NOTES

chloric acid after removing ethanol. The yield of precipitated acid was 24.29 g. or 94.2%. It was very sparingly soluble in water. After one recrystallization from ether, the acid sintered above 200° and melted at 268–275° and after an additional recrystallization it melted at 277–280° (lit.<sup>2</sup> 277–278°).

Fluorenone-3-carboxylic acid. Alder et al.<sup>2</sup> give few details so these were worked out again. The cyclization in sulfuric acid gives yields of 79-87%. It was found to be temperature sensitive and should not be heated over  $45^{\circ}$  or further reaction occurs. Twenty g. of finely powdered phenyl terephthalic acid was stirred with 180 ml. of concentrated sulfuric acid at 25-30° until all was dissolved. The resulting dark solution was then kept at 40° (internal temp.) for 20-30 min. It was poured into ice water, and the precipitated acid filtered, washed, and dried. A yield of 15.17 g. or 81.9% of acid was obtained which sintered at 265° with melting 270-300°. Hydrolysis of the purified methyl ester and recrystallization from aqueous acetone gave a product of m.p. 299-304° with previous sintering (lit.<sup>4</sup> 304°).

Methyl fluorenone-3-carboxylate. The acid was esterified by refluxing for 1 day a mixture of 8.0 g. acid with 5 ml. concentrated sulfuric acid and 750 ml. of methanol. After the usual isolation, a yield of 7.66 g. or 90% was obtained. Four recrystallizations from aqueous acetone gave a product sintering at 133° and melting at 146–147° (lit.<sup>4</sup> 145°). Recrystallization eliminates any phenyl terephthalate or other impurities. The ester is decomposed by hot concentrated potassium hydroxide solution, giving a dark brown solution, and for hydrolysis, short contact with warm alkali is necessary.

Fluorene-3-carboxylic acid. A solution of 8.24 g. of methyl fluorenone-3-carboxylate in 300 ml. of acetic acid was mixed with 9 g. of red phosphorus and 10 ml. of 47-50% hydriodic acid and the liquid refluxed 45 hr. Most of the solvent was distilled and the residue diluted with 450 ml. of water and ice cooled several hours. The solids were filtered and then extracted with an excess of dilute potassium carbonate solution. The carbonate extract was filtered and acidified and the precipitated acid filtered off, washed, and dried. It weighed 7.18 g. or 98.7%. This preparation melted at 220-230° with previous sintering. Three recrystallizations from acetone-water with a minimum of heating gave a product of m.p. 229.5-231.5° with sintering at 222° (lit.<sup>4</sup> 230 and 231°).

Methyl fluorene-3-carboxylate. 10 g. of the above acid with 8 ml. of concentrated sulfuric acid and 350 ml. of methanol were refluxed 24 hr. and the ester isolated as usual. The light brownish ester was washed with alkali and dried. It was then distilled from a small short-path still at 1 mm. and the solid distillate recrystallized from acetone-water and dried. The yield of white product was 10.1 g. or 94.7%. After four recrystallizations from aqueous acetone, the ester had m.p. 79-80°.

Anal. Caled. for C<sub>15</sub>H<sub>12</sub>O<sub>2</sub>: C, 80.36; H, 5.36. Found: C, 80.13; H, 5.32.

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### **Preparation of**

**Diethyl 4-Phosphonovalero-4-lactone** 

### J. A. CADE

#### Received January 31, 1958

The preparation of esters of 1-hydroxyalkanephosphonic acids by the base-catalyzed interaction of carbonyl compounds with dialkyl hydrogenphosphonates is well known,<sup>1</sup> but the behavior of 1-ketocarboxylic acids in this reaction does not appear to have been examined hitherto. Interest in such a reaction was provoked during a search for new methods of obtaining methanediphosphonates and related derivatives, *i.e.*, compounds containing a P-C-P bridge.<sup>2</sup>

It had been shown,<sup>8</sup> that trialkyl phosphite reacts with a lactone to give predominantly the trialkyl ester of a phosphonocarboxylic acid, *e.g.*:

$$CH_{2}CH_{2}C=0 + (C_{2}H_{5}O)_{3}P \xrightarrow{160^{\circ}} (CHO)CHCHCHCOCH$$

