

1036. *The Transmission of Polar Effects through Aromatic Systems. Part IV.¹ Some Effects of Solvent in the Alkaline Hydrolysis of Ethyl Phenylacetates.*

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The rates of alkaline hydrolysis of a number of substituted phenylacetic esters are reported, extending our study of systems in which the substituent and functional centre are prevented from mesomeric interaction. The results are discussed in relation to the Hammett equation, and are compared with two other series of reactions involving "insulated" systems. The electronic effects of certain substituents are shown to be affected to some extent by the solvent, and other reactions are cited which suggest that this phenomenon is a general one. Attention is drawn particularly to the relative effects of *p*-Me and *p*-Bu^t and to the trimethylammonio-substituent.

IN Part III,¹ the rates of alkaline hydrolysis of ethyl phenylacetate and nine of its mono-substituted derivatives, in aqueous acetone solution at 25°, were reported. The results, discussed in relation to the Hammett equation, were shown to support the theory of van Bekkum, Verkade, and Wepster,² that the σ -value of a substituent depends on the nature of the reaction from which it is derived, and that there is one series of σ -values, designated σ^n , which is appropriate to reaction series where there is no direct resonance interaction between the substituent and the reaction centre. We have extended this investigation to thirteen more substituents, four of which have not previously been studied in systems where the substituent is insulated from the reaction centre by an intervening methylene group. Application of the Hammett equation to the results reveals changes in the electronic effects of substituents with change of solvent. These changes are then examined in the light of similar findings concerning the solvent-dependence of the relative reactivities of benzenoid compounds.

RESULTS AND DISCUSSION

Second-order rate constants for the alkaline hydrolysis of ethyl phenylacetate and thirteen substituted derivatives are set out in Table 1.

TABLE 1.

Rate constants (l. mole⁻¹ sec.⁻¹) for the alkaline hydrolysis of ethyl phenylacetates at 25°.

Subst.	H	<i>p</i> -Bu ^t	<i>p</i> -NMe ₂	<i>o</i> -NO ₂	<i>p</i> -NH ₂	<i>m</i> -OMe	3,4-Benzo
10 ² <i>k</i>	4.48	2.19	2.58	2.60	3.11	4.63	4.88
Subst.	<i>p</i> -Ph	<i>p</i> -I	<i>m</i> -Cl	<i>m</i> -F	<i>p</i> -CN	<i>p</i> -NMe ₃ ⁺ I ⁻	<i>m</i> -NMe ₃ ⁺ I ⁻
10 ² <i>k</i>	4.95	6.89	8.97	9.59	21.7	51.7	90.8

The rate constant for ethyl phenylacetate in Table 1 is a re-determined value which was obtained to ensure a meaningful comparison with those of the *p*-phenyl-substituted and 3,4-benzo-analogue, since the values in these cases are so similar. The new value differs by less than 2% from that previously recorded by us,¹ which is within the limits of the reproducibility that we have reported for these measurements.¹

Certain conclusions may be drawn from the rate constants themselves.

(1) *p*-Ph behaves as a weakly electron-attracting group, for it increases the rate of hydrolysis by about 10% relatively to that of the unsubstituted compound. This effect is an inductive one ($-I$). This result is in contrast to the electron-releasing property indicated by the small negative σ -value of *p*-Ph, as derived by McDaniel and Brown from the

¹ Part III, *J.*, 1961, 3247.

² van Bekkum, Verkade, and Wepster, *Rec. Trav. chim.*, 1959, **78**, 815.

ionization constant of biphenyl-4-carboxylic acid,³ but this is in accord with the theory of van Bekkum, Verkade, and Wepster as σ^n -values for mesomerically electron-releasing groups are uniformly more positive than the corresponding σ -values.² The $-I$ effect of *p*-Ph in biphenyl-4-carboxylic acid is evidently more than offset by the greater resonance energy in the free acid than in the anion which arises from mesomeric interaction of *p*-Ph with CO_2H and $-\text{CO}_2^-$, respectively. The deactivation of the *meta*-position of biphenyl in electrophilic aromatic substitution has also led to the conclusion that the phenyl substituent has an electron-withdrawing inductive effect.⁴

(2) The 3,4-benzo-group behaves analogously, in that the present results indicate it to be weakly electron-withdrawing. The activation of the β -position of naphthalene in electrophilic aromatic substitution⁵ is due to the ability of the nucleus to release electrons by a time-variable mechanism. Fischer *et al.* have assessed the polar properties of the 3,4-benzo-group and similarly shown it to be weakly electron-withdrawing.⁶

