Substituent Effects on Spectral Properties and Hydrogen–Deuterium Exchange in Protonated Benzophenones

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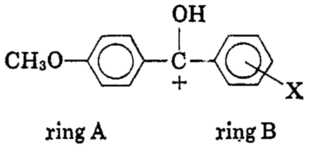
Going from the ketone to protonated ketone involves extensive downfield shifts in the nmr. The chemical shifts of protons in ring A, the visible spectrum, and the exchange rates were all sensitive to the electron-donating character of substituents in ring B. Steric effects involving the coplanarity of the rings affect the spectra and exchange rates in the opposite manner.

In a recent, comprehensive review article, Deno pointed out that protonated ketones have many properties that would be expected for hydroxy carbonium ions.[1] Earlier work[2,3] had shown that carbonium ion systems were capable of hydrogen–deuterium exchange. The exchange occurs readily in the highly reactive 1,1-dianisylethyl cation systems and may involve a transient dication.[3]

The present work involves a study of the effect of the substituent in ring B of system **1** on (i) the visible spectra of the protonated ketone,[4] (ii) the nmr chemical shifts[1,5] in rings A and B, and (iii) hydrogen–deuterium exchange in the two rings.



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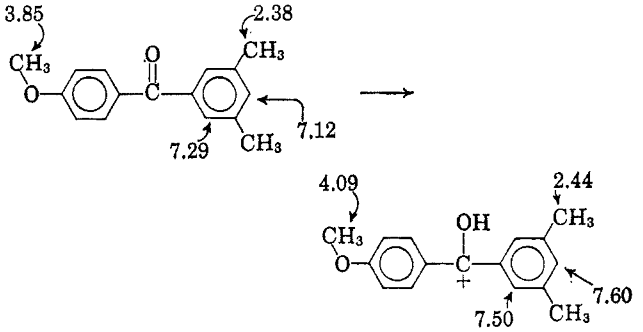
The nmr spectra of carbonium ions has been a particularly useful tool used to determine the degree of charge delocalization and as a criterion of stability in various systems.[6-8] In the present study, it is of interest to observe the extent to which the electronic effect of the substituent X in the ring B can be transmitted through the system of p orbitals to affect the chemical shifts in ring A.

Results and Discussion

The spectral data are given in Table I. Comparison of the nmr spectra of **8** in CCl_4 and in 96% H_2SO_4 illustrates the effect of the resonating charge in the latter (Scheme I). In the cation form the *para* proton (ring B) occurs downfield from the *ortho*. In the ketone, the relative positions of the two are reversed, owing in part to the anisotropy of the carbonyl which deshields the *ortho* proton.[9]

SCHEME I
CHEMICAL SHIFTS FOR THE INDICATED PROTONS
(PARTS PER MILLION)



It is tentatively suggested that a resonance form of the cation, involving a carbon–oxygen double bond, may not be too important.

As Scheme I shows, every group in **8** suffers a substantial downfield shift going from the ketone to the cation. This shift must be ascribed to the effect of the charge in the various resonance forms (or strictly speaking the lack of shielding electrons at these various positions). As previously shown,[10,11] the deshielding is most extensive in the *ortho* and *para* positions of the rings, the same positions that exist in direct resonance interaction with the cationic center. It is noteworthy that the *meta* methyl groups are slightly deshielded going to the cation, whereas the methoxy group is extensively deshielded, showing the importance of a resonance form involving a positive charge on the ether oxygen. Reversible protonation of the ether oxygen may likewise be important.

The chemical shift of various groups in the cations **3**, **7**, **9**, and **10** is given in Scheme II. In this series of compounds, the effect of steric hindrance to ring coplanarity is clearly evident. The ultraviolet $\lambda_{\max}$ decreases drastically in the order **10** > **3** > **7** > **9**. As the classical case of the difference in $\lambda_{\max}$ between *trans*-stilbene (320 mμ) and *cis*-stilbene (305 mμ) illustrates,[12] the longer $\lambda_{\max}$ occurs in systems where ring coplanarity is possible. The extinction coefficient, which is even more sensitive to ring coplanarity in resonating systems,[13] decreases by almost a factor of 2.

