ortho, para directing groups and the log of the hydrogen uptake. However, this relationship may be fortuitous.

Since the rate of hydrogenation varies with the nature of the substituent groups we conclude that the colloidal iridium catalyst causes the hydrogen to add to the nitro group in an ionic form as was found to be the case with rhodium.[1h]

**Acknowledgment.**—This investigation was carried out under the auspices of the Office of Naval Research. The noble metal salts were obtained through the courtesy of Baker and Co. Inc., Newark 5, N. J.

## IV. Summary

1. A method has been described for the preparation of an iridium–polyvinyl alcohol catalyst.
2. A kinetic study of hydrogenations carried out with this catalyst has been undertaken.

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[CONTRIBUTION FROM THE ROSS CHEMICAL LABORATORY, ALABAMA POLYTECHNIC INSTITUTE]

# Alkylation of Triethyl Phosphonoacetate and Related Esters

BY GENNADY M. KOSOLAPOFF AND J. STEPHEN POWELL

A number of years ago Arbuzov and his coworkers discovered the possibility of alkylation of triethyl phosphonoacetate in a manner analogous to that used for alkylation of dialkyl malonates.[1] However, no further investigations of this useful reaction existed until the present, while the work of Arbuzov and Razumov covered but a few examples. A more thorough study of the possibilities of this reaction was undertaken in this Laboratory in order to provide the necessary intermediates for the synthesis of "phosphono" analogs of naturally occurring amino acids and to clear up several points of identification of phosphonocarboxylic acids which have been left from the work of Arbuzov and Razumov, as well as from some earlier studies of Michaelis.

Triethyl phosphonoacetate may be alkylated readily, *via* its potassium derivative, in satisfactory yields, especially when a relatively high-boiling solvent, such as xylene, is used.

$$(EtO)_2P(O)CHKCO_2Et + RX \longrightarrow (EtO)_2P(O)CHRCO_2Et + KX$$

Furthermore, it has been found that dialkylation is also feasible and several disubstituted compounds were readily prepared. This finding was useful in the final identification of the oxidation product of the "diacetonephosphinic" acid of Michaelis,[2] which was provisionally given the structure of dimethylphosphonoacetic acid by Anschütz, Klein and Cermak.[3]

While triethyl phosphonoacetate reacts quite readily with potassium metal on heating, the mono-alkylated esters react even more readily and their metal derivatives are obtainable without external heating. These react with alkyl halides to yield the dialkylated esters. The separation of the alkylation products is not a difficult task when the alkyl groups employed are fairly large, but the methylated derivatives present a particularly difficult problem, since the monomethylated derivative boils at essentially the same temperature as the unsubstituted ester; the dimethylated ester boils lower than these and may be separated rather readily. The monomethylated product, reported by Arbuzov and Razumov,[1] was stated to yield on hydrolysis a free acid, the melting point of which was reported as 119–132°; the paper of Arbuzov and Dunin[1] described the acid as a hygroscopic sirup. These unsatisfactory results are readily explainable by contamination of the monomethylated ester with, probably, small amounts of the starting material. Our results were similar to those of Arbuzov and his coworkers. The only other reference to this acid is given by Nylen,[4] who obtained the acid by hydrolysis of the triethyl ester, which in turn was secured by the reaction of triethyl phosphite with ethyl $\alpha$-bromopropionate in an extremely poor yield; Nylen's acid also had an unsatisfactory melting point (75–95°) and was admittedly impure. Nylen mentioned that his triethyl methylphosphonoacetate lost a considerable part of its phosphorus content during hydrolysis in the form of phosphorous acid. Neither Arbuzov and Razumov nor the present investigation confirm such dephosphonation of the ester prepared by alkylation of triethyl potassiumphosphonoacetate. The appearance of phosphorous acid during hydrolysis of Nylen's product is explainable by the contamination of the desired ester, in the course of its preparation, by tetraethyl hypo- and pyrophosphates, which form a rather difficultly separable mixture which boils in the range of the methylphosphonoacetate. The formation of the hypo- and pyrophosphates is a common side reaction in the interaction of secondary halides with reagents of the phosphite class and appears to involve the formation of $(RO)_2PO$, which dimerizes and also undergoes oxidation–reduction reactions.[5]