(3) The rate-constants in Table I show the electron-withdrawing inductive effect of the NMe_3^+ substituent to be greater from the *meta*- than from the *para*-position, in accord with the conclusions of Roberts, Clement, and Drysdale.⁷

Coloration during Ester Hydrolysis.—When solutions of alkali and ethyl *p*-cyanophenylacetate were mixed, an intense red colour was observed. This decreased in intensity and, when hydrolysis was complete, the resulting colourless solution gave *p*-cyanophenylacetic acid after acidification. Colours were also observed with other esters substituted with mesomerically electron-withdrawing groups. In ethanolic sodium ethoxide, in which the intensity of the colour did not decrease significantly with time, the maximum absorptions were at: *p*- NO_2 , 540; *p*-CN, 535; *p*-COMe, 440; *o*- NO_2 , 600 μ . These groups apparently activate the methylene group with respect to proton-abstraction and a conjugated, coloured anion results. The red colour of an alkaline solution of 4-nitrobenzyl cyanide is due to an anion of similar type.⁸

The *p*-nitro-substituent should activate the methylene protons more strongly than any other group examined, and the following evidence shows that ionization has no effect on the measured rate of hydrolysis, which follows strictly second-order kinetics.

The optical density of a solution of ethyl *p*-nitrophenylacetate in ethanol rose to a maximum as the concentration of added sodium ethoxide was increased. The maximum value, corresponding to complete ionization of the ester, gave $\epsilon = 2.76 \times 10^4$. It was assumed that this value was not greatly solvent-dependent, for the corresponding anion from 4-nitrobenzyl cyanide has $\epsilon_{\text{max}} 2.59 \times 10^4$ in ethanol⁹ and 2.89×10^4 in water.¹⁰ The proportion of the ester ionized at the start of the hydrolyses, calculated by extrapolation of the optical density to zero time, was then estimated as 1.5 and 0.5% in 56% acetone* and 85.4% ethanol, respectively, when the initial concentrations of ester and alkali were $M/100$. Further, these values were the maximum extents of ionization during the reaction. Thus, the rate-constants in the hydrolyses are not invalidated by the occurrence of these acid-base equilibria.

Application of the Hammett Equation to the Results.—A plot of the $\log k$ values for all the substituents we have now studied (except the NMe_3^+ substituents) against σ^n -values is approximately linear (ρ 0.970), but the correlation is unusually poor ($r = 0.976$, $s =$

* The solvent compositions quoted in this paper refer to the percentage by weight of the organic solvent in the aqueous-organic solution.

³ McDaniel and Brown, *J. Org. Chem.*, 1958, **23**, 420.

⁴ de la Mare and Ridd, "Aromatic Substitution," Butterworths Scientific Publns., London, 1959, p. 157.

⁵ Ref. 4, p. 176; see also Eaborn and Taylor, *J.*, 1961, 1012.

⁶ Fischer, Packer, Vaughan, Wilson, and Wong, *J. Org. Chem.*, 1959, **24**, 155.

⁷ Roberts, Clement, and Drysdale, *J. Amer. Chem. Soc.*, 1951, **73**, 2181.

⁸ Caldin and Harbron, *J.*, 1962, 2314.

⁹ Bruylants, Braye, and Schonne, *Helv. Chim. Acta*, 1952, **35**, 1127.

¹⁰ Stearns and Wheland, *J. Amer. Chem. Soc.*, 1947, **69**, 2025.

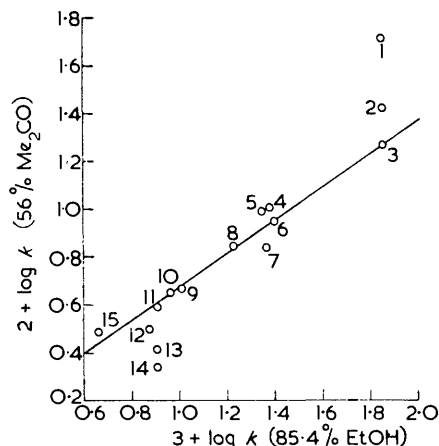
0.07). If the NMe_3^+ substituents are included, the correlation is even worse. This is in marked contrast to the excellent correlation with σ^+ of the ionization constants of phenyl-acetic acids in aqueous solution measured by Fischer and his co-workers¹¹ ($r = 0.994$, $s = 0.019$).

