde thus obtained, 4 g. of malonic acid, 8 ml. of pyridine, and 1 ml. of piperidine was treated in the same manner as described for 11-hydroxy-*trans*-2-undecenoic acid, and 1 g. of crude hydroxy acid, m.p. 58–60° was obtained. Recrystallizations from a mixture of petroleum ether (b.p. 40–60°) and ethyl ether gave 9-hydroxy-*trans*-2-nonenoic acid, m.p. 64.5–65.5°, ν_{max} (Nujol) at 3365, 1686, 1658, 984 cm.$^{-1}$.

Anal. Calcd. for $C_9H_{16}O_3$: C, 62.76; H, 9.36. Found: C, 62.88; H, 9.45.

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Electrolysis of Quaternary Phosphonium Salts

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Received May 8, 1962

Horner and co-workers[1,2] have recently reported the formation of tertiary phosphines from the electrolysis of various quaternary phosphonium halides. The present note describes the electrolysis of some other quaternary phosphonium salts under different conditions.

We have found that the electrolysis of several substituted triphenylphosphonium nitrates and trifluoroacetates at an aluminum cathode and a gold or platinum anode in a single-compartment cell yields triphenylphosphine oxide. This is in contrast to the results of Horner who found that, in a divided cell, phosphines were formed at a mercury or lead cathode.

The original purpose of this work was to investigate the use of quaternary phosphonium salts in the dimerization reaction previously described for ammonium salts.[3,4] Although bibenzyl was obtained in 31% yield (along with 35% of triphenylphosphine oxide) from the electrolysis of benzyltriphenylphosphonium nitrate in dimethylformamide, no dimer was obtained from the electrolysis of allyltriphenylphosphonium nitrate or 9-fluorenyltriphenylphosphonium nitrate. Each of these electrolyses afforded substantial amounts of triphenylphosphine oxide. The reaction mixtures were in general much less convenient to work with than those resulting from the electrolysis of quaternary ammonium salts.

It is possible that the quaternary phosphonium salt is first cleaved to a hydrocarbon radical and triphenylphosphine which is then oxidized to triphenylphosphine oxide. In actual fact, the electrolysis of benzyltriphenylphosphonium nitrate in methanol gave 5% of triphenylphosphine in addition to 44% of triphenylphosphine oxide.

Further evidence in support of such a reaction path is obtained from the electrolysis of triphenylphosphine in methanol in the presence of ammonium nitrate. In an undivided cell with an aluminum cathode and a platinum anode a yield of 54% of triphenylphosphine oxide is obtained.

Another possible mechanism for the formation of triphenylphosphine oxide is the oxidation of triphenylphosphine by nitrate ion. That such a reac-

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[2] L. Horner and A. Mentrup, *Ann.*, **646**, 65 (1961).

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tion is not required is shown by the isolation of 51% of triphenylphosphine oxide (in addition to 14% of toluene) from the electrolysis of benzyltriphenylphosphonium trifluoroacetate in methanol.

Since it has now been shown that triphenylphosphine can be electrolytically oxidized under the same conditions that phosphonium salts are cleaved there appears to be no discrepancy between this work and that of Horner. Horner used an electrolysis cell having separate cathode and anode compartments which effectively prevented diffusion of the initially formed phosphines. In the present work, however, the triphenylphosphine is free to diffuse and undergo anodic oxidation to the phosphine oxide.

Experimental

Electrolysis Procedure.—In the experiments designated (A) the procedure was that previously used for quaternary ammonium compounds.[4]

In the experiments designated (B) the electrolysis cell consisted of a jacketed tall-form beaker 10 cm. high and 5 cm. in diameter with an enlarged top 1 cm. high. The electrodes were attached to a circular piece of Bakelite which fitted in the enlarged top. Two strips of aluminum 2.5 cm. apart served as cathodes with a platinum wire anode centered between them. The immersed area of each cathode was 12.5 cm.^{2} (5c m. high and 2.5 cm. wide) and the anode also was immersed to a depth of 5 cm. Tap water was constantly circulated through the jacket and stirring was provided by a Teflon-covered magnetic bar.

In both procedures the current was provided by a variable voltage-regulated power supply and an ammeter was connected in series with the electrolysis cell. The current was maintained constant at 0.40 amp. throughout each electrolysis and the initial applied voltage was generally about 100 volts.

In each experiment 0.050 mole of salt was dissolved or suspended in 130 ml. of solvent. At the conclusion of each electrolysis the reaction mixture was poured into a liter of water and worked up as described for each compound.

Quaternary Phosphonium Compounds.—The salts were prepared in good yield by refluxing equimolar quantities of triphenylphosphine and the appropriate halide in acetone and subsequent reaction of the phosphonium bromide with either silver nitrate or silver trifluoroacetate.