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(1) Arbuzov and Razumov, *J. Russ. Phys.-Chem. Soc.*, **61**, 623 (1929). A previous communication by Arbuzov and Dunin (*Ber.*, **60**, 291 (1927)) stated that such a reaction had been carried out but gave no information whatever about the procedure used or results obtained.

(2) Michaelis, *Ber.*, **17**, 1273 (1884); **18**, 898 (1885); **19**, 1009 (1886).

(3) Anschutz, Klein and Cermak, *ibid.*, **77**, 726 (1911).

(4) Nylen, *ibid.*, **57**, 1023 (1924).

(5) Chavanne and Rumpf, *Compt. rend.*, **225**, 1322 (1947).

## Experimental

The molecular refractions of the esters described below were calculated with the recently published refractivities of phosphorus in various organic derivatives.[6] The titrations of the free acids were performed at 0° with 0.1 *N* sodium hydroxide in 10% sodium chloride solutions, analogously to the titrations of diphosphonates done by Kabachnik.[7]

Triethyl phosphonacetate was prepared conventionally from diethyl sodiophosphite and ethyl chloroacetate,[8] with a 65% yield being attained when xylene was used as the solvent. The product boiled at 83–84° at 0.5 mm.; $n^{30}_{\text{D}}$ 1.4280, $d^{30}_{4}$ 1.1125; *MR* found, 51.861; calcd., 51.665.

**Triethyl Methylphosphonoacetate.**—Triethyl phosphonoacetate (40 g.) in 200 ml. of xylene was heated gently, with stirring, with 7.0 g. of potassium and the resulting solution of the potassium derivative was treated over thirty minutes with 40 g. of methyl iodide with stirring. After three hours at 60–70°, the mixture was filtered (28 g. of potassium iodide was obtained; the theoretical amount is 29.6 g.), and the filtrate was distilled yielding 27.3 g. (64%) of the product, b. p. 84–86° at 0.5 mm., $n^{30}_{\text{D}}$ 1.4290, $d^{30}_{4}$ 1.0890; *MR* found, 56.393; calcd., 56.283. Repetition of the synthesis with 14.8 g. of the phosphonacetate gave a 51% yield of the product, b. p. 76–77°, at 0.2 mm., having the same constants as cited above. Hydrolysis of the product by refluxing for eight hours with concentrated hydrochloric acid (no phosphorous acid appeared in the solution), followed by evaporation under an infrared lamp yielded the free acid in the form of very hygroscopic waxy solid, which melted indefinitely above 70°.

**Triethyl Dimethylphosphonacetate.**—A suspension of 3.6 g. of potassium in 200 ml. of xylene was treated dropwise, with stirring, with 22 g. of triethyl methylphosphonoacetate (above). Evolution of hydrogen and formation of the potassium derivative was rapid without external application of heat and was complete within forty minutes. A deliberate excess of methyl iodide (25 g., against theoretical 13.1 g.) was added over one hour to the stirred solution and the mixture was refluxed gently for two hours. After standing overnight, the precipitated potassium iodide was filtered and the filtrate yielded, upon vacuum distillation, 16.2 g. of the product, which after two redistillations boiled at 74° at 0.2 mm.; $n^{30}_{\text{D}}$ 1.4286, $d^{30}_{4}$ 1.0752; yield 70%; calcd.: P, 12.3; *MR*, 60.90. Found: P, 12.20, 12.18; *MR*, 60.431.