The rates of alkaline hydrolysis of ethyl phenylacetates have been measured in 85.4% ethanol by Watkinson *et al.*¹² Their results are also not well correlated with σ^+ , or with the corresponding results for hydrolysis in 56% acetone (see Figure). The latter unsatisfactory correlation is evidently the result of the change of solvent, for it is only in this respect that the two sets of hydrolyses differ. We note in particular the following:

(1) The straight line drawn in the Figure is closely defined ($r = 0.999$) by the points for hydrogen and the three *meta*-substituents which have been studied in both solvents. The points for *para*-substituents, however, cannot be properly accommodated either by this line or by one constructed specifically for these substituents. The deviations from both the *meta*-line and the "best" straight line through all the points are in most cases well outside the experimental error: in the extreme cases, *p*-Bu^t and *p*-NMe₃⁺, the rates of hydrolysis in 56% acetone would have needed to be faster and slower, respectively, by a

Plot of $\log k$ (56% acetone) against $\log k$ (85.4% ethanol).

Substituents: 1, *p*-NMe₃⁺. 2, *p*-NO₂. 3, *m*-NO₂.
4, *p*-Br. 5, *p*-Cl. 6, *m*-Cl. 7, *p*-I. 8, *p*-F.
9, *m*-OMe. 10, H. 11, *p*-OMe. 12, *p*-Me.
13, *o*-NO₂. 14, *p*-Bu^t. 15, *p*-NH₂.



factor of about 2 in order to be fitted by the *meta*-line. The solvent evidently affects the rate-retarding or rate-enhancing property of a substituent more strongly when it is *para* than when it is *meta* to the functional centre.

(2) In 56% acetone an order of rate constants $\text{H} > \text{Me} > \text{Bu}^t$ obtains, whereas in 85.4% ethanol the order is $\text{H} > \text{Bu}^t > \text{Me}$.¹² This reversal of the relative effects of alkyl groups has been observed in similar systems. Berliner *et al.*¹³ reported the following relative rates for the alkaline hydrolysis of ethyl *p*-alkylbenzoates: (a) in 56% acetone, $\text{H} > \text{Me} > \text{Et} > \text{Pr}^i > \text{Bu}^t$; (b) in 85% ethanol, $\text{H} > \text{Bu}^t > \text{Pr}^i > \text{Et} > \text{Me}$. Again, whereas *p*-Me is more strongly rate-retarding than *p*-Prⁱ in the hydrolysis of ethyl cinnamates in 85.4% ethanol,¹⁴ the order $\text{H} > \text{Me} > \text{Pr}^i$ occurs in the hydrolysis of 4-alkylbenzyl acetates in 56% acetone.¹⁵ Shiner and Verbanic¹⁶ observed a similar reversal for *m*-Me and *m*-Bu^t with change of solvent from 90% ethanol to aqueous acetone in the solvolysis of *m*-alkylbenzhydryl halides.

An analogous situation is encountered in the electrophilic substitution of toluene and

¹¹ Fischer, Mann, and Vaughan, *J.*, 1961, 1093.

¹² Watkinson, Watson, and Yates, following paper.

¹³ Berliner, Beckett, Blommers, and Newman, *J. Amer. Chem. Soc.*, 1952, **74**, 4940.

¹⁴ Brynmor Jones and Watkinson, *J.*, 1958, 4064.

¹⁵ Tommila and Hinshelwood, *J.*, 1938, 1801; Tommila, *Ann. Acad. Sci. Fennicae*, 1942, **59**, A. No. 4.

¹⁶ Shiner and Verbanic, *J. Amer. Chem. Soc.*, 1957, **79**, 369.

