tion of 5.2 g. (0.05 mole) of sodium carbonate in 50 ml. of water. After thirty minutes of refluxing, a yellow liquid product began to separate on the walls of the flask. Refluxing was continued for a total of twelve hours. The aqueous solution was removed by decantation and the yellow residue dissolved in ether. The aqueous layer was extracted with ether and the ethereal solutions combined and dried over magnesium sulfate. The ether was allowed to evaporate at room temperature in a vacuum desiccator, the final traces being removed by cautious evacuation. The viscous liquid material was then yellow-orange in color and was readily soluble in benzene, ether, and methanol, but insoluble in water. The yield was 4.8 g. (57.0%). The nitrogen analysis indicates a D. P. of 8 to 12.

Anal. Calcd. for $C_9H_{16}N_2O$: C, 64.25; H, 9.59; N, 16.65. Found: C, 64.17; H, 9.85; N, 14.99.

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Raman Spectroscopic Investigation of the Isomerization of *n*-Hexane

BY SAN-ICHIRO MIZUSHIMA, HIDETOSHI OHNO AND TAKEHISA SAKURA

The isomerization of *n*-hexane in the presence of aluminum chloride has been studied. A mixture of 500 cc. of *n*-hexane (Fischer–Tropsch product), 100 g. of aluminum chloride (Takeda's pure sample) and 2 cc. of water was placed in a flask equipped with a reflux condenser and a mechanical stirrer and maintained at a constant temperature of 45°.[1] The purity of the *n*-hexane used was confirmed by its Raman effect.[2,3]

The liquid product of the reaction was separated by fractional distillation into several fractions and the Raman spectrum of each was photographed. The intensity of the Raman lines characteristic of each of the component hydrocarbons allowed an analysis of the reaction product to be made.[3] Several experiments were made with differing speeds of stirring. For one of them (reaction period four hours) Raman analysis gave this result: isobutane 9%, isopentane 7%, 2,2-dimethylbutane 4%, 2,3-dimethylbutane 2%, 2-methyl- and 3-methylpentane 6%, and *n*-hexane 72%.

The isomerization undergoes an induction period during which no apparent change such as the evolution of bubbles can be observed. In one example stopped immediately after this induction period (110 minutes), 5% of *n*-hexane had reacted to yield isobutane (0.2%), isopentane (0.2%), 2,2-dimethylbutane (1%), 2,3-dimethylbutane (1%), and 2-methyl- and 3-methylpentane (2%). The Raman analysis is very useful for the detection of such small changes. A similar result was obtained when the induction period was changed by altering the speed of stirring. It is seen that during the induction period the isomerization proceeds to some extent, but the amount of cracking is very small. Isomerization appears to precede cracking and is the predominant reaction during the induction period, after which cracking becomes important. This conclusion is also supported by the following two facts: (1) In the cracked product isoparaffins but no normal paraffin have been found; (2) in the presence of aluminum chloride isoparaffins are cracked more easily than normal paraffins.

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[1] For previous investigations see Ellis, "The Chemistry of Petroleum Derivatives," Vol. II, 1937, and also Calingaert and Beatty, THIS JOURNAL, 58, 51 (1936).

[2] For a description of our Raman apparatus see *e. g.* Mizushima and Morino, *Proc. Ind. Acad. Sci.*, 8, 315 (1938), Raman Jubilee Volume.

[3] Recent data on the Raman spectra of *n*-hydrocarbons are given in: Mizushima and Shimanouchi, THIS JOURNAL, 71, 1320 (1949).

The Action of Grignard Reagents on Diaryl Phosphinyl Chlorides[1]

BY D. C. MORRISON

In connection with work on incorporation of radioactive phosphorus into organic molecules, it was found necessary to study the action of Grignard reagents on the chlorides of aromatic phosphinic acids. This reaction has not been examined previously. The product of the reaction is an unsymmetrical alkyldiarylphosphine oxide of the type Ar_2RPO (where R refers to alkyl and Ar is aryl), and is formed apparently by simple replacement of the halogen atom by an alkyl group according to the equation

$$Ar_2P(O)Cl + RMgX \longrightarrow Ar_2RP(O) + MgXCl$$

The reaction proceeds smoothly to give fair to good yields of the phosphine oxides. The melting points of these compared reasonably well with previous literature values and are recorded in Table I. The phosphinyl chlorides were not isolated as such, but were used as obtained in toluene solution by the action of thionyl chloride on the free acid in this solvent. One of the phosphine oxides which was prepared was not previously described in the literature. This is diphenylbutylphosphine oxide, and for characterization was converted into the dinitro derivative.

TABLE I

Compound	M. p., °C., lit.	M. p., °C., uncor. Found	Yield, %
$C_2H_5(C_6H_5)_2PO$	121[a]	123–124	67.2
i-$C_3H_7(C_6H_5)_2PO$	145–146[b]	144–146	44.6
i-$C_4H_9(C_6H_5)_2PO$	137.5–138[b]	132.5–134	75.2
$C_6H_5\cdot CH_2(C_6H_5)_2PO$	192–193[b]	189–190	69.0
$CH_3(p$-$CH_3\cdot C_6H_4)_2PO$	143[c]	145.5–146.5	63.8
$C_4H_9(C_6H_5)_2PO$	....	89.5	68.0
$C_4H_9(NO_2\cdot C_6H_4)_2PO$	....	124–125.5	68.4

[a] Michaelis and Soden, *Ann.*, **229**, 295 (1885). [b] Arbusov, *J. Russ. Phys.-Chem. Soc.*, **42**, 395 (1910); *C.A.*, **5**, 1397. [c] Michaelis, *Ann.*, **315**, 84 (1901).

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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 $C_{16}H_{17}N_2PO_6$: C, 55.17; H, 5.46. Found: C, 55.50; H, 5.04.

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[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).

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

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[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).