Hydrolysis of the ester, as described above, yielded the dimethylphosphonoacetic acid in the form of colorless needles, which were purified by precipitation from dry ether with petroleum ether, followed by prolonged vacuum drying. The acid is not very hygroscopic and may be exposed to the normal atmospheric humidity for several hours without liquefaction, once it has been thoroughly dried. The product, m. p. 170–172°, on titration gave the equivalent weight of 56.3; calculated, 56.03; P found, 18.35, 18.48%; calculated, 18.4%.

Preparation of 4-methylpentan-2-one-4-phosphonic acid, from mesityl oxide and phosphorus trichloride in the presence of acetic anhydride, was performed according to Conant and Cook's procedure,[9] using the specific directions of Drake and Marvel.[10] It may be noted that the intermediate phosphonyl chloride reacted with cold water quite sluggishly, which agreed with Michaelis' observation.[2] The keto phosphonic acid (2 g.) was treated with 25 ml. of fuming nitric acid and, following the vigorous oxidation which was initiated by a brief warming of the mixture, the solution was evaporated to dryness under an infrared lamp. After two re-evaporations with small amounts of water, the crude solid mixture of the resulting acids was separated *via* the barium salts, as directed by Michaelis,[2] and the barium salt of the carboxy phosphonic acid was taken up in 200 ml. of water with the addition of the least necessary amount of hydrochloric acid. After careful removal of the barium ion by addition of dilute sulfuric acid, the clear filtrate was evaporated to dryness under an infrared lamp and the residue was purified by ether–petroleum ether treatment, as described above. After thorough drying in vacuum, the product showed the same behavior on melting as the authentic dimethylphosphonoacetic acid: resinification at 166° and melting at 170–172°; mixed melting point of the two specimens revealed no depression.

**Triethyl *n*-Butylphosphonacetate.**—The reaction, carried out as described above, utilizing 10.0 g. of potassium, 56 g. of triethyl phosphonoacetate and 50 g. (deliberate excess) of *n*-butyl bromide in xylene, with a five hours refluxing period, yielded 53.1 g. (75.9%) of the product, which boiled at 101–103° at 0.2 mm.; $n^{30}_{\text{D}}$ 1.4322; $d^{30}_{4}$ 1.0321; calcd.: *MR*, 70.137; P, 11.05. Found: *MR*, 70.465; P, 10.9, 11.0.

Hydrolysis of the ester by refluxing for eight hours with concentrated hydrochloric acid, followed by treatment with warm benzene and petroleum ether, yielded *n*-butylphosphonacetic acid, in the form of colorless needles, which showed very little hydroscopicity after vacuum drying, and melted at 110–112°; calcd.: equiv. wt., 65.36; P, 15.8. Found: equiv. wt., 65.43; P, 15.7, 15.7.

**Triethyl Di-*n*-butylphosphonoacetate.**—The general procedure was followed, using 50.5 g. of the above ester, 7.3 g. of potassium and 40 g. (excess) of *n*-butyl bromide; refluxing period was five hours. The initial distillation gave 45.2 g. (74.5%) of crude product, b. p. 111–115° at 0.25 mm., which on redistillation gave 27.4 g. of the pure material, b. p. 112° at 0.2 mm.; $n^{30}_{\text{D}}$ 1.4408, $d^{30}_{4}$ 0.9978; calcd.: *MR*, 88.609; P, 9.2. Found: *MR*, 88.994; P, 9.1, 9.2.

The ester was hydrolyzed by refluxing for six hours with concentrated hydrochloric acid, followed by refluxing for one hour with 48% hydrobromic acid. After evaporation to dryness, solution of the residue in warm benzene, re-evaporation to dryness and prolonged trituration with cold petroleum ether there was obtained the free di-*n*-butylphosphonoacetic acid, in the form of colorless needles, which, after drying in vacuum, melted at 140–141°, with resinification at 138°; calcd.: equiv. wt., 84.1; P, 12.3. Found: equiv. wt., 83.9; P, 12.1, 12.2.

