Effect of Structure on Basicity.—When the data of Table I are considered for use in making ρ–σ correlations, the general nature of the correlation pattern is evident, and indeed has been anticipated in the preceding discussion. However, as the protonation equilibria do not follow H_0 with unit slope (*i.e.*, the slope of a plot of log $[BH^+/B]$ *vs.* H_0 is not unity), there is some ambiguity in the value to be gained from a complete numerical treatment of the basicities of the substituted benzoylbenzoic acids. In addition to the data which we have presented here Vinnik[47] recently reported data on two other substituted benzoylbenzoic acids. His reported data for *o*-(3,4-dimethylbenzoyl)benzoic acid and *o*-(2-chlorobenzoyl)benzoic acid are in accord with ours, with the exception of the value for the parent compound.

Hammett Base Character of the Protonated Benzoylbenzoic Acids.—The summarized slopes of log $[BH^+/B]$ *vs.* H_0 show that the benzoylbenzoic acids are not behaving as ideal Hammett indicators. Such deviation from ideality is also shown by substituted benzophenones; the slope for benzophenone is *ca.* 0.86, and that for *p,p'*-dimethoxybenzophenone is 0.87.

Such deviations have been ascribed to differences in the solvation requirements of ions of different structure. The difference between primary and tertiary amines has been ascribed to changes in solvation requirements,[5] and similar arguments have been advanced as an explanation of the behavior of amides as weak bases.[16a] It would appear reasonable that a like explanation is valid also in the present instance. Unfortunately the spectral changes accompanying the protonation of benzoylbenzoic acid are complex. There is a considerable bathochromic medium shift (apparently common for oxygen bases; *cf.* benzalacetophenone[8] and benzoic acid[41]). This factor, coupled with the subsequent structural changes in more concentrated sulfuric acid, precludes the determination of extremely precise data for this family of compounds. Hence the general pattern is clear, but the precision of the data is only moderate. Benzoylbenzoic acids are weak bases, protonate at the ketonic carbonyl group, and generally do not behave as primary aniline Hammett bases; the effect of substituents on basicity is in accord with this expectation.

[47] M. I. Vinnik, R. S. Ryabova, and N. M. Chirkov, *Zh. Fiz. Khim.*, **33**, 1992 (1959); *Russ. J. Phys. Chem.* (Eng. Transl.), **33**, 253 (1959); M. I. Vinnik, R. S. Ryabova, and G. V. Belova, *Zh. Fiz. Khim.*, **36**, 942 (1962); *Russ. J. Phys. Chem.*, (Eng. Transl.), **36**, 495 (1962); M. I. Vinnik, R. S. Ryabova, Zh. E. Grabovskaya, Kh. Koslov, and I. Kubar, *Zh. Fiz. Khim.*, **37**, 94 (1963); R. S. Ryabova and M. I. Vinnik, *ibid.*, **37**, 2529 (1963).

The Effect of Substituents upon the Formation of the Lactol Carbonium Ion of Benzoylbenzoic Acid[1–4]

DONALD S. NOYCE AND PAUL A. KITTLE[4]

Department of Chemistry, University of California, Berkeley, California 94720

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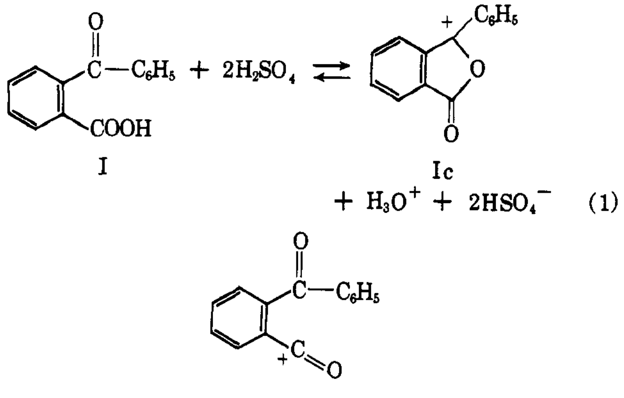
It is shown by consideration of structural effects and spectral characteristics that the lactol carbonium ion (Ic) is the best representation of *o*-benzoylbenzoic acid in concentrated sulfuric acid. Correlations of the effect of structure on the ease of formation of Ic are best with σ^+ values, ρ being 1.83.

