hydroxy-α-methyl-β-phenylbutyramide and 75 ml. of 88% formic acid there was obtained 14.8 g. (80%) of N,N-diethyl-α,β-dimethylcinnamamide, b.p. 123–126° (1 mm.) and at 117–118° (0.75 mm.) on redistillation.

Anal. Calcd. for $C_{15}H_{21}ON$: C, 77.88; H, 9.15; N, 6.06. Found: C, 77.40; H, 9.08; N, 6.02.

DURHAM, N. C.

[CONTRIBUTION FROM THE MARION EDWARDS PARK LABORATORY OF BRYN MAWR COLLEGE]

The Hydrolysis of Substituted Ethyl *p*-Biphenylcarboxylates

BY ERNST BERLINER AND LIANG HUANG LIU[1]

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The rates of hydrolysis of substituted ethyl *p*-biphenylcarboxylates have been determined at 25 and 40° and compared with those of substituted ethyl benzoates. The substituent effects are qualitatively the same in both systems, but the transmission of the effects is only about one-fourth as large in the biphenyl esters as in ethyl benzoates.

As a result of a study of the dissociation constants of various substituted *p*-biphenylcarboxylic acids,[2] it was concluded that substituent effects can be transmitted through the biphenyl system. Substituents in the ring not carrying the carboxyl group influence the dissociation constants qualitatively in the same way in which the same substituents influence the dissociation constants of benzoic acids. Quantitatively the transmission is appreciably less in the biphenyl than in the benzene system, *i.e.*, rho[3] is only about one-third as large for the dissociation of biphenylcarboxylic acids as for benzoic acids. Because dissociation constants are concerned with permanent polarities only, it seemed worthwhile to study the behavior of the biphenyl system in a chemical reaction, where polarizability effects can also be observed. In order to make the comparison between the benzene and the biphenyl structure expressible in terms of the reaction constant, ρ, the rates of the alkaline hydrolysis were determined for the esters of those substituted biphenylcarboxylic acids whose dissociation constants had previously been measured.

In Table I are listed second-order rate constants at 25 and 40° for the alkaline hydrolysis of these esters, as well as energies of activation and log *PZ* factors. The reactions were conducted with equal concentrations of ester and hydroxide ion in 88.7% by weight aqueous ethanol. The conditions were similar to those employed by Evans, Gordon and Watson,[4] and by Kindler,[5] except that the alcohol concentration was somewhat larger, because of the low solubility of some of the esters.

TABLE I

RATES OF HYDROLYSIS OF SUBSTITUTED ETHYL *p*-BIPHENYLCARBOXYLATES IN 88.7% ETHANOL

Substituent	$k_2^{25} \times 10^4$, l.m.$^{-1}$ sec.$^{-1}$	$k_2^{40} \times 10^3$, l.m.$^{-1}$ sec.$^{-1}$	*E*, kcal.	log *PZ*, l.m.$^{-1}$ sec.$^{-1}$
4'-OCH_3	3.55 ± 0.03	1.56 ± 0.005	18.3 ± 0.2	9.96
4'-CH_3	4.37 ± .05	1.90 ± .02	18.2 ± .3	9.98
4'-H	5.50 ± .06	2.32 ± .02	17.8 ± .2	9.79
4'-Cl	7.52 ± .05	3.13 ± .02	17.6 ± .2	9.78
4'-Br	7.60 ± .05	3.18 ± .01	17.7 ± .2	9.85
3'-Br	9.32 ± .1	3.88 ± .03	17.6 ± .2	9.87
3'-NO_2	....	5.95 ± .03	....	...
4'-NO_2	15.8 ± .15	6.58 ± .05	17.6 ± .2	10.10

The substituents have the same qualitative effect on the biphenyl esters that they have on ethyl benzoate hydrolysis. The rate-determining step is a nucleophilic attack, and the favorable effect of electron-attracting groups is relayed through the two benzene rings. The 4'-methoxy compound is the slowest and the 4'-nitro compound the fastest, even though the over-all spread between these two extreme compounds is considerably less than in the corresponding ethyl benzoates. The spread in activation energies between the fastest and the slowest compounds is only 0.7 kcal., compared to 4.15 kcal. in benzoate hydrolysis,[6] but the log *PZ* factors are of similar magnitude, indicating no unusual differences in a steric sense between the two systems. Although the differences in activation energies are small, the general pattern of rate differences being determined by differences in activation energies, with the log *PZ* factors remaining constant, is discernible.