**Triethyl Benzylphosphonoacetate.**—The general procedure was followed, utilizing 28 g. of triethyl phosphonoacetate, 6 g. of potassium and 40 g. of benzyl chloride; refluxing period six hours. The mixture yielded 12.5 g. (32%) of the product, b. p. 133–135° at 0.2 mm.; $n^{30}_{\text{D}}$ 1.4830, $d^{30}_{4}$ 1.1099; *MR* found, 80.878; calcd., 80.390. Hydrolysis of the ester by refluxing for seven hours with concentrated hydrochloric acid, followed by evaporation and treatment with petroleum ether, yielded benzylphosphonoacetic acid in the form of colorless plates, which were not noticeably hygroscopic after vacuum drying, contrary to the observation of Arbuzov and Razumov,[1] and which melted at 150–152° (Arbuzov and Razumov give the melting point of 137.145° for their preparation); calcd.: equiv. wt., 76.72; P, 13.45. Found: equiv. wt., 76.6; P, 13.3, 13.4.

**Triethyl Benzyl-*n*-butylphosphonoacetate.**—The general procedure was used with 22 g. of triethyl *n*-butylphosphonoacetate, 3.1 g. of potassium and 20 g. (excess) of benzyl chloride, with a nine hours refluxing period; 10 g. (35%) of the product, a viscous oil, b. p. 141–144° at 0.2 mm., was obtained. Better results were secured by a similar reaction of 16.4 g. of triethyl benzylphosphonoacetate, 2.3 g. of potassium and 16.0 g. of *n*-butyl bromide, with reflux for six hours; this gave 10.5 g. (54%) of the product, b. p. 143–145° at 0.2 mm.; $n^{30}_{\text{D}}$ 1.4832; $d^{30}_{4}$ 1.0650; calcd.: *MR*, 98.862; P, 8.4. Found: *MR*, 99.366; P, 8.3, 8.35. Hydrolysis of the ester gave the free acid only in the form of a very viscous resin.

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(6) Kabachnik, *Izvest. Akad. Nauk S. S. S. R., Otdel Khim Nauk*, No. 2, 219 (1948).

(7) Kabachnik, *ibid.*, No. 6, 631 (1947).

(8) Kosolapoff, THIS JOURNAL, **68**, 1103 (1946).

(9) Conant and Cook, *ibid.*, **42**, 830 (1920).

(10) Drake and Marvel, *J. Org. Chem.*, **2**, 387 (1937).

## Summary

Mono- and dialkylation of triethyl phosphonoacetate was investigated and several new esters and free acids were isolated. Benzylphosphonoacetic acid was obtained in a state of higher purity than the material reported earlier by Arbuzov and Razumov. The difficulty of securing pure methylphosphonoacetic acid by any of the available methods is discussed. The final link of structure determination of Michaelis' "diacetonephosphinic" acid was achieved.

AUBURN, ALABAMA RECEIVED JANUARY 3, 1950

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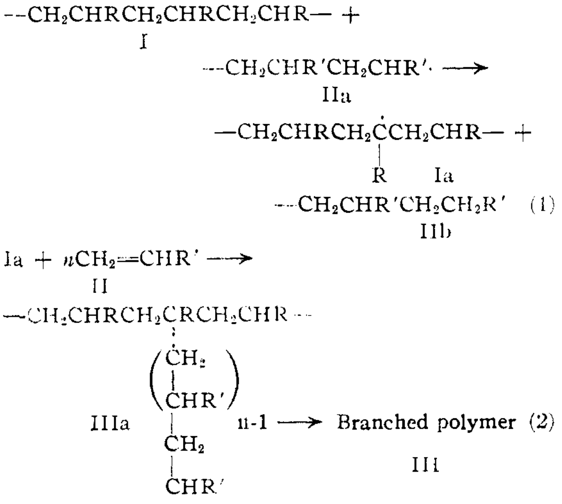
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CARNEGIE INSTITUTE OF TECHNOLOGY]

# The Polymerization of *p*-Chlorostyrene in the Presence of Polymethylacrylate. II[1]

BY ROBERT B. CARLIN AND DUANE L. HUFFORD[2]

