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 $[(C_2H_5O)_2P(O)C(CH_3)\text{-}O\text{-}CO]_2$ 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.[5] 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. 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.$^{-1}$ region characteristic of P-H bond stretching is noteworthy.

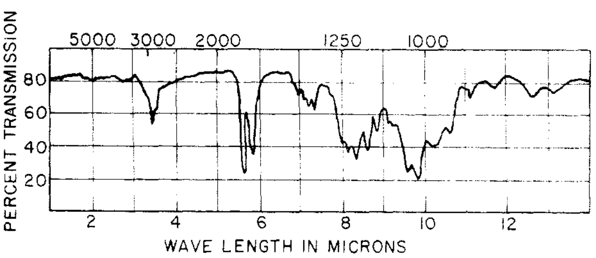

Fig. 1. Infrared absorption spectrum of diethyl 4-phosphonovalero-4-lactone

TABLE I

PRINCIPAL ABSORPTION PEAK ASSIGNMENTS

Cm.$^{-1}$	Assignment
763	P—C
856 900	C—C═O or C—O—C
1020 1045	P—O—C
1134	C—O—C
1203	P═O
1252	Epoxy in C—O—C═O
1368 1393	Multiple —CH_3
1445	Assymetric C—CH_3
1721 1786	C═O
2900 2950	Aliphatic C—H

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

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Received February 7, 1958

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,[1] a correction for the effect of product water being applied to the rate equation. Tommila and Hinshelwood's[2] method was used in following ester hydrolysis. Results are given in Tables I and II together

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

[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).

TABLE I

RATE CONSTANTS FOR THE ESTERIFICATION OF ACIDS IN METHANOL

	$k \times 10^4$ (L. mole^{-1} sec.$^{-1}$)				Derived Data	
Acid	25°	40°	50°	60°	E (kcal. mole^{-1})	$\log_{10}B$
Benzoic	2.10 2.13	7.05 7.06 7.08 7.13	14.82 15.00 15.12	30.0 30.7	15.01 ± 0.03	7.33 ± 0.02
1-Naphthoic	0.859	2.78	6.05 6.25	12.43 12.55	15.15 ± 0.11	7.03 ± 0.07

TABLE II

RATE CONSTANTS FOR THE ALKALINE HYDROLYSIS OF ESTERS IN 56% (w/w) ACETONE-WATER

	$k \times 10^3$ (L. mole^{-1} sec.$^{-1}$)				Derived Data	
Ester	15°	25°	40°	50°	E	$\log_{10}B$
Ethyl benzoate	1.303 1.311	2.98 2.99 3.00 3.03	9.75 9.90	19.87 19.87	14.44 ± 0.03	8.07 ± 0.02
Ethyl 1-naphthoate	0.436	1.000 1.005	3.20 3.20	6.73 6.73	14.46 ± 0.05	7.61 ± 0.03
Methyl benzoate	4.17 4.20	9.62 9.67	30.6 30.8	63.0 63.1	14.33 ± 0.01	8.49 ± 0.01
Methyl 1-naphthoate	1.52	3.46 3.47	11.33	22.87 23.33	14.44 ± 0.04	8.13 ± 0.03

with the derived values of the Arrhenius parameters E and $\log_{10}B$. Rate constants are accurate to 1%.

Taft[3] has shown that the polar substituent constant (σ^*) of ortho groups in *o*-substituted benzoates may be evaluated from the equation

$$\log (k/k_0)_B - \log (k/k_0)_A = \sigma^*(\rho_B^* - \rho_A^*)$$

Using the data of Tables I and II and Jaffé's[4] values of ρ for the unhindered *m*- and *p*- derivatives, the σ^* value for the 2:3-benzo group relative to hydrogen (the relevant k_0 refers to the reaction of the corresponding unsubstituted benzoic ester) has been evaluated. With this σ^* value, the nonpolar contribution (E_s) to the relative rate, has been evaluated (again relative to hydrogen) using the equation

$$E_s = \log k/k_0 - \sigma^*\rho^*$$

Values for both parameters are given in Table III. These figures are derived using log k values obtained from Arrhenius plots of the data in Tables I and II. It should be noted that Taft's σ^* and E_s values for ortho substituents are relative to the methyl group.