When the logarithms of the rate constants are plotted against Hammett's σ-values, the usual linear relationship is obtained (Fig. 1).[3] The least square line has a slope (ρ) of $+0.623$ with a median deviation of 0.0089. At 40°, ρ is $+0.594$ and r is 0.0066. The most comparable literature data for the alkaline hydrolysis of substituted ethyl benzoates at 25° are those reported for reaction in 85% by weight ethanol.[4,6] For that reaction ρ is calculated to be $+2.567$ ($n = 14$, $r = 0.043$). Assuming that the small difference in solvent composition will not alter ρ appreciably, in ester hydrolysis the biphenyl system transmits only about one-fourth as much of the effect of substituents as can be relayed through the benzene system, compared to the value of one-third found in the case of the dissociation constants.

It might have been expected that the relative ρ-values for dissociation constants and ester hydrolysis would be more nearly alike. However, in Table II are collected data for similar systems, in which ρ-values for dissociation constants are compared with those of ester hydrolysis. The reaction constant for the hydrolysis of ethyl phenylpropionates was calculated from the data of Kindler,[7]

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(1) Helen Schaeffer Huff Memorial Post-doctorate Fellow, 1949–1950.

(2) E. Berliner and E. A. Blommers, THIS JOURNAL, **73**, 2479 (1951).

(3) L. P. Hammett, "Physical Organic Chemistry," McGraw–Hill Book Co., Inc., New York, N. Y., 1940, Chapter VII.

(4) D. P. Evans, J. J. Gordon and H. B. Watson, *J. Chem. Soc.*, 1430 (1937).

(5) K. Kindler, *Ann.*, **450**, 1 (1926).

(6) C. K. Ingold and W. S. Nathan, *J. Chem. Soc.*, **222** (1936).

(7) K. Kindler, *Ann.*, **452**, 90 (1927). ρ is $+0.488$, n is 4 and r is 0.025.

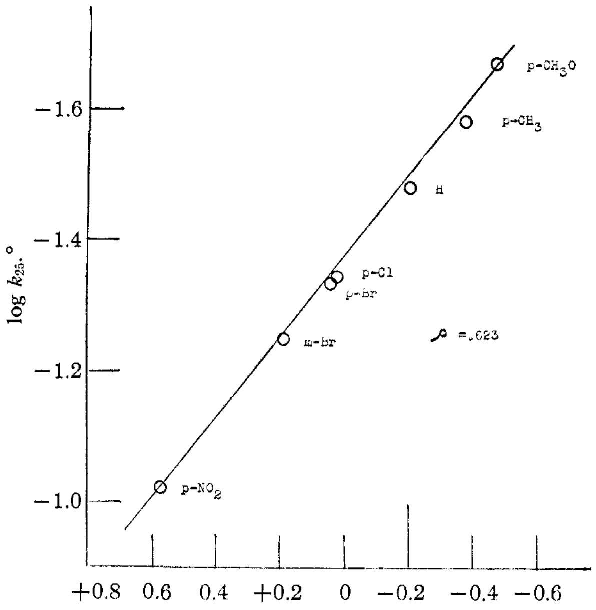

Fig. 1.—A plot of log k_{25} against Hammett's σ-constants.

but only four points are available. In every case, except one, the relative ρ is less in ester hydrolysis than in the equilibrium between the acid and its anion, *i.e.*, in those systems in which substituent effects are transmitted beyond one benzene ring, the transmission appears stronger when the substituents affect the dissociation constants than when they affect the ester hydrolysis. This is perhaps due to the fact that some extent of transmission occurs in both the acids and their anions, and substituents that favor removal of the proton also stabilize the anion, so that the substituent effect is magnified. In ester hydrolysis only the approach of the reagent is affected by the substituent,[8] and transmission is broken in the transition state. The conjecture that polarities are transmitted through saturated chains (and the benzene ring) better than polarizabilities is in fact not supported by other evidence. But in the ethyl cinnamates, the high polarizability of the double bond must be responsible for the relatively large ρ in hydrolysis, and the extent of transmission, therefore, comes closest to that in benzene. The second phenyl ring in biphenyl appears then to be less polarizable than the olefinic double bond.[9]

TABLE II

ρ-VALUES FOR DISSOCIATION CONSTANTS AND ESTER HYDROLYSIS

Acid or ethyl ester	ρ (acid dissociation)	ρ (ester hydrolysis)	Rel. ρ (ester hydrolysis)
Benzoic	1	2.498	1
Phenylacetic	0.471	0.824	0.330
Cinnamic	.466	1.329	0.532
Biphenylcarboxylic	.37	0.623[a]	0.243[a]
Phenylpropionic	.212	0.488	0.195

[a] At 25°; the other ρ-values for the ester hydrolyses refer to reaction at 30°. Data taken from reference 3.