 $(C_2H_5O)_2P(O)CH_2CH_2CO_2C_2H_5$ 

Such a reaction might be expected to produce a *gem*-bis(dialkyl phosphono)carboxylic ester, II, from a dialkyl phosphonolactone in which the phosphorus atom is joined to the same carbon atom as the oxygen bridge; especially since the presence of the dialkyl phosphono group should enhance the electrophilic power of this atom:

$$I \qquad \begin{array}{c} O & CH_{3} \\ (C_{2}H_{5}O)_{2}P - C - CH_{2}CH_{2} - C = O + (C_{2}H_{5}O)_{3}P \longrightarrow \\ I \\ [(C_{2}H_{5}O)_{2}P(O)]_{2}C(CH_{3})CH_{2}CH_{2}CO_{2}C_{2}H_{5} \\ II \end{array}$$

This aspect of the investigations had to be suspended before it was brought to satisfactory completion, but an example of the type of lactone required *viz*. diethyl 4-phosphonovalero-4-lactone, I, was made from levulinic acid by the reactions:

$$CH_{3}CO \cdot CH_{2}CH_{2}CO_{2}H + (C_{2}H_{5}O)_{2}P(O)H \xrightarrow{\text{NaUC}_{2}H_{1}} \\ O CH_{3} \\ (C_{2}H_{5}O)_{2}P \xrightarrow{[]}{-} C \xrightarrow{-} CH_{2}CH_{2}CO_{2}Na \xrightarrow{p-CH_{3}C_{5}H_{4}SO_{3}H} \\ OH I \\ OH$$

Because of competition from the carboxyl group for the base, more than one equivalent of the latter is necessary to effect interaction, whereas with ordinary ketones a trace suffices. The product, I, is very sensitive to water and alcohols, and could not be isolated in a sufficiently pure condition to warrant quoting a value for the molecular refraction, even after repeated redistillation. It is acknowledged that most 1-hydroxyalkanephosphonates are not stable and easily revert to equilibrium with the components from which they are derived,<sup>4</sup> but one would have expected ring formation in the lactone to prevent this. The triethyl ester obtained by in-

<sup>(1)</sup> R. L. McConnell and H. W. Coover, Jr., J. Am. Chem. Soc., 78, 4450 (1956) and references.

<sup>(2)</sup> Atomic Energy Research Establishment reports C/R 2011; C/R 2012 (1957).

<sup>(3)</sup> R. L. McConnell and H. W. Coover, Jr., J. Am. Chem. Soc., 78, 4453 (1956).

<sup>(4)</sup> V. S. Abramov and N. A. Ilyina, J. Gen. Chem. (U.S.S.R.) (Consultants Bureau English Translation), 24, 121 (1956).

teraction of I with absolute ethanol was even less stable to distillation, but its composition, refractive index, and infrared spectrum were substantially the same as those of the substance produced by the reaction between diethyl hydrogenphosphonate and ethyl levulinate in the presence of a trace of sodium ethoxide.

Two other keto acids were examined. No identifiable product was obtained when pyruvic acid was used in place of levulinic acid although reaction took place; the dimer  $[(C_2H_5O)_2P(O)C(CH_3)-O-CO]_2$  was sought.

Benzoylformic acid (0.1 mole) in ether reacted readily with dimethyl, diethyl, diallyl, diisopropyl, di-n-butyl, di(3,3,5-trimethyl)hexyl, or di-2-phenylethyl hydrogen phosphonates (0.12 mole) in the presence of pyridine (0.12 mole). Subsequent addition of cyclohexylamine (0.1 mole) to the reactions precipitated white crystalline solids with ill-defined melting points, which approximated in composition to the salts with this base of the correspondphenyl(dialkyl phosphono)glycollic acids. ing  $C_{6}H_{11}NH_{3}+$  $(RO)_2P(O)C(OH)(C_6H_5)CO_2^{-1}$ and which were obtained in yields of 95, 75, 49, 61, 50, 42, and 45%, respectively. Recrystallization from a variety of solvents only had the effect of increasing the melting range and lowering its upper limit.