t-butylbenzene at their *para*-positions. In most substitutions the Baker-Nathan order of reactivity ($p\text{-Me} > p\text{-Bu}^t > \text{H}$) is observed, but the inductive order ($p\text{-Bu}^t > p\text{-Me} > \text{H}$) occurs in nitration,¹⁷ while in detritiation the relative activating effects depend on the nature of the solvent.¹⁸ The occurrence of the Baker-Nathan order has often been attributed to hyperconjugation, and it is possible that the reversal of the rate-retarding effects of $p\text{-Me}$ and $p\text{-Bu}^t$ in the hydrolyses is due to a reduction in (or elimination of) the hyperconjugative polar effect of $p\text{-Me}$ when the solvent is changed from 85% ethanol to 56% acetone. An explanation based on hyperconjugation is, however, much less probable here than it is for electrophilic substitution, for two reasons. (i) Formation of the electron-deficient transition state in substitutions may bring about preferential release of electrons from $p\text{-Me}$ by a time-variable mechanism (a polarisability effect) which is absent for the unexcited aromatic compound, whereas the greater retarding power of $p\text{-Me}$ than of $p\text{-Bu}^t$ in hydrolysis in 85% ethanol would require that hyperconjugation be present in the isolated molecule since the transition state is electron-rich. (ii) In electrophilic substitution $p\text{-Me}$ is conjugated to the electron-deficient centre, while in the hydrolyses of ethyl phenylacetates it is insulated by a methylene group from the functional centre.

(3) The substituents which deviate most from the *meta*-line include one which is close to the reaction centre ($o\text{-NO}_2$) * and also the largest groups investigated ($p\text{-I}$, $p\text{-Bu}^t$, and $p\text{-NMe}_3^+$). Price and Lincoln suggested that the Bu^t group could, even from the *para*-position, impede solvation of the transition state by a "bulk" effect,¹⁹ and this is possibly relevant to the present results in that use of the solvent of greater polarity, 56% acetone,¹³ where the transition state should be more strongly solvated, and presence of *ortho*-substituents¹² and two of the bulky *para*-substituents ($p\text{-I}$ and $p\text{-Bu}^t$), but not $p\text{-NMe}_3^+$, cause hydrolysis to proceed at a rate which is slow by comparison with that than in the less polar solvent.

(4) The polar substituent, $p\text{-NMe}_3^+$, causes hydrolysis in 56% acetone to be very much faster than expected by comparison with the rate in the less polar solvent: in 56% acetone, the rate-constant for the $p\text{-NMe}_3^+$ ester is greater than those of the *m*- and the $p\text{-NO}_2$ ester¹ by factors of about 3 and 2, respectively, whereas in 85.4% ethanol it is actually slightly less than those of the two nitro-esters.¹² The $p\text{-NO}_2$ substituent shows a similar, but much smaller, rate-enhancement in 56% acetone relative to the *m*- NO_2 group. The *m*- NMe_3^+ substituent, which was not studied by Watkinson *et al.*, shows a very large deviation (as does $p\text{-NMe}_3^+$) in the correlation of the results in 56% acetone with σ^n . (Trimethylanilinium iodide showed no detectable uptake of base in the hydrolytic conditions. A reaction involving attack of base on the trimethylammonio-group would not be facilitated by the presence of *m*- or $p\text{-CH}_2\text{CO}_2\text{Et}$, for this substituent is weakly electron-releasing, as judged by its activation of the *meta*-position of the nucleus in nitration.²⁰ The fast rates cannot therefore be accounted for by such a side-reaction.) Similar large variations in the effect of the NMe_3^+ group with change of solvent have been noted by Roberts and his co-workers⁷ and by Ritchie and Lewis.²¹ The solvent-dependence of the polar effect of $p\text{-NO}_2$ has been noted by Taft,²² who reports σ^a -values (which are similarly based to σ^r -values) of 0.82 for aqueous solution and 0.73 for non-hydroxylic media and most mixed aqueous-organic solvents. This is consistent with this group's more powerful rate-enhancing effect in the more aqueous and polar of the two media compared here. Thus the effect by means of which $p\text{-I}$ and $p\text{-Bu}^t$ cause hydrolysis to be relatively slow in 56% acetone may be less significant, in the case of the polar NMe_3^+ substituents and the

* The behaviour of this and other *ortho*-substituents in these reactions is discussed in detail by Watkinson *et al.*¹²

¹⁷ Knowles, Norman, and Radda, *J.*, 1960, 4885.

¹⁸ Eaborn and Taylor, *J.*, 1961, 247.

¹⁹ Price and Lincoln, *J. Amer. Chem. Soc.*, 1951, **73**, 5836.

²⁰ Knowles and Norman, *J.*, 1961, 2938.

²¹ Ritchie and Lewis, *J. Amer. Chem. Soc.*, 1962, **84**, 591.

²² Taft, *J. Phys. Chem.*, 1960, **64**, 1805.

dipolar *p*-NO₂, than the solvent-dependence of the inherent electron-attracting capacities of these groups.