As with the acids, the ρ-values for the biphenyl esters fall between phenylacetates (and cinnamates) and phenylpropionates. If biphenyl were as good a conductor of substituent effects as benzene, which one could be led to believe from inspecting the conventional resonance forms, a higher ρ-value would have been expected. That this is not so, does not necessarily mean that there is no conjugation across the rings. The same combination of electrostatic and resonance effects of substituents—reflected in their σ-values—that is responsible for the changes in the rates of hydrolysis of ethyl benzoates, must also be responsible for the analogous, but weaker, changes in the biphenyl system. The extent of weakening through the biphenyl system, may be a measure of both the long distance of the substituents from the reaction center, which will dampen electrostatic effects appreciably, and the lack of complete coplanarity of the two rings. Complete coplanarity might manifest itself in the activation entropies, for it would entail the "freezing" of the molecule in a fixed position. Such loss of free rotation should lower the frequency factor as compared to that in the benzene reaction, unless freedom of rotation were already restricted in the ground state. However, the log *PZ* factors are of the same order of magnitude as those in benzoate hydrolysis (9.79 to 9.73[6] or 9.78[4] for the two unsubstituted esters). It is therefore concluded that while some of the dampening of the substituent effects is a distance effect, some might be due to the absence of appreciable coplanarity, which is necessary for effective conjugation.[10] In spite of the weakening of the relay effect, substituent effects *can* be transmitted through the biphenyl system and the conjugation of the two rings does exist, contrary to what could be expected by merely considering the directive influence on benzene of substituted phenyl groups in electrophilic aromatic substitution.[2] The conclusion is complementary to that obtained from the measurement of the dissociation constants.

From the data obtained for the hydrolysis of ethyl biphenylcarboxylates and for the dissociation of the corresponding acids, as well as the ρ-values for the same reactions of benzoic acids, it is possible to calculate σ-constants for substituted *p*-phenyl groups. The data thus obtained are assembled in Table III. For ρ of ethyl benzoate hydrolysis Kindler's data[5] at 30° in 87.83% ethanol were used, and the present data were recalculated to 30°. This, as well as the slightly different solvent composition will introduce some errors, but considering the smallness of the constants, the agreement between the two sets of data in Table III is not bad. The constants show the same relative order as the σ-constants of the substituents proper, but the spread is much less. Roughly, the whole group of

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[8] J. N. E. Day and C. K. Ingold, *Trans. Faraday Soc.*, **37**, 686 (1941).

[9] See also "Physical Aspects of Organic Chemistry," 4th Ed., by W. A. Waters, D. Van Nostrand Co., Inc., New York, N. Y., 1950, p. 287.

[10] For a recent example of the lack of complete coplanarity in biphenyl and the effect of this on absorption spectra, see R. B. Sandin, R. Melby, A. S. Hay, R. N. Jones, E. C. Miller and J. A. Miller, THIS JOURNAL, **74**, 5073 (1952).

TABLE III

SIGMA CONSTANTS FOR SUBSTITUTED 4-PHENYL GROUPS

Substituent	σ (from hydrolysis)	σ (from diss. constant)[2]	σ (av.)	Deviation from mean
4-*p*-Aminophenyl		−0.303	(−0.303)	
4-*p*-Hydroxyphenyl		− .242	(− .242)	
4-*p*-Methoxyphenyl	−0.0627	− .114	− .088	0.025
4-*p*-Methylphenyl	− .0284	− .0682	− .048	.02
4-Phenyl	+ .011	− .0455	− .017[a]	.028[a]
4-*p*-Chlorophenyl	+ .0644	+ .0985	+ .081	.017
4-*p*-Bromophenyl	+ .0668	+ .0985	+ .083	.016
4-*m*-Bromophenyl	+ .102	+ .0833	+ .093	.01
4-*m*-Nitrophenyl	+ .177[b]	+ .189	+ .183	.006
4-*p*-Nitrophenyl	+ .194	+ .265	+ .229	.036

[a] Hammett's value for *p*-phenyl is +0.009 with a median deviation of 0.22. If the experimental value for pK of benzoic acid, rather than the one extrapolated from the least square line, is used, sigma (from diss. constant) for *p*-phenyl becomes −0.008. [b] Calculated assuming an activation energy of 17.6 kcal.

