The possibility of forming a similar class of compounds by the reaction of Grignard reagents with aromatic phosphonyl chlorides ($ArPOCl_2$) has not been examined, but this may be expected to form the other class of mixed alkyl aryl oxides of the type R_2ArPO.

As a control experiment the action of ethylmagnesium bromide on diphenyl phosphinic acid was tried to see if the acid chloride is actually a necessary intermediate. No phosphine oxide was obtained after several hours of refluxing in ether and the acid was recovered unchanged, indicating that direct replacement of hydroxyl in the acid by the alkyl radical is not possible under the conditions used.

This reaction of the diaryl phosphinyl chlorides can be compared to the reaction of Grignard reagents with sulfonyl chlorides which produces sulfones.[2] Unlike the latter, however, no halogenation was observed in the reaction with phosphinyl chlorides. This may be due to the fact that both the phosphine oxides and phosphinic acids are very stable compounds and difficult to reduce.

Experimental

The phosphinic acids used as starting materials were obtained by either of the methods of Kosolapoff.[3,4] They were recrystallized from water and air-dried. The diphenyl acid had m. p. 192–193° while the di-*p*-tolyl acid had m. p. 135.5–136.5°.

Preparation of the Phosphine Oxides.—Since the experimental conditions for these preparations were all very similar, only a description of the method used for obtaining ethyldiphenylphosphine oxide is given. Runs were usually carried out in 0.001–0.01 mole amounts.

A solution of 0.22 g. (0.001 mole) of the diphenyl acid in toluene was treated with 0.5 ml. (0.007 mole) of thionyl chloride and the solution refluxed for one to two hours. The excess thionyl chloride was then removed by distilling away about half the toluene and the remaining liquid cooled and diluted with benzene. This solution was then added dropwise to an excess of ethylmagnesium bromide in ether at room temperature. The Grignard reagent was made from 0.25 g. (0.011 mole) of magnesium and 2.5 ml. (0.032 mole) of ethyl bromide. The time of addition of the phosphinyl chloride solution was one-half hour and the resulting liquid was heated to reflux for one to two hours. It was then cooled and hydrolyzed by ice and hydrochloric acid.

The organic layer was separated and the aqueous phase extracted with ether. The extract was combined with the organic layer and ether was removed on the water-bath. The residue was then steam distilled for several hours, cooled and extracted with ether several times. The combined extracts, after drying and evaporating left a residue which was either crystalline or became so on standing. This was decolorized in acetone solution with Norit and recrystallized from ether–petroleum ether or acetone–water.

The butyldiphenylphosphine oxide showed no unusual properties when compared to other members of the series, except perhaps in melting point. The m.p. of 89.5° is the lowest of the group.

Anal. Calcd. for $C_{16}H_{19}PO$: C, 74.42; H, 7.37. Found: C, 74.28; H, 7.33.[5]

Nitration of Butyl Diphenyl Phosphine Oxide.—The nitrating mixture used was a mixture of two to two and one-half volumes of concentrated sulfuric acid and one volume of fuming nitric acid. The oxide (0.065 g.) was added to 10 ml. of this mixed acid at 0° and the solution left in an ice-bath for two hours. It was then poured into water and the product extracted with ether. The ether solution was washed repeatedly with water to remove acids and then evaporated. The residue was recrystallized from ether and ether–petroleum ether. By analogy with the case of the nitration of triphenylphosphine oxide which was shown to yield a meta nitro derivative,[6] it was assumed that the orientation in this compound is also meta.

Anal. Calcd. for $C_{16}H_{17}N_2PO_5$: C, 55.17; H, 5.46. Found: C, 55.50; H, 5.04.

Acknowledgment.—The author is indebted to Professor Melvin Calvin and to Drs. K. G. Scott, R. M. Lemmon and W. M. Garrison for advice during the course of this work and to Dr. J. G. Hamilton for making available the use of his laboratory.

---

[2] Gilman and Fothergill, This Journal, 51, 3501 (1929). Earlier work is referred to here and the mechanism of the reaction is discussed.

[3] G. M. Kosolapoff, *ibid.*, 64, 2982 (1942).

[4] G. M. Kosolapoff, *ibid.*, 71, 369 (1949).

[5] Microanalyses by C. W. Koch and V. H. Tashinian.

[6] Challenger and Wilkinson, *J. Chem. Soc.*, 125, 2675 (1924).