In conjunction with other studies[2,5] we have had occasion to examine the behavior of a group of substituted *o*-benzoylbenzoic acids in 90–100% sulfuric acid. Newman, Kuivila, and Garrett[6] have shown that *o*-benzoylbenzoic acid (I) undergoes "complex ionization" (eq. 1) in 100% sulfuric acid in support of the earlier suggestion of Newman[7] that the dominant species in such solutions is Ic. Newman considered it less likely that the major species in 100% sulfuric acid is the open-chain acylium ion Id, since a mixture of normal and pseudo-ester is obtained on pouring a solution of I in 100% sulfuric acid into methanol. Long and Paul[8] have pointed out that the cryoscopic results[6] do not serve to distinguish between Ic and Id. Vinnik, Ryabova, and Chirkov[9] have obtained data showing that the product of complex ionization is formed to the extent of 50% in 96% sulfuric acid, though they prefer to describe it in terms of structure Id.



I

Ic

$$+\ H_3O^+ + 2HSO_4^- \qquad (1)$$

Id

It is the purpose of the present report to describe the results of measurements relating to the effect of substituents on the ease of formation of the lactol carbonium ion Ic; it will also be clear that Ic is the better structure for the dominant species in solution in 100% sulfuric acid.

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[1] Previous paper: D. S. Noyce and P. A. Kittle, *J. Org. Chem.*, **30**, 1896 (1965).

[2] Supported in part by grants from the National Science Foundation, NSF G-13125 and NSF GP-1572.

[3] Grateful acknowledgement is also made to the Petroleum Research Fund for a grant in partial support of this research.

[4] National Science Foundation Cooperative Fellow, 1961–1962; National Institutes of Health Predoctoral Fellow, 1962–1963.

[5] D. S. Noyce and P. A. Kittle, manuscript in preparation.

[6] M. S. Newman, H. G. Kuivila, and A. B. Garrett, *J. Am. Chem. Soc.*, **67**, 704 (1945).

[7] M. S. Newman, *ibid.*, **64**, 2324 (1942).

[8] F. A. Long and M. A. Paul, *Chem. Rev.*, **57**, 984 (1957).

[9] M. I. Vinnik, R. S. Ryabova, and N. M. Chirkov, *Zh. Fiz. Khim.*, **33**, 1992 (1959); *Russ. J. Phys. Chem.*, (Eng. Transl.), **33**, 253 (1959).