substituents, from the 4-*p*-methoxyphenyl to the 4-*p*-nitrophenyl groups, can be placed between the *p*-alkyl groups and the *p*-halogens.[11]

Some interest attaches itself to the character of the phenyl group itself, when it acts as a substituent. The present σ-value of the phenyl group (+0.009) indicates a very small electron attraction and was obtained from Kindler's data on the hydrolysis of ethyl biphenylcarboxylate in 87.83% ethanol at 30°,[5] under which conditions the biphenyl ester reacted slightly faster than ethyl benzoate (0.0536:0.0490). Although the solvents are not strictly comparable, a recalculation of the present value to 30° gives the almost identical rate constant of 0.0541 l.m.$^{-1}$ min.$^{-1}$. The activation energies for the alkaline hydrolysis of ethyl biphenylcarboxylate and ethyl benzoate are almost identical.[4,6] How close the rate constants of the two compounds are can be seen from the fact that in 56% acetone, ethyl biphenylcarboxylate is reported to react actually somewhat slower than ethyl benzoate (2.68:2.89), but the difference is not due to a corresponding difference in the activation energies.[12] The pK for biphenylcarboxylic acid is practically indistinguishable from that of benzoic acid (5.66:5.65), and the phenyl group is, if anything, slightly electron releasing. In all these cases the effect of the phenyl group is very small.

Because of the greater electronegativity of aromatic carbon compared to aliphatic carbon, the phenyl group is an intrinsic electron attractor when attached to saturated carbon.[13] In conformity, phenylacetic acid is a stronger acid than acetic acid,[14] and ethyl phenylacetate is hydrolyzed faster than ethyl acetate.[7] The situation is different, however, when the phenyl group is attached directly to the carboxyl group, and when comparison is made between formic and benzoic acid. Formic acid is appreciably stronger than benzoic acid and ethyl formate is hydrolyzed many times faster than ethyl benzoate.[7] The reason is the conjugation between the phenyl and the carboxyl groups which is present in benzoic acid.[15] This conjugation is partly destroyed in the benzoate ion and is wholly eliminated in the transition state of ester hydrolysis. The phenyl group therefore acts as if it had an electron releasing effect, but the reason for the reversal is the preservation of conjugation between the phenyl and the carboxyl group. The second benzene ring in biphenyl should assist that process and should have a slight electron releasing effect if the conjugation effect is stronger than that produced by the electronegativity of the phenyl group. As with biphenylcarboxylic acid, the *p*-phenyl group has very little, but if anything an electron releasing, effect on the dissociation constant of benzeneboronic acid (pK 10.80:10.79).[16] But *m*-biphenylboronic acid and *m*-biphenylcarboxylic acid, where the phenyl group cannot be of much assistance in preserving conjugation, are both stronger than benzeneboronic and benzoic acid, respectively.[16,17] That the *p*-phenyl group, by distributing a positive charge, can act as an electron releasing and the *m*-phenyl as an electron attracting group, has recently also been stated by Lichtin and Glazer.[18]

The small effect of a phenyl group, discussed here, is not necessarily a true indication of the effect of a phenyl group in all possible situations. As with many substituents, the effects are much greater where strong resonance interaction of the substituent and the reacting group is possible (which is not the case with acid derivatives), or where it can be enhanced in the transition state. 4-Aminobiphenyl is an appreciably weaker base than aniline (σ is +0.11),[19] and *p*-phenylphenol is over seven times stronger than phenol (σ +0.419).[20] The *p*-phenyl group has also a strong electron attracting effect in the reaction of 2,4-dinitrochlorobenzene with substituted anilines (σ +0.179).[21,22] In these cases the *p*-phenyl group appears to be more strongly electron attracting than is indicated by its σ-value. No comparative data are available for reactions in which the phenyl group appears electron releasing by accommodating a positive charge. It increases the dissociation of triphenylmethyl chloride in sulfur dioxide by a factor of about six,[23] and in preparative chemistry biphenyl is known to be appreciably more reactive toward electrophilic substitution than benzene and can be acetylated in benzene as a sol-

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(11) The constants in Table III probably only apply to reactions and equilibria involving biphenylcarboxylic acids or their derivatives.

(12) E. Tommila, L. Brehmer and H. Elo, *Ann. Acad. Sci. Fennicae*, **59**, No. 9, 3 (1942) [*C. A.*, **38**, 6174 (1944)].