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[1] N. C. Deno, "Progress in Organic Chemistry," Vol. 2, Interscience Publishers, Inc., New York, N. Y., 1964, p 182.

[2] N. C. Deno and W. L. Evans, *J. Am. Chem. Soc.*, **78**, 582 (1956).

[3] C. A. Kingsbury, *Tetrahedron Letters*, 2539 (1966).

[4] Extensive work on the visible spectra of various carbonium ion systems has been reported: N. C. Deno, J. J. Jeruzelski, and A. Schriesheim, *J. Am. Chem. Soc.*, **77**, 3044 (1955), and related papers.

[5] Some work has been reported on substituent effects on aromatic carbonium ion spectra; see ref 1; also R. W. Taft and J. Rakshys, Jr., *ibid.*, **87**, 4387 (1965).

[6] G. Olah and C. U. Pittman, Jr., *ibid.*, **88**, 3310 (1966).

[7] R. Breslow, H. Höver, and H. Chang, *ibid.*, **84**, 3168 (1962).

[8] H. G. Richey, Jr., L. Rennick, A. Kushner, J. Richey, and J. Phillips, *ibid.*, **87**, 4017 (1965).

[9] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press Ltd., London, 1959, pp 122–124.

[10] (a) G. Olah, *J. Am. Chem. Soc.*, **86**, 932 (1964), and many earlier papers; (b) D. G. Farnum, *ibid.*, **86**, 934 (1964).

[11] Earlier work on the triphenylcarbonium ion, which showed anomalous *meta* proton absorption is apparently due to ring-current effects from the other rings:[10b] (a) D. E. O'Reilley and H. Leftin, *J. Phys. Chem.*, **64**, 1555 (1960); (b) P. R. Moodie, T. Connor, and R. Stewart, *Can. J. Chem.*, **37**, 1402 (1959).

[12] B. Pullman and A. Pullman, "Les Théories Electronique de la Chimie Organique," Masson et C^{IE}, Ed., Paris, 1952, p 465.

[13] (a) E. J. Moriconi, W. F. O'Connor, and W. F. Forbes, *J. Am. Chem. Soc.*, **82**, 5454 (1960); (b) L. L. Ingraham in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p 481.

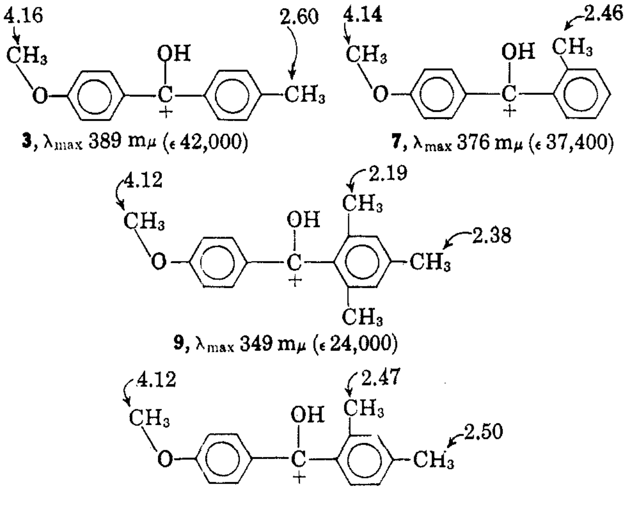
TABLE I

SPECTRAL PROPERTIES AND EXCHANGE HALF-LIVES IN SYSTEM 1

		Anisyl ring protons			λ_{max},		Exchange half-lives in D_2SO_4, min	
Ion	X	δ_o, ppm[a]	δ_m, ppm[a]	$\Delta\delta$	mμ	ε	Ring A	Ring B
2	p-CH_3O	8.10	7.32	0.78	400	42,800	36[b]	
3	p-CH_3	8.22	7.33	0.89	389	42,000	83	
4	p-Cl	8.21	7.30	0.91	389	42,600	300	
5	H	8.31	7.36	0.95	379	35,000	190	
6	m-CH_3	8.28	7.32	0.96	382	35,000	200	
7	o-CH_3	8.25	7.28	0.99	376	27,400	980	9400 (*meta*)
8	3,5-$(CH_3)_2$	8.25	7.27	0.98	387	32,000	500	1500 (*ortho* + *para*)
9	2,4,6-$(CH_3)_3$	8.23	7.22	1.01	349	24,000	480	<4 (*meta*)
10	2,4-$(CH_3)_2$	8.21	7.28	0.93	395	29,400	*ca.* 150	*ca.* 20

[a] The chemical shifts on the basis of tetramethylsilane as 0 ppm. Owing to the insolubility of TMS, tetramethylammonium bromide was used as internal standard. [b] Statistical factor of 2 has been applied.