Electrolyses. Benzyltriphenylphosphonium Trifluoroacetate in Methanol (B).—The solution was electrolyzed for 24 hr. at which time analysis by vapor phase chromatography indicated the formation of toluene in 14% of the theoretical yield. The aqueous mixture was extracted four times with chloroform and twice with hexane. The combined organic layer was washed with water, dried over magnesium sulfate, and the solvents distilled at the water pump under nitrogen. The dark residue was dissolved in benzene and chromatographed on alumina. A total of 7.1 g. (51%) of triphenylphosphine oxide was obtained from the various fractions on elution with benzene. Crystallization from benzene–hexane gave a m.p. 153–154°; mixed m.p. with triphenylphosphine oxide was 153–155°.

Benzyltriphenylphosphonium Nitrate in Methanol (B).—The solution was electrolyzed for 23.5 hr. The aqueous mixture was extracted six times with chloroform and once with hexane. The combined organic layer was washed with water, dried over magnesium sulfate, and the solvents distilled through a Vigreux column. After removal of all of the solvent at the aspirator the dark residue was dissolved in methanol and crystals were obtained as follows. Hexane was boiled with the methanol solution and decanted. The hexane was concentrated with an air jet and periodically decanted from any tar which settled. When no more tar deposited the hexane was completely evaporated to give clean crystals. This procedure was repeated several times to give 5.0 g., m.p. 152–154°. Five more digestions gave another 1.4 g., m.p. 149–153°. The combined crops were washed with a small amount of warm ether, the ether was evaporated, and the residue was crystallized from methanol with cooling by Dry Ice–acetone, 0.6 g. obtained, m.p. 79–80°.

Coincidence of infrared spectra established that the higher melting material was triphenylphosphine oxide (44% yield) and the lower melting was triphenylphosphine (5%).

Benzyltriphenylphosphonium Nitrate in Dimethylformamide (A).—The solution was electrolyzed for 18.7 hr. The aqueous mixture was extracted four times with a total of 1 l. of ether. The ether extract was washed twice with water, dried over magnesium sulfate, and distilled through a Vigreux column. The residue was digested once with hexane, the hexane was evaporated, and the solid was crystallized from methanol (Dry Ice–acetone cooling) to give 1.43 g. (31.4%) of bibenzyl, m.p. 51–52°. The material which was insoluble in the hexane digestion was treated as in the previous experiment to isolate triphenylphosphine oxide. A total of 4.7 g. (35%) was obtained. After crystallization from benzene–hexane the m.p. was 154–155° and a mixed m.p. with triphenylphosphine oxide was 153–154°.

Allyltriphenylphosphonium Nitrate in Dimethylformamide (A).—The solution was electrolyzed for 23.5 hr. The aqueous mixture was extracted four times with ether and twice with hexane. The combined extract was dried over magnesium sulfate and the solvent removed by distillation through a Vigreux column. The solid obtained, 3.2 g. (23%), was crystallized twice from benzene–hexane to give a m.p. 150–152°; mixed m.p. with triphenylphosphine oxide was 151–152°.

9-Fluorenyltriphenylphosphonium Nitrate in Dimethylformamide (A).—The suspension was electrolyzed for 20 hr. The aqueous mixture was extracted twice with ether, twice with hexane, and three times with chloroform. The extracts were combined, dried over magnesium sulfate, and distilled *in vacuo* to remove the solvents. The dark solid was digested repeatedly with hexane to give 2.7 g. of crude triphenylphosphine oxide. The residue after digestion was dissolved in methanol and treated as previously described for the isolation of triphenylphosphine oxide; an additional 4.1 g. was obtained. The total yield was 50%. The combined product was crystallized twice from benzene–hexane to give a m.p. of 153–154° which was undepressed on mixture with triphenylphosphine oxide.

Triphenylphosphine in Methanol (B).—A suspension of 13.1 g. (0.05 mole) of triphenylphosphine in a solution of 8 g. (0.1 mole) of ammonium nitrate in 140 ml. of methanol was electrolyzed for 25 hr. At this time all of the solid had dissolved. The dark electrolysis mixture was poured into a liter of water and extracted four times with 200-ml. portions of chloroform. The combined extract was dried over magnesium sulfate and the chloroform was distilled *in vacuo.* The dark residue was digested repeatedly with boiling ether and boiling hexane until evaporation of the solvent afforded no additional crystals. More solid was obtained, however, by dissolving the residue in methanol and treating it as previously described for the isolation of triphenylphosphine oxide. All of the crystals were combined, washed with a small amount of ether, and filtered to give 7.54 g. (54%) which had a m.p. of 152–154°. The melting point was undepressed on mixture with triphenylphosphine oxide.

Two experiments attested to the stability of triphenylphosphine under the work-up conditions: (1) A solution of triphenylphosphine in hexane was refluxed for 23 hr. and the triphenylphosphine was recovered unchanged. (2) A solution of triphenylphosphine was boiled and concentrated to dryness by an air jet. This was repeated four times and triphenylphosphine was recovered uncontaminated by triphenylphosphine oxide.