(13) A. D. Walsh, *Disc. Faraday Soc.*, **2**, 18 (1947).

(14) J. F. J. Dippy, *Chem. Revs.*, **25**, 151 (1939).

(15) A. E. Remick, "Electronic Interpretations of Organic Reactions," 2nd ed., John Wiley and Sons, Inc, New York, N. Y., 1949, p. 420 ff. M. J. S. Dewar, "The Electronic Theory of Organic Chemistry," The Clarendon Press, Oxford, 1949, p. 159.

(16) D. L. Yabroff, G. E. K. Branch and B. Bettman, THIS JOURNAL, **56**, 1850 (1934).

(17) N. N. Lichtin and H. P. Leftin, *ibid.*, **74**, 4207 (1952).

(18) N. N. Lichtin and H. Glazer, *ibid.*, **73**, 5537 (1951); also ref. 17.

(19) N. F. Hall and M. R. Sprinkle, *ibid.*, **54**, 3469 (1932).

(20) E. O. Woolfolk, C. Golumbic, R. A. Friedel, M. Orchin and H. H. Storch, *Bulletin 487*, Bureau of Mines, United States Government Printing Office, Washington, 1950.

(21) H. J. Van Opstadt, *Rec. trav. chim.*, **52**, 901 (1933).

(22) At 200° only 15% of iodobenzene, but 28% of *p*-iodobiphenyl reacts with piperidine. Unpublished results with Mrs. P. Jones Edgerton.

(23) Reference 18 and N. N. Lichtin and P. D. Bartlett, THIS JOURNAL, **73**, 5530 (1951).

vent.[24] It is halogenated many times more rapidly[25] and benzoylated several times faster than benzene.[26] It has, of course, always been stated that the phenyl group can act both as an electron sink and source[27]; whether it reacts one way or the other depends on the system and the reaction, and it is therefore also clear that the phenyl group has to be classified with those substituents to which at least two σ-values, including some of opposite sign, have to be assigned.

Experimental

Preparation of Esters.—All acids were prepared by hypohalite oxidation of the corresponding methyl ketones by the methods described before.[2,28] 4'-Methyl-*p*-biphenylcarboxylic acid was obtained in 73% yield and melted at 244–246° (lit.[29] 245°). The necessary ketone, *p*-tolylacetophenone, was prepared in 75% yield from *p*-methylbiphenyl[30] by a Friedel–Crafts acylation in carbon bisulfide, m.p. 121–121.4° (cor.), white plates from ligroin. *Anal.* Calcd. for $C_{15}H_{14}O$: C, 85.68; H, 6.71. Found: C, 85.43; H, 6.52. (This analysis was carried out by Miss J. Leeds.)

The acids were esterified by the usual method with absolute ethanol and concentrated sulfuric acid.[31] The esters were crystallized several times from absolute ethanol, except for the unsubstituted and the *p*-methyl compounds, which were crystallized from petroleum ether. The corrected melting points, neutralization equivalents and analyses of the new esters are listed below.

Substituent in ethyl *p*-biphenylcarboxylate	M.p., °C.	Neut. equiv. Found	Neut. equiv. Calcd.
4'-OCH_3	105.6–105.8[a]	257	256.3
4'-CH_3	80.0–80.5[b]	239.5	240.3
4'-H	49.2–49.6 (lit.[32] 46)	224.3	226.3
4'-Cl	73.3–73.8[c]	259.4	260.7
4'-Br	74.8–75.5[d]	304.5	305.2
3'-Br	70.0–70.5 (lit.[2] 69.3–70.1)	305	305.2
3'-NO_2	114.0–114.5 (lit.[2] 113.7–114.4)	268.3	271.3
4'-NO_2	115.3–115.6 (lit.[33] 112)	273.2	271.3

[a] *Anal.* Calcd. for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29. Found: C, 75.24; H, 6.54. [b] *Anal.* Calcd. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 80.25; H, 6.81. [c] *Anal.* Calcd. for $C_{15}H_{13}O_2Cl$: C, 69.10; H, 5.03. Found: C, 69.09; H, 5.20. [d] *Anal.* Calcd. for $C_{15}H_{13}O_2Br$: C, 59.03; H, 4.29. Found: C, 59.33; H, 4.50.