SCHEME II



3, λ_{max} 389 mμ (ε 42,000)

7, λ_{max} 376 mμ (ε 37,400)

9, λ_{max} 349 mμ (ε 24,000)

10, λ_{max} 395 mμ (ε 29,400)

The nmr chemical shifts of the various methyl groups show similar differences. The *para* methyl in **3** occurs considerably downfield of the similar group in the mesityl compound **9**. Presumably resonance structures involving charges in ring B of **3** and **7** are more important than similar structures with charges in the mesityl ring, **9**, probably owing to the out-of-plane character of the latter.

The *ortho* methyls of **9** may actually be shielded by the ring current of the anisyl ring to the extent that these groups lie above the anisyl ring.[11b,14] The *ortho* methyls in **9** occur considerably upfield of the *para* methyl in the same ring and far upfield of the *ortho* methyl in **7**. In **7** and **10** the *ortho* methyls probably lie near the hydroxy function.

A useful condensation of the chemical shift data centers around a function, $\Delta\delta$, which is defined as the difference in chemical shift between the *ortho* ring protons (*i.e.*, *ortho* to the cationic center) and the *meta* ring protons. Tentatively it is proposed that this function is related to the degree of delocalization of charge in the ring. The $\Delta\delta$ values for the various cations are recorded in Table I. Thus $\Delta\delta$ is rather small (0.89) for **3**, in which both rings share the charge. In the *ortho* tolyl cation **7**, in which slight steric hindrance to coplanarity exists, $\Delta\delta$ is larger (0.97). This function reaches its highest value in **9**, in spite of ring-current effects. Apparently the anisyl ring carries the bulk of the charge.

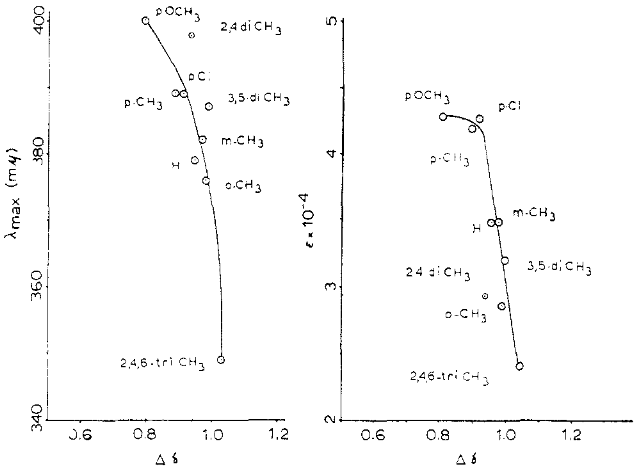


Figure 1.—Ultraviolet λ_{max} and ultraviolet extinction coefficient *vs.* nmr $\Delta\delta$ for the substrates indicated.

The function $\Delta\delta$ is sensitive to the electronic character of the substituents X. In **2**, X = OCH_3, the charge is equally distributed over both rings; the $\Delta\delta$ has a small value (0.78). In **3**, X = p-CH_3, $\Delta\delta$ for ring A is higher (0.89). In **4**, X = p-Cl, the trend is continued and $\Delta\delta$ is 0.91. The trend of $\Delta\delta$ in ring B is the reverse. Thus, as X becomes poorly electron donating, ring A carries more charge (the *ortho* proton particularly becomes increasingly deshielded).

The ultraviolet λ_{max} and extinction coefficient are similarly sensitive to the character of X. Both decrease in the order **2** > **4** > **3** > **5**. A plot of λ_{max} *vs.* $\Delta\delta$ is given in Figure 1.