Table IV gives energy factors for the formation and hydrolysis of 1-naphthoic esters at 25°. The values of σ^* and E_s (25°) used are the mean values −0.026 and −0.402, respectively.

TABLE III

POLAR AND NONPOLAR CONTRIBUTIONS TO RELATIVE RATE

	σ^{*ac}	$E_s{}^a$	σ^{*bc}	$E_s{}^b$
25°	−0.018	−0.401	−0.033	−0.404
40°	−0.019	−0.396	−0.036	−0.399
50°	−0.022	−0.393		

[a] From formation and hydrolysis of methyl 1-naphthoate; [b] from formation of methyl 1-naphthoate and hydrolysis of ethyl 1-naphthoate; [c] mean value and median deviation of the five σ^* values are −0.026 ± 0.004.

At first sight, it would appear, from Table IV, that (1) the polar and nonpolar contributions to the relative heats of activation are both very small and (2) kinetic energy steric effects ($T\Delta\Delta S^\ddagger$) constitute the dominant factor in reducing the rates of reaction of the 1-naphthyl derivatives. However, the nonpolar contribution to the relative heat of activation is a composite of two terms, one due to resonance effects ($\Delta\Delta E\psi^\ddagger$) and the other due to steric strain ($\Delta\Delta E_R{}^\ddagger$). It seems likely that these two effects are of approximately equal magnitude but of opposing sign, so that the total nonpolar contribution is zero. (The steric requirements of the ester transition state would be expected to be at least comparable with those of the transition state for the Menschutkin reaction of quinoline and methyl iodide, for which $\Delta\Delta E_R{}^\ddagger = 1$ *k*cal.[5]) Upper and lower limits for the rate-increasing resonance effect and hence for the rate-retarding steric strain term may be readily estimated. The loss of resonance energy in passing from ground to

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(3) R. W. Taft in M. S. Newman *Steric Effects in Organic Chemistry*, John Wiley & Sons, Inc., New York, 1956, Chapter 13.

(4) H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

(5) J. Packer, J. Vaughan, and E. Wong, *J. Am. Chem. Soc.*, **80**, 905 (1958).

TABLE IV

ENERGY TERMS (RELATIVE TO BENZOIC ESTERS) FOR 1-NAPHTHOIC ESTER FORMATION AND HYDROLYSIS

Reaction	$\Delta\Delta H^{\ddagger a}$	$-2.303\ RT\ \sigma^*\rho^{*b}$	$-T\Delta\Delta S^{\ddagger c}$	$-2.303\ RT\ E_s{}^d$	$\Delta\Delta H^{\ddagger} + 2.303\ RT\sigma^*\rho^{*e}$
Formation of methyl ester	0.14 ± 0.11	−0.01	0.41	0.54	0.15
Hydrolysis of methyl ester	0.11 ± 0.04	0.06	0.49	0.54	0.05
Hydrolysis of ethyl ester	0.02 ± 0.06	0.06	0.62	0.54	−0.04

[a] Relative heat of activation (ΔE). [b] Relative polar energy of activation ($\Delta\Delta E_0^{\ddagger}$). [c] 2.303 $RT\ \Delta \log B$. [d] Nonpolar contribution to the relative free energy of activation. [e] Nonpolar contribution to the relative heat of activation ($\Delta\Delta H^{\ddagger} - \Delta\Delta E_{\sigma}^{\ddagger}$).