Kinetic Measurements.[4,5]—Sufficient carbon dioxide-free aqueous ethanol (d^{25}_{25} 0.81943, 88.7% by weight) was prepared from purified absolute ethanol[34] to last for all kinetic runs. The alcoholic hydrolyzing agent was made up from metallic sodium and the aqueous ethanol in small quantities. Because the sodium salts of some of the acids precipitated as hydrolysis proceeded, the usual technique of withdrawing samples was replaced by the following method: Approximately 60 ml. of the hydrolyzing solution was thermostated, and 5-ml. portions were pipetted into twelve 50-ml. erlenmeyer flasks provided with ground-glass stoppers. Two samples were immediately titrated with standard hydrochloric acid. An exact amount of ester was dissolved in the solvent, and after thermostating, 10-ml. samples of ester solution, each exactly equivalent to 5 ml. of the sodium hydroxide solution, were pipetted into each flask. The half-delivery time of the ester solution was recorded and, after suitable time intervals, 10 ml. of standard hydrochloric acid was added to a flask and the excess acid was back-titrated with standard barium hydroxide solution after addition of 3 ml. of pure carbon tetrachloride. Phenolphthalein was used as an indicator. Rate constants were calculated from the integrated form of the second-order rate equation for equal concentrations. The concentrations of reactants were between 0.025 and 0.03 *M*, except for the nitro compounds, when they were between 0.01 and 0.015 *M*. In order to correct any error due to hydrolysis of ester during solution in aqueous ethanol, the following procedure was used with each run: To 5 ml. of sodium hydroxide solution was added 10 ml. of hydrochloric acid, followed by 10 ml. of ester solution. This was cooled and titrated with *B* ml. of barium hydroxide of normality *N*. If the volume of barium hydroxide, equivalent to 10 ml. of hydrochloric acid, is *A*, the initial concentration of ester and alkali is $(A - B) \times N \times {}^1/_{15}$ and the barium hydroxide titer at infinite time is $A - B$. Two typical runs are recorded above. The errors recorded in Table I are average errors, and the errors in *E* are estimated from the largest and smallest values of *k* at the two temperatures. Runs were usually conducted in duplicate.

THE ALKALINE HYDROLYSIS OF ETHYL 4'-METHYL-*p*-BIPHENYLCARBOXYLATE AT 25°

[Ester] = [OH^-] = 0.02857 *M*

Time, min.	$Ba(OH)_2$, ml.	*x*	k_2, l.m.$^{-1}$ min.$^{-1}$
0	0.748	...	....
406.9	2.837	2.089	0.0261
501.7	3.220	2.472	.0266
596.3	3.540	2.792	.0266
688.9	3.820	3.072	.0265
1329	5.200	4.452	.0260
1449	5.514	4.666	.0262
1595	5.625	4.877	.0262
1726	5.808	5.060	.0263
∞	8.962		

THE ALKALINE HYDROLYSIS OF ETHYL 4'-NITRO-*p*-BIPHENYLCARBOXYLATE AT 40°

[Ester] = [OH^-] = 0.01164 *M*

Time, min.	$Ba(OH)_2$, ml.	*x*	k_2, l.m.$^{-1}$ min.$^{-1}$
0	1.980	...	...
59.5	3.615	1.635	0.397
86.3	4.133	2.153	.395
105.1	4.442	2.467	.395
164.2	5.230	3.255	.394
207.2	5.670	3.695	.395
256.0	6.075	4.095	.395
312.4	6.460	4.480	.397
∞	7.578		

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(24) W. S. M. Grieve and D. H. Hey, *J. Chem. Soc.*, 969 (1933). This reaction, however, does not lend itself to large scale preparations. See L. F. Fieser, M. T. Leffler, *et al.*, THIS JOURNAL, **70**, 3174 (1948), part VI.

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(27) C. K. Ingold, *Chem. Revs.*, **15**, 225 (1934).

(28) We are indebted to Dr. H. E. Schroeder of E. I. du Pont de Nemours and Co., Wilmington, Del., for samples of 4-biphenylcarboxylic acid and 4'-nitro-*p*-biphenylcarboxylic acid, and to Dr. D. T. Mowry of the Monsanto Chemical Company, Dayton, Ohio, for samples of *p*-acetylbiphenyl and *p*-chlorobiphenyl.

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(30) W. E. Bachmann and R. A. Hoffman in Adams, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 224.

(31) L. F. Fieser, "Experiments in Organic Chemistry," 2nd ed., D. C. Heath and Co., Boston, Mass., 1941, p. 62.

(32) O. Doebner, *Ann.*, **172**, 114 (1874).

(33) W. S. M. Grieve and D. H. Hey, ref. 24.

(34) Reference 31, p. 358.