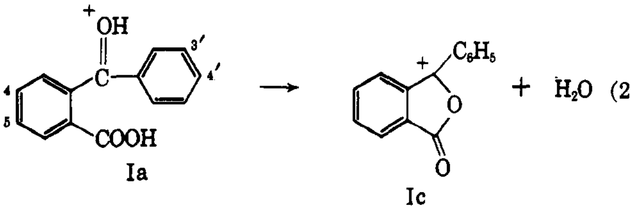
TABLE I

Substituent	λ_{max}, Å.	ϵ_{max}	log ϵ	log K^a	% H_2SO_4^{b}	σ^+
H	4100	28,200	4.45	4.88	96.91	0
H^c	4100	. . .	. . .	4.74	. . .	0
3′-Methoxy^d	. . .	. . .	. . .	5.1	. . .	+0.047
3′-Methyl	4100	29,800	4.47	4.66	96.10	−0.066
3′-Nitro	3950	20,600	4.31	6.27	99.43	+0.674
4′-Methoxy (III)	4400	48,300	4.68	3.22	87.18	−0.778
4′-Methyl	4300	33,100	4.52	4.28	94.10	−0.311
4′-Methyl^e	4300	32,300	. . .	4.33	. . .	. . .
4′-Bromo	4450	38,800	4.59	4.88	96.91	+0.150
4′-Chloro^e	4400	34,600	. . .	4.95	97.0	+0.114
3′,4′-Dimethyl^f	4300	35,700	. . .	4.16	. . .	(−0.377)
4-Methoxy (V)	3975	23,000	4.36	5.22	97.81	+0.047
4-Methyl	4050	26,800	4.43	4.86	96.90	−0.066
4-Nitro (VI)	4000	25,700	4.41	5.30	97.90	+0.674
5-Methoxy (IV)	4900	61,500	4.79	3.34	87.92	−0.778
5-Methyl	4250	27,000	4.43	4.43	94.80	−0.311
5-Nitro	4000	38,500	4.59	5.91	99.10	+0.790
5-$NH_3$$^{+g}$	4500	24,000	4.38	6.44	. . .	. . .

[a] Expressed on the activity of water scale; data for activity of water from W. F. Giauque, *et al.*, *J. Am. Chem. Soc.*, **82**, 62 (1960). [b] Per cent H_2SO_4 at which (Ia)/(Ic) = 1. [c] Ref. 9. [d] This value is determined from the kinetics of the cyclization of 2-(3′-methoxybenzoyl)benzoic acid (ref. 5), and is therefore less precise. [e] R. S. Ryabova and M. I. Vinnik, *Zh. Fiz. Khim*, **37**, 2529 (1963). [f] M. I. Vinnik, R. S. Ryabova, and G. V. Belova, *ibid.*, **36**, 942 (1962). [g] See Vinnik, *et al.*, ref. 14.

Results and Discussion

The solutions of *o*-benzoylbenzoic acid in sulfuric acid more concentrated than 90% show the appearance of a new, long-wave-length absorption band with a maximum at 4100 Å. In agreement with Vinnik, Ryabova, and Chirkov we find that benzoylbenzoic acid is one-half converted to the species responsible for this band in 96.9% sulfuric acid. As I is converted to the cation Ia in 90% sulfuric acid the subsequent equilibrium is represented by eq. 2. We express the equilibrium constant for eq. 2 as eq. 3. If activity coefficient terms may be neglected, then the ratio of the concentration of Ic to the concentration of Ia may be directly related to the activity of water in the medium. There are several indications that such an activity coefficient ratio remains nearly constant above 85% sulfuric acid.[10] The success of Deno and Taft[10] and of Brand[11] is germane. However, strict constancy does not appear to hold invariably, as shown by the results on the isomerization of chalcones in concentrated sulfuric acid solutions.[12] Long and Bakule have also commented on this question.[13]



(2)

$$K_{c^+} = \frac{(\mathrm{Ia})}{(\mathrm{Ic})a_{H_2O}}\frac{f_{\mathrm{Ia}}}{f_{\mathrm{Ic}}} \qquad (3)$$

Neglecting activity coefficients, then, the equilibrium constant for the formation of the lactol carbonium ion may be conveniently expressed in terms of the activity of water in the medium.[14]

$$\log K = \log [(\mathrm{Ia})/(\mathrm{Ic})] - \log a_{H_2O} \qquad (4)$$

The variation of the ratio Ic/Ia is very satisfactorily correlated with the activity of water in concentrated sulfuric acid; we have therefore chosen to report our data in this form. The summarized results are presented in Table I.

The introduction of electron-donating substituents into the 4′-position or the 5-position results in the analogous lactol carbonium ions (*e.g.*, IIIc or IVc) being formed at substantially lower sulfuric acid concentrations. Such a result is inconsistent with structures like Id, and therefore supports Ic as the dominant structure, *i.e.*, the lactol carbonium ion.

From another point of view as well, the structure Ic is more in accord with the facts. The new absorption band at 4100 Å. in Ic bears close resemblance to the visible band which characterizes the benzhydryl cation, formed when benzhydrol is dissolved in concentrated sulfuric acid.[15] Again the introduction of electron-donating substituents *para* to the cationic center results in a substantial bathochromic shift (*cf.* Table I). This pattern of spectral changes is inconsistent with Id as the typical structure.