# EXPERIMENTAL

Diethyl 4-phosphonovalero-4-lactone. Sodium (7.9 g., 0.345 mole) was dissolved in ethanol (180 cc.) contained in a 1 liter 3-necked flask fitted with a reflux condenser, a dropping funnel, and a mechanical stirrer. To the cooled solution, diethyl hydrogen phosphonate (45.2 g., 0.328 mole) was added, followed by levulinic acid (38 g., 0.328 mole) in alcohol (50 cc.). The mixture was heated under reflux for 1 hr., the bulk of the alcohol was distilled (180 cc.), and the residue was sucked dry for several hours at the water-pump. Toluene (250 cc.) was then added to the dry product which was dispersed by means of the stirrer and the mixture was heated while toluene (ca. 75 cc.) distilled until the boiling point indicated the absence of alcohol.<sup>5</sup> At this stage, ptoluenesulphonic acid (59 g., 0.343 mole) in toluene (500 cc.) was added by means of a dropping funnel. The distillation of solvent was continued, while the suspension was stirred to prevent serious bumping, until the boiling point indicated the complete removal of water. The mixture was allowed to cool, was then filtered, and the filtrate was distilled, first at atmospheric pressure to remove toluene and then at low pressure, the fraction b.p. 90-140° (0.1-0.2 mm.) being collected. Redistillation gave 50 g. of almost pure lactone, b.p. 100-104° (0.2 mm.),  $n_{\rm D}^{20}$  1.442. Yield 64%

Anal. Calcd. for  $C_8H_{17}O_8P$ : C, 45.77; H, 7.25; P, 13.11. Found: C, 45.63; H, 7.44; P, 13.00.

Acknowledgment. Thanks are due to Mr. P. J. Fydelor for recording the infrared spectrum of the product which is shown in Fig. 1. It was obtained from a cap layer between rock salt plates in a Hilger H 800 double beam instrument. The absence of an absorption peak in the 2410 cm.<sup>-1</sup> region

characteristic of P-H bond stretching is note-worthy.

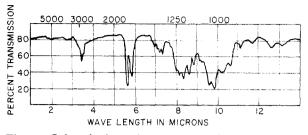


Fig. 1. Infrared absorption spectrum of diethyl 4-phosphonovalero-4-lactone

TABLE I	

PRINCIPAL ABSORPTION PEAK ASSIGNMENTS

Cm1	Assignment	
763 856 900 1020 1045 1134 1203	PC CC=0 or C0C P0C C0C P=-0	
$1252 \\ 1368 \\ 1393 \\ 1445 \\ 1721 \\ 1786 \\ 2900 \\ 2950 \\ 1250 \\ $	Epoxy in C—O—C==O Multiple —CH <sub>3</sub> Assymetric C—CH <sub>3</sub> C==O Aliphatic C—H	

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# Polar, Resonance, and Steric Effects of the 2:3-Benzo Substituent

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We have determined the rate constants of (1) acid-catalyzed esterification, in methanol, of benzoic and 1-naphthoic acids, and (2) alkaline hydrolysis(with sodium hydroxide) of methyl and ethyl benzoates and 1-naphthoates in 56% (w/w) acetone-water. Kinetics of esterification, with hydrogen chloride as catalyst, were followed by a method similar to that of Hartman and Borders,<sup>1</sup> a correction for the effect of product water being applied to the rate equation. Tommila and Hinshelwood's<sup>2</sup> method was used in following ester hydrolysis. Results are given in Tables I and II together

<sup>(5)</sup> It is imperative to remove the alcohol completely, otherwise that remaining reacts with the lactone to give triethyl 4-phosphono-4-hydroxyvalerate.

<sup>(1)</sup> R. J. Hartman and A. M. Borders, J. Am. Chem. Soc., 59, 2107 (1937).

<sup>(2)</sup> E. Tommila and C. N. Hinshelwood, J. Chem. Soc., 1801 (1938).