



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 corresponding phenyl(dialkyl phosphono)glycollic acids,  $(RO)_2P(O)C(OH)(C_6H_5)CO_2^- C_6H_{11}NH_3^+$ , 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, *p*-toluenesulphonic 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.),  $n_D^{20}$  1.442. Yield 64%.

*Anal.* Calcd. for  $C_9H_{17}O_5P$ : 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. Fydeler 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  $cm^{-1}$  region

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

characteristic of P-H bond stretching is noteworthy.

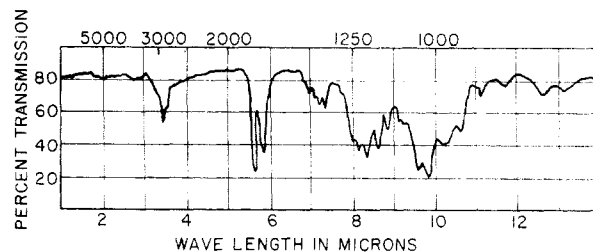


Fig. 1. Infrared absorption spectrum of diethyl 4-phosphonovalero-4-lactone

TABLE I  
PRINCIPAL ABSORPTION PEAK ASSIGNMENTS

$cm^{-1}$	Assignment
763	P—C
856	C—C=O or C—O—C
900	
1020	P—O—C
1045	
1134	C—O—C
1203	P=O
1252	Epoxy in C—O—C=O
1368	Multiple —CH <sub>3</sub>
1393	
1445	Assymmetric C—CH <sub>3</sub>
1721	C=O
1786	
2900	Aliphatic C—H
2950	

CHEMISTRY DIVISION  
ATOMIC ENERGY RESEARCH ESTABLISHMENT  
HARWELL, BERKS, ENGLAND

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

J. PACKER, J. VAUGHAN, AND E. WONG

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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

(1) R. J. Hartman and A. M. Borders, *J. Am. Chem. Soc.*, **59**, 2107 (1937).

(2) E. Tommila and C. N. Hinshelwood, *J. Chem. Soc.*, 1801 (1938).