transition state in the hydrolysis of ethyl benzoate, relative to a simple aliphatic ester, is 6 *k*cal. mole^{-1}.[6] If resonance between the ring and side-chain in a 1-naphthoic ester were completely inhibited owing to the steric effect of the fused ring, then the 1-naphthoate would resemble an aliphatic ester in giving a $\Delta\Delta E\psi^{\ddagger}$ value of -6 *k*cal. mole^{-1}. A lower limit for $\Delta\Delta E\psi^{\ddagger}$ may be estimated from relative pK_a values for benzoic (4.20) and 1-naphthoic (3.69) acids. Resonance interaction between ring and side chain is less in the anion than in the parent acid. Some steric inhibition of such resonance in the case of naphthoic acid leads to a smaller decrease in resonance energy for 1-naphthoic acid ionization than for benzoic acid ionization. If this were the sole reason why 1-naphthoic acid is a stronger acid than benzoic acid, then $\Delta\Delta E\psi^{\ddagger}$ for the ionization of 1-naphthoic acid (relative to benzoic) would be -0.7 *k*cal. mole^{-1} (*cf.* ref. 7). This may be accepted as a lower limit for $\Delta\Delta E\psi^{\ddagger}$ for the ester hydrolysis because in this reaction all resonance interaction is frozen out in the transition state. Thus, the strain in the transition states, for hydrolysis and esterification involving simple 1-naphthoic esters, lies between 0.7 and 6 *k*cal. mole^{-1}.

In view of the small value for σ^* (Table III) it would appear that the relative reactivities of 1-naphthyl and phenyl derivatives will usually be governed more by steric than by polar factors.

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[6] M. M. Kreevoy and R. W. Taft, *J. Am. Chem. Soc.*, **79**, 4016 (1957).

[7] Ref. 3, p. 581.

Synthesis of Some New 8,8′-Disubstituted 2,2′-Biquinolines

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Received February 10, 1958

It has been shown[1] that when 2,2′-biquinoline is substituted in the 3-position with a methyl or ethyl group the molar absorptivity of the copper (I) complex is greatly reduced. However, substitution of a phenyl group in this position increases the value of the molar absorptivity. It has been proposed that the molar absorptivity and the stability of the complex are a function of the planarity of the biquinoline molecule and the electron density about the nitrogen atoms of the quinoline nuclei. Substitution of any of these substituents in the 3-position introduces a steric factor that causes distortion from planarity of the 2,2′-biquinoline molecule by rotation of the quinoline moieties about the bond between the 2,2′-positions. The stability of the complex and the molar absorptivity should then decrease. The anomalous behavior of 3-phenyl-2,2′-biquinoline was attributed to increased electron density about the nitrogen atoms of the quinoline nuclei by electron donation of the phenyl group. The resulting increased stability of the copper (I) complex would account for the increase in the value of the molar absorptivity of the complex.

To further test this proposal it was decided to prepare 2,2′-biquinolines substituted in the 8,8′-positions with the methyl, ethyl, and phenyl groups. Spatial models of these compounds indicate that formation of the copper (I) complex would require a similar rotation of the quinoline moieties about the bond between the 2,2′-positions of the biquinoline.

The preparation of 8,8′-dimethyl-2,2′-biquinoline from the reaction of 8-methylquinoline with sodium is claimed in the literature.[2] However, it has since been shown[3] that the application of this method to quinoline yields 2,3′-biquinoline and not the expected 2,2′-biquinoline. Although the yields vary widely when the method of Ueda[4] (reductive coupling using palladium and hydrazine) or the Ullmann reaction[5–7] is applied to the corresponding haloquinolines or haloisoquinolines for the preparation of biquinolines or biisoquinolines products of predictable structure are obtained. Application of the method of Ueda to 2-bromo-8-methylquinoline gave a product indicated by analysis to be 8,8′-

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[1] G. F. Smith and D. H. Wilkins, *Anal. Chim. Acta*, **10**, 139 (1954).

[2] E. Conolly, *J. Chem. Soc.*, 2083 (1925).

[3] K. Ueda, *J. Pharm. Soc. Japan*, **57**, 817 (1937); *Chem. Abstr.*, **32**, 1265 (1938).

[4] K. Ueda, *J. Pharm. Soc. Japan*, **57**, 180 (1937); *Chem. Abstr.*, **33**, 608 (1939).

[5] J. G. Breckenridge, *Can. J. Research B*, **28**, 593 (1950).

[6] F. H. Case and G. Maerker, *J. Am. Chem. Soc.*, **75**, 4920 (1953).

[7] F. H. Case, *J. Org. Chem.*, **17**, 471 (1952).