(5) Ethyl *p*-chlorophenylacetate is hydrolysed faster ($k = 9.71 \times 10^{-2}$ l. mole⁻¹)¹ than the *meta*-isomer under our conditions, in contradistinction to the customary observation that the chloro-substituent is more strongly electron-withdrawing from the *meta*- than from the *para*-position. This unexpected result prompted us to resynthesize the *p*-chloro-ester to check its purity. The new sample proved identical in both physical properties and rate of hydrolysis with that previously used by us.¹

Finally, the unsatisfactory Hammett plot for hydrolysis in 56% acetone is examined by application of the procedure of van Bekkum, Verkade, and Wepster² to the results. This gives $\rho = 0.957$, $r = 0.995$, $s = 0.035$, $n = 7$ (H, *m*-Me, *m*-F, *m*-Cl, *m*-NO₂, *p*-NO₂, *p*-COMe), from which the following σ -values are derived and compared with the corresponding σ^n -values (in parentheses) where these have been computed:² *p*-Bu^t, -0.303; *p*-NMe₂, -0.229 (-0.172); *p*-NH₂, -0.144 (-0.172); *p*-Me, -0.134 (-0.129); *p*-OMe, -0.038 (-0.111); *m*-OMe, 0.036 (0.076); 3,4-benzo, 0.062; *p*-Ph, 0.067; *p*-I, 0.217 (0.299); *p*-F, 0.221 (0.168); *p*-Cl, 0.372 (0.232); *p*-Br, 0.390 (0.265); *p*-CN, 0.737 (0.674); *p*-NMe₃⁺, 1.131 (0.800); *m*-NMe₃⁺, 1.387 (0.885). The σ^n -values for *p*-NMe₂ and *p*-NH₂ are subject to some uncertainty,² and Taft²² gives σ° -values of -0.44 and -0.38, respectively. Even when these groups, and *m*- and *p*-NMe₃⁺, are omitted, however, the mean difference between these σ -values and σ^n -values is 0.07 unit, whereas for the ionization constants of phenylacetic acids the corresponding difference is only 0.01 unit. In particular, in addition to the anomalies discussed above, we find that (a) the σ -values of *p*-OMe, *p*-F, *p*-Cl, and *p*-Br are significantly more positive than their σ^n -values, and (b) *p*-CN shows an enhanced electron-attracting capacity in 56% acetone which may be due a solvent-dependence of its σ^n -value,²² comparable with that of *p*-NO₂.²²

At present, no explanation can be advanced for the effects which have been discussed. Our results emphasize, however, the inherently approximate nature of the Hammett equation, which takes no account of the nature of the solvent. The processes of statistical averaging customarily used in the application of the equation can obscure interesting effects. For example, the change in the relative influence of *p*-Me and *p*-Bu^t with change of solvent is apparently a general phenomenon, yet in terms of the Hammett equation each group should be assigned a unique σ -value.

It also becomes apparent that the unambiguous discernment of small and subtle effects by simple application of the Hammett equation is not always possible. Thus, we suggested earlier that the polar effect of a substituent can affect the resonance interaction of a functional centre with the nucleus, basing the conclusion on deviations from a Hammett plot in which were included certain *para*-substituents which we now realize may behave anomalously in 56% acetone solution.¹ Other independent evidence is therefore necessary to confirm that this effect is significant.

EXPERIMENTAL

Materials.—Most of the substituted phenylacetic esters were prepared by recorded methods. Liquid esters were purified by fractional distillation, and solid esters by chromatography on alumina, followed by recrystallization from light petroleum (b. p. of various ranges). Physical data and references are in Table 3.

Ethyl p-dimethylaminophenylacetate. A mixture of ethyl *p*-nitrophenylacetate¹ (10 g.), 40% aqueous formaldehyde (25 ml.), and 5% palladium-charcoal (5 g.), in ethanol (150 ml.), was shaken under 5 atm. of hydrogen for 45 min. The mixture was filtered and the catalyst extracted with boiling ethanol. Distillation yielded *ethyl p*-dimethylaminophenylacetate (7.1 g., 70%), b. p. 116°/0.25 mm. (Found: C, 69.4; H, 8.35; N, 6.7. C₁₂H₁₇NO₂ requires C, 69.6; H, 8.25; N, 6.75%). The material was converted into its *methiodide*, m. p. 178° (from ethanol) (Found: C, 45.0; H, 5.8; N, 4.2; I, 35.9. C₁₃H₂₀INO₂ requires C, 44.7; H, 5.8; N, 4.0; I, 36.35%).