Preliminary experiments have provided evidence that the polymerization of *p*-chlorostyrene in the presence of polymethylacrylate produces some polymer molecules in which both *p*-chlorostyrene and methyl acrylate units are chemically combined.[3] The work reported here was undertaken in an effort to extend and expand the available body of information supporting the postulate that chain branching reactions of the following type may occur in simple vinyl polymerizations.



$$\underset{\text{I}}{-CH_2CHRCH_2CHRCH_2CHR-} + \underset{\text{IIa}}{-CH_2CHR'CH_2CHR'\cdot} \longrightarrow \underset{\text{Ia}}{-CH_2CHRCH_2\overset{\cdot}{C}(R)CH_2CHR-} + \underset{\text{IIb}}{-CH_2CHR'CH_2CH_2R'} \quad (1)$$

$$\text{Ia} + \underset{\text{II}}{n\,CH_2{=}CHR'} \longrightarrow \underset{\text{IIIa}}{-CH_2CHRCH_2CRCH_2CHR-\,(CH_2CHR')_{n-1}CH_2CHR'} \longrightarrow \underset{\text{III}}{\text{Branched polymer}} \quad (2)$$

When a pure vinyl monomer polymerizes, reactions such as those formulated above can lead only to branched polymers (III, R = R') which would be extremely difficult to separate and distinguish from the purely linear polymers (I or IIb, R = R'). If, on the other hand, a vinyl monomer (II) is polymerized in the presence of a polymer which is composed of units of a different kind (R ≠ R'), then branched polymers (III, R ≠ R') comprising chains of units of one kind and attached branches formed from units of another kind, might be produced. In the work described here, as in the preliminary work,[3] *p*-chlorostyrene (II, R' = *p*-$C_6H_4Cl$) was polymerized in the presence of polymethylacrylate (I, R = $COOCH_3$) at 50°. The polymerizations were carried out in the absence of solvents so that reactions of growing polymer chains (IIa, R' = *p*-$C_6H_4Cl$) with substances other than polymethylacrylate might be minimized. In an effort to discover whether the presence of a polymerization catalyst affects the reaction which produces polymers composed of units of both kinds, 0.7–0.9% of benzoyl peroxide was added to some reaction mixtures but not to others.

After polymerization of *p*-chlorostyrene in the presence of polymethylacrylate, the products were separated into three fractions by means of a solvent extraction scheme. Methyl acrylate units in the polymers were first hydrolized to acrylic acid units, and polyacrylic acid was separated from the mixture by extraction with water. The water-insoluble polymers were then extracted with benzene until the soluble poly-*p*-chlorostyrene was removed. Chlorine analyses of the water-soluble and of the benzene-soluble fractions proved that the former contained only traces of poly-*p*-chlorostyrene and that the latter was essentially pure poly-*p*-chlorostyrene. The polymer fractions which were insoluble both in water and in benzene were shown by chlorine analyses to possess both *p*-chlorostyrene and acrylic acid units. For the most part, the units of different kinds must have been present in chemical combination, because intimate physical mixtures prepared from solutions containing both pure *p*-chlorostyrene and pure polymethylacrylate gave only relatively small amounts of water- and benzene-insoluble fractions when submitted to the separation scheme. The formation of very highly branched poly-*p*-chlorostyrene, which might be insoluble in benzene and which might thereby complicate the separation scheme, was avoided in all runs by stopping the polymerization of *p*-chlorostyrene at low conversions.

## Experimental

**Polymethylacrylate.**—Dioxane solutions of the crude polymer[3] were freed of insoluble material, and the polymer was reprecipitated into methanol. After another repre-

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[1] Abstracted from a doctor's thesis by Duane L. Hufford; presented before the Organic Division, A. C. S., Philadelphia, Pa., April, 1950.

[2] General Tire and Rubber Co. Fellow, 1947–1949.

[3] Carlin and Shakespeare, THIS JOURNAL, **68**, 876 (1946).