The spectrum of the acylium ion from mesitoic acid shows a major absorption band at 2800 Å.[16] In only one instance did we observe increasing absorption in this region of the spectrum (~2800 Å.) as the sulfuric acid concentration was increased past 95%. In the case of 4-methoxy-2-benzoylbenzoic acid (V) in addition to the long-wave-length band [3975 Å. (ϵ 23,000)], another band appeared at 2700 Å. (ϵ 20,000). Unfortunately, this region of the spectrum (2500–3000 Å.) becomes very complex as the acid strength is lowered. Consequently, other than at high acidities, the peak at 2700 A. is obscured.

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(10) N. C. Deno and R. W. Taft, Jr., *J. Am. Chem. Soc.*, **76**, 244 (1954).

(11) J. C. D. Brand, *J. Chem. Soc.*, 1002 (1950).

(12) D. S. Noyce and M. J. Jorgenson, *J. Am. Chem. Soc.*, **85**, 2422 (1963).

(13) F. A. Long and R. Bakule, *ibid.*, **85**, 2313 (1963).

(14) M. I. Vinnik, R. S. Ryabova, Zh. E. Grabovskaya, Kh. Koslov, and I. Kubar [*Zh. Fiz. Khim*, **37**, 94 (1963)] have recently reported a similar treatment of data for substituted benzoylbenzoic acids. They have also pointed out the potential utility of substituted benzoylbenzoic acids as J_0 indicators, a possibility which we have considered independently.

(15) N. C. Deno, J. J. Jaruzelski, and A. Schreisheim, *J. Am. Chem. Soc.*, **77**, 3044 (1955); N. C. Deno and A. Schreisheim, *ibid.*, **77**, 3051 (1955).

(16) W. M. Schubert, J. Donohue, and J. D. Gardner, *ibid.*, **76**, 9 (1954); H. Hosoya and S. Nagakura, *Spectrochim. Acta*, **17**, 324 (1961).

It is consistent with these observations to suggest that in 100% sulfuric acid V exists partly as the lactol carbonium ion (Vc) and partly as the acylium ion (Vd). Consistent with this view is the lessened absorption at 3975 Å. compared with the other methoxy benzoylbenzoic acids. One further attempt to obtain insight into this question was unsuccessful. The n.m.r. spectrum of V in 100% sulfuric acid revealed the methoxyl signal as a sharp singlet. The fluorine n.m.r. spectrum of 2-(4′-fluorobenzoyl)benzoic acid also showed the fluorine signal as a singlet in 100% H_2SO_4. Hence, there is no n.m.r. evidence for two species, but rapidly equilibrating species may be present.

ρ–σ Correlations.—The general pattern of the ρ–σ type of correlations is clear in Table I. Plotting the equilibrium constants against σ^+ values for the substituents gives a reasonably good single straight line for substituents in both rings. The value for 4-nitro-2-benzoylbenzoic acid (VII) lies distinctly off the line. It is to be noted that nitro compounds often give difficulty in such determinations of equilibria by spectral means. Omitting VII, the least-squares correlation gives $\rho = 1.83$, $\sigma = 0.977$.

Experimental

The preparation and characterization of the compounds used in this study have been described previously. The methods for determining the ionization ratios have been described previously.[17]

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[17] D. S. Noyce and M. J. Jorgenson, *J. Am. Chem. Soc.*, **84**, 4312 (1962)

Synthesis and Isomerization of 2,6-Dimethyl-*n*-butylbenzene

F. E. Condon[1] and Andreas A. Zavitsas

Department of Chemistry, The City College of the City University of New York, New York, New York