Acknowledgment.—The vapor phase chromatographic analysis was performed by Dr. R. C. Petersen and the benzyltriphenylphosphonium trifluoroacetate was prepared by Dr. S. D. Ross.

The Reaction of 2,3-Dichloro-*p*-dioxane with Phenyllithium

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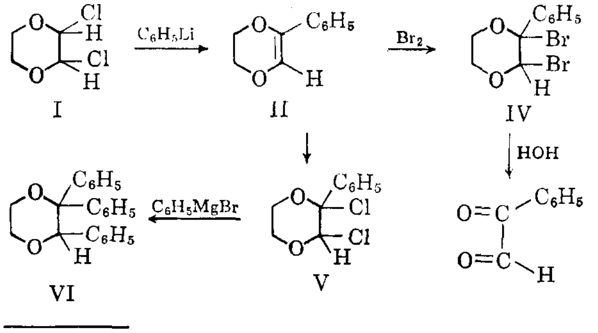
Received May 10, 1962

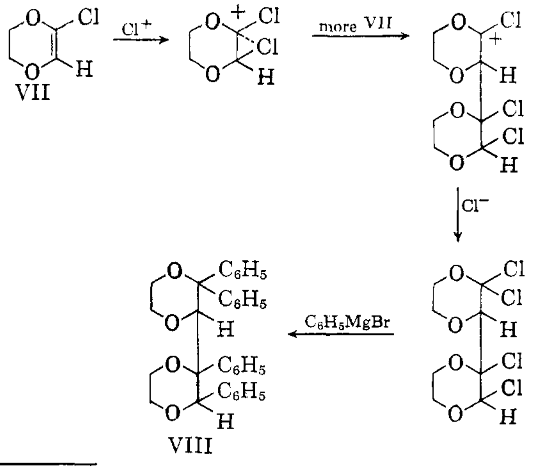
Organometallic compounds react with 2,3-dichloro-*p*-dioxane (I) in a variety of ways. Aryl Grignard reagents give mixtures of isomeric 2,3-diaryl-*p*-dioxanes in excellent yields.[3-5] The dominant isomer was assigned a *cis* structure by Stumpf,[5] but later strong evidence for a *trans* structure was presented.[6] The *trans* product predominates whether the starting material I is *cis* or *trans*.[7] The reaction of compound I with alkyl Grignard reagents is primarily one of dehalogenation,[4] dioxene and disproportionation products of the alkyl group resulting. The very small yields of mixtures of isomeric dialkyldioxanes produced from the alkylmagnesium halides can be markedly increased[8] by employing the Blaise[9] modification of the Grignard reagent utilising unisolated alkylzinc intermediates. Even better yields are obtained from similar alkylcadmium compounds, but dialkylmercury or alkylmercuric halide reagents are inert toward I. In the present study, phenyllithium has been found to react with I in yet another way, the product being 2-phenyl-*p*-dioxene (II).



The unsymmetrical 2-phenyl-*p*-dioxene is an extremely unstable and fugacious substance, in sharp contrast to the closely related, but symmetrical 2,3-diphenyl-*p*-dioxene (III).[6] Samples of III have now been kept for several years in ordinary shelf storage without modification, but II changes from a white crystalline solid to a light green liquid on standing at room temperature, often in a matter of hours. The nature of the change taking place in II is as yet obscure. Some sort of polymerization occurs, as the average molecular weight of a modified sample was found to be about 1400. That the reaction was not simply polymerization was indicated by the change in analysis, the percentages of carbon decreasing as modification proceeds. Addition of one oxygen atom for each phenyldioxene unit would account roughly for the change in composition. The infrared spectra indicate loss of double bond and a slight, but by no means proportional, formation of carbonyl during the transition.

Characterization and proof of structure of the 2-phenyl-*p*-dioxene were complicated by its unstable character but are quite definite. It adds one mole of bromine to yield 2-phenyl-2,3-dibromo-*p*-dioxane (IV). This readily undergoes hydrolysis to phenylglyoxal, which was isolated in the form of the osazone. The chlorine addition product, 2-phenyl-2,3-dichloro-*p*-dioxane (V), was converted by phenylmagnesium bromide to 2,2,3-triphenyl-*p*-dioxane (VI), which was also prepared by an independent synthesis from the known 2,2,3-trichloro-*p*-dioxane.[10]

When 2,2,3-trichloro-*p*-dioxane was treated with phenylmagnesium bromide, two products rather than the expected one were produced. Since the major one had the correct analysis and molecular weight for 2,2,3-triphenyl-*p*-dioxane, it was assigned that structure. The less soluble one, formed in minor amount, was reminiscent of by-products



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