CROCKER LABORATORY, UNIVERSITY OF CALIFORNIA
DIVISION OF RADIOLOGY
UNIVERSITY OF CALIFORNIA MEDICAL SCHOOL
BERKELEY AND SAN FRANCISCO, CALIFORNIA

RECEIVED MARCH 9, 1950

A Direct-Current Conductance Method[1,2]

BY RAY F. PALMER[3] AND ALLEN B. SCOTT

Several direct-current methods for the measurement of electrolytic conductance have been reported.[4,5,6,7] Of these, only the work of Andrews and Martin has been done since the generally accepted standardization of reference potassium chloride solutions by Jones and Bradshaw.[8] In general, the direct-current values of Andrews and Martin for potassium chloride do not agree satisfactorily with the alternating current values of Shedlovsky,[9] differing by as much as 0.5% at some concentrations. A method has been developed in this Laboratory which eliminates to a large degree errors due to polarization during passage of the direct current, and gives conductance values showing satisfactory agreement with existing alternating current data.

Experimental

The cell and circuit shown in Fig. 1 were similar to those used by Eastman[6] except that hydrogen electrodes were used in place of calomel electrodes. Direct current was passed through a column of solution across two hydrogen electrodes, called the primary electrodes. The potential

---

[1] From a thesis submitted by Ray F. Palmer in partial fulfilment of the requirements for the M.S. degree at Oregon State College; published with the approval of the Oregon State College Monographs Committee, Research Paper No. 160, Department of Chemistry, School of Science.

[2] Presented at the Pacific Northwest Regional Meeting of the American Chemical Society, Richland, Washington, June 10, 1950.

[3] General Electric Co., Hanford Works, Washington.

[4] Andrews and Martin, This Journal, 60, 871 (1938).

[5] Marie and Noyes, *ibid.*, 43, 1095 (1921).

[6] Eastman, *ibid.*, 42, 1648 (1920).

[7] Newbery, *J. Chem. Soc.*, 113, 701 (1918).

[8] Jones and Bradshaw, This Journal, 55, 1780 (1933).

[9] Shedlovsky, *ibid.*, 54, 1411 (1932).

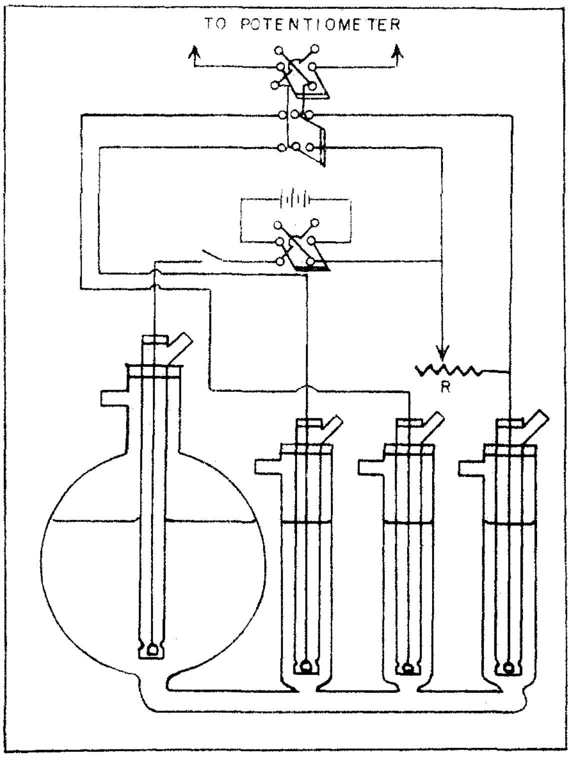

Fig. 1.—Direct-current conductance cell and measuring circuit.

difference across a portion of the solution was measured by means of two other ("secondary") hydrogen electrodes contained in sidearms along the column. By means of a reversing selection switch, the potential difference across either the secondary electrodes or a resistor (R) in series with the cell was measured for current flow in either direction. The resistance of the cell is readily computed from the potential differences across the cell and R and from the known value of R, which remained at 5000 ohms throughout the experiment.

As practically no current is drawn through the secondary electrodes, and as they are theoretically reversible, they should remain free of polarization during passage of the current. Further, there will be no concentration changes occurring in the portion of solution across which the potential difference is measured. Experimentally it was discovered that a small polarization developed on the secondary electrodes, which became nearly constant after a short time. The effect of this polarization was eliminated by making potential difference measurements first with the primary current in one direction and then in the reverse direction; the average gave the potential difference free of the polarization potential. In spite of time drifts in the polarization, the average was found to remain constant except for small random observational errors.