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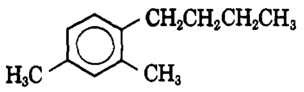
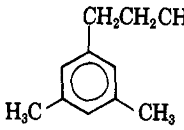
A new hydrocarbon, 2,6-dimethyl-*n*-butylbenzene, has been synthesized and its isomerization–disproportionation by aluminum chloride at 100° has been studied and compared with that of 2,4-dimethyl-*n*-butylbenzene. Both isomerisates contain at least 17 components and are much more complex than indicated by previous work. Migration and intermolecular transfer of methyl groups as well as the *n*-butyl group were noted. The *n*-butyl group is not rearranged. A time study of the isomerization of 2,6-dimethyl-*n*-butylbenzene showed the early formation of xylenes as potential intermediates for the formation of isomers by butyl group transfer, suggested that 2,4-dimethyl-*n*-butylbenzene is an intermediate in the transformation of 2,6- to 3,5-dimethyl-*n*-butylbenzene, and indicated that the disappearance of 2,6-dimethyl-*n*-butylbenzene is kinetically second order in the parent hydrocarbon.

It is now well established that the aluminum chloride catalyzed isomerization of 2,4-dimethyl-*n*-butylbenzene (I) takes place without rearrangement of the *n*-butyl group and gives 3,5-dimethyl-*n*-butylbenzene (II) as the major product.[2] An earlier report[3] that 3,5-dimethyl-*t*-butylbenzene (III) was the major product—an identification based on physical properties and the preparation of derivatives—seems now to have been incorrect. In related work, the aluminum chloride catalyzed disproportionation of *n*-butylbenzene has been shown to take place without rearrangement of the *n*-butyl group and to give mainly 1,3-di-*n*-butylbenzene, and the aluminum chloride catalyzed alkylation of benzene with 1,3-di-*n*-butylbenzene gives solely *n*-butylbenzene.[4]



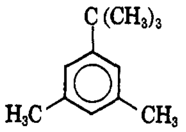
I



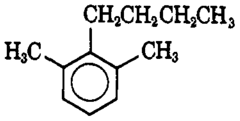
II

Much controversy has centered around the question whether the isomerization of alkylbenzenes takes place intramolecularly or intermolecularly, and at least five distinct mechanisms have been proposed. Some of these will be referred to later in the discussion.

In order to extend knowledge in this area and to try to resolve some of the controversy regarding the mechanism of alkylbenzene isomerization, we have synthesized 2,6-dimethyl-*n*-butylbenzene (IV) and made a time study of its isomerization by aluminum chloride at 100°. At the same time, we have repeated the synthesis and isomerization of I, in order to be able to compare the behavior of I and IV toward aluminum chloride.



III



IV

Synthesis.—The synthesis of IV made use of *t*-butyl as a removable blocking group[5] as shown in the accompanying sequence (Scheme I). Compounds IV–VIII are new. An attempt to reduce V to VIII by the Clemmensen method failed, perhaps because of steric hindrance.[6]

Comparative Isomerizations of 2,4- and 2,6-Dimethyl-*n*-butylbenzene.—The isomerization of 2,6-dimethyl-*n*-butylbenzene was carried out as described previously for 2,4-dimethyl-*n*-butylbenzene[2,3] by heating it 3.5 hr. on a steam bath with 22% of its weight of anhydrous aluminum chloride. Isomerization of 2,4-dimethyl-*n*-butylbenzene was conducted similarly except that only 17% by weight of aluminum chloride was used. Each reaction mixture was washed, dried, and distilled under reduced pressure. Each yielded a volatile fraction distilling to 132° at 17 mm. and com-

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[1] To whom communications should be sent.

[2] D. V. Nightingale and J. M. Shackelford, *J. Am. Chem. Soc.*, **76**, 5767 (1954).

[3] D. Nightingale and L. I. Smith, *ibid.*, **61**, 101 (1939).

[4] R. E. Kinney and L. A. Hamilton, *ibid.*, **76**, 786 (1954).

[5] M. J. Schlatter, *ibid.*, **76**, 4952 (1954).

[6] *Cf.* F. C. Whitmore and C. T. Lester, *ibid.*, **64**, 1251 (1942).