Methiodide of ethyl m-dimethylaminophenylacetate. Attempted preparations similar to the

TABLE 3.
Phenylacetic acids and their ethyl esters.

Subst.	Acid		Ethyl ester			
	M. p.	Ref.	M. p.	Ref.	B. p./mm.	Ref.
<i>o</i> -NO ₂			65·5°	23		
<i>p</i> -Bu [†]					98°/0·5	24
<i>m</i> -F					110—111°/12	24
<i>m</i> -Cl	75—76°	25			142°/12 *	26
<i>p</i> -Cl	104—105	27	33—33·5	28		
<i>p</i> -I	136—137	29			124°/0·7 †	
<i>m</i> -OMe					143°/12	30
3,4-Benzo	141·5—142·5	31	30	32	158—160°/1·4	
<i>p</i> -Ph	158—159	33	22—22·5	‡		
<i>p</i> -CN	153	34	87—88	§		
<i>p</i> -NH ₂			49—50	35		

* Found: C, 60·8; H, 5·45; Cl, 17·6. Calc. for C₁₀H₁₁ClO₂: C, 60·45; H, 5·6; Cl, 17·85%.
 † Found: C, 41·2; H, 3·9; I, 43·0. C₁₀H₁₁IO₂ requires C, 41·4; H, 3·8; I, 43·7%. ‡ Found: C, 79·55; H, 6·8; C₁₀H₁₀O₂ requires C, 79·95; H, 6·7%. § Found: C, 70·0; H, 5·75; N, 7·6. C₁₁H₁₁NO₂ requires C, 69·8; H, 5·85; N, 7·4%.

above, with ethyl *m*-nitrophenylacetate,¹ were unsuccessful. The product was an intractable, partially methylated mixture. The compound was synthesized as follows. Ethyl *m*-nitrophenylacetate (5 g.), in ethanol (50 ml.), with 5% palladium and charcoal (5 g.), was reduced under 5 atm. of hydrogen for 20 min. The resultant amine was isolated and boiled for 1 hr. with three successive portions of methyl iodide (15 ml.). After the first two treatments the mixture was poured into alkali and extracted with ether. The ether layer was dried (Na₂SO₄) and the ether distilled off. After the third treatment the excess of methyl iodide was distilled off, and the product recrystallized repeatedly from 1 : 1 ethanol–light petroleum (b. p. 60—80°), giving the *methiodide* (3·2 g., 38%), m. p. 115° (Found: C, 44·9; H, 5·8; N, 3·95; I, 36·25%).

Rate Measurements.—The procedure has already been described.¹

Simulated ester hydrolyses were performed with trimethylanilinium iodide. This salt did not react measurably with alkali in $\frac{1}{2}$ hr.

From the hydrolysis of ethyl *p*-cyanophenylacetate, the acidic material was isolated and identified as *p*-cyanophenylacetic acid, m. p. and mixed m. p. 150—151°.

The time-variable coloration of ethyl *p*-nitrophenylacetate in alkali was followed by visible spectrophotometry, a Unicam S.P. 500 instrument being used. The solutions in aqueous ethanol were made up as described by Brynmor Jones and Watkinson.¹⁴ With ester and alkali both *N*/100, 2 mm. cells were used. Graphs of (optical density)⁻¹ against time were linear, and were extrapolated to zero time.

A *M*/200-solution of ethyl *p*-nitrophenylacetate in ethanol was diluted 100-fold and 2 ml. of the resultant solution were added to solutions containing varying concentrations (up to about 1*N*) of sodium ethoxide in ethanol. A graph of the optical density of such solutions against ethoxide concentration was a smooth curve whose maximum was used to estimate the extinction coefficient.

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²⁶ Boon, Carrington, Greenhalgh, and Vasey, *J.*, 1954, 3263.

²⁷ Straus, *Annalen*, 1912, **393**, 317.

²⁸ Mehner, *J. prakt. Chem.*, 1900, **62**, 565.

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³⁰ Pschorr, *Annalen*, 1912, **391**, 45.

³¹ Newman, *J. Org. Chem.*, 1944, **9**, 518.

³² Wislicenus and Elvert, *Ber.*, 1916, **49**, 2827.

³³ Schwenk and Papa, *J. Org. Chem.*, 1946, **11**, 798.

³⁴ Jaeger and Robinson, *J.*, 1941, 744.

³⁵ Pyman, *J.*, 1917, **111**, 169.