Potential differences were measured by a Leeds and Northrup Type *K* potentiometer. The entire conductance cell, which, in addition to the column of solution constituting the cell proper, included a one-liter vessel for preparing and storing solutions, was thermostated at a temperature of 25.000 ± 0.002°, as determined by a platinum-resistance thermometer calibrated by the Bureau of Standards. The resistor R was calibrated by the manufacturer; however, its exact value was not important, as it was included in the calculation of the cell constant and remained unchanged throughout the experiment.

The cell constant was obtained from the resistance of the cell when filled with 0.1 and 0.01 demal potassium chloride solutions, using the specific conductances of Jones and Bradshaw for these reference solutions. The potassium chloride used was J. T. Baker Analyzed, Special, ignited to 700° in a platinum crucible and cooled over phosphorus pentoxide before weighing. All solutions were made from water collected steaming from a tin-lined still and stored under nitrogen, and having a specific conductance in the neighborhood of 1.4 × 10^{-6} ohm^{-1} cm.^{-1} when first prepared. The water conductivity was determined by an alternating current bridge for each solution at the time of preparation and again on a sample of water, handled in the same manner as the solution, at the conclusion of measurements. The average was taken as the proper correction, and in all cases the difference between initial and final values was barely of significance. Tank hydrogen, used for the hydrogen electrodes, was passed through solutions of potassium permanganate and potassium hydroxide and finally through a thermostated solution of the same composition as that in the cell. The hydrogen also served to manipulate the solution from the one-liter reservoir into the tube serving as the cell and to exclude the atmosphere. All volumetric equipment was calibrated by weight methods.

Observed results for the determination of the cell constant and equivalent conductances of 0.01 *N* and 0.001 *N* potassium chloride are given in Table I.

TABLE I

Concn., demal.	Resistance, ohms	κ of solute,[8] ohm^{-1} cm.^{-1}	κ H_2O, ohm^{-1} cm.^{-1}	Cell constant, cm.^{-1}
0.1	1139	0.012856	1.90 × 10^{-6}	14.65 ± 0.01
.1	1138	.012856	2.40 × 10^{-6}	14.63 ± 0.04
.01	10347	.0014088	2.78 × 10^{-6}	14.61 ± 0.004
			Av.	14.63 ± 0.01

Concn. (*N*)	Resistance (ohm)	κ H_2O (ohm^{-1} cm.^{-1})	Equivalent conductance (ohm^{-1} cm.^{-1} eq.^{-1}) a. c.	d. c.[a]
0.01	10334	2.10 × 10^{-6}	141.4 ± 0.1	141.36
.001	98740	1.44 × 10^{-6}	146.7 ± 0.1	146.97

[a] Values of Shedlovsky[9] recomputed on the basis of Jones and Bradshaw's standardizing values.

The estimated errors in the three cell constants are based solely on observational deviations in the course of about 10 measurements at each concentration. These deviations arose principally because of insufficient galvanometer sensitivity and could be reduced substantially by a redesign of the cell and measuring circuit. The estimated error in the average cell constant is based only upon the deviations of the three different solutions (the two 0.1 *d* solutions having been independently prepared) from the mean. The estimated error in Λ for the 0.1 and 0.01 *N* solutions is based upon observational errors in measured resistance and the estimated error in the cell constant.

The reasonable constancy of the cell constant with concentration and the agreement between the direct and alternating current values at 0.01 *N* indicate that the method described is capable of work of precision very nearly comparable to the best modern a. c. methods, and further indicates that there is no fundamental difference between resistance measured by direct and alternating currents. The difference at 0.001 *N* (0.2%) is probably due to inaccuracy in the water correction in this experiment; the elaborate precautions for the preparation and handling of dilute solutions described by Shedlovsky could readily be adapted for use with this cell.

It must be remarked that the necessity of making several measurements for current of both directions in order to reduce observational errors renders the method described here much less convenient than conventional alternating current methods. Its principal advantage lies in the reduction in cost because of the elimination of features necessary in the alternating current bridge to overcome errors due to reactance.

DEPARTMENT OF CHEMISTRY
OREGON STATE COLLEGE
CORVALLIS, OREGON

RECEIVED MAY 8, 1950