The protonated ketones of this study readily exchange hydrogen for deuterium, usually in the *meta* position of the anisyl ring. Table I lists the half-lives for exchange in D_2SO_4. The dianisyl compound **2** exchanges very rapidly, whereas the exchange is slower where the remote substituent is poorly electron donating. The half-lives of exchange correlate fairly well with σ^+ parameters.[15]

In some cases exchange occurs in both rings of the protonated benzophenone. Exchange first becomes observable in the ring B of **7** (two protons only exchange) but at a rate one-tenth as fast as that in the anisyl ring. In **8** exchange occurs quite rapidly in the ring B but still one-third as fast as that in the anisyl ring. It is interesting that the rate of exchange of the

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(14) R. Breslow and H. W. Chang, *J. Am. Chem. Soc.*, **83**, 2367 (1961).

(15) H. C. Brown and Y. Okamoto, *J. Org. Chem.*, **22**, 485 (1957).

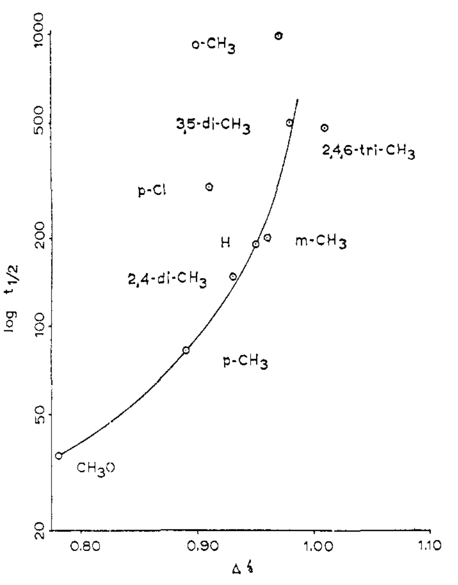

Figure 2.—A plot of log $t_{1/2}$ *vs.* $\Delta\delta$ for the substituents indicated.

ortho ring B protons is about the same as that of the *para* proton. Finally, in **9** the activated mesityl ring exchanges extremely rapidly, over 100 times as fast as the anisyl ring. Exchange is aided by the out-of-plane character of the mesityl ring which renders it less deactivated by the resonating charge.

The various possibilities for exchange are shown in Scheme III. In a previous study in diarylethyl cation systems at least some exchange directly on the cation itself was considered likely. However in the present system, exchange *via* pathway 2 does not seem likely except possibly in the dianisyl system **2** or the mesityl system **9**

Scheme III

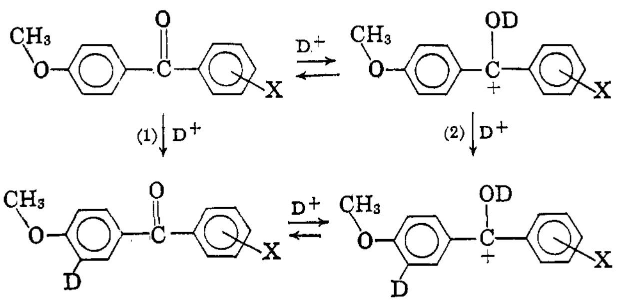

Figure 2 shows a plot of the exchange half-life in ring A *vs.* the nmr chemical shift parameter $\Delta\delta$, ring A. The chemical shifts of protons in ring A previously were shown to be sensitive to the electron-donating character of substituents in ring B, even though no resonance structure can be drawn in which the nonbonding electrons of substituent X in ring B interact with ring A. The rates of hydrogen–deuterium exchange in ring A are likewise sensitive to the substituents in ring B.

Experimental Section

The substrates **2** and **5** were commercial preparations (Aldrich) recrystallized, mp 143–144° and 61–62° (lit. 144°[16] and 62°[17], respectively). The other substrates were prepared by Friedel–Crafts acylations. A typical preparation (of **8**) is given below. The substrate 3,5-dimethylbenzoic acid (5 g, 3.3×10^{-2} mole) was placed in 100 ml benzene and mixed with PCl_5 (5.0 g, 3.3×10^{-2} mole). The solution was stirred until the evolution of HCl ceased. The excess benzene and $POCl_3$ were distilled off. Benzene was readded and distilled off. Then 100 ml of CH_2Cl_2 and 25 ml of anisole were added and the solution was cooled with an ice bath; $AlCl_3$ (4.6 g, 3.6×10^{-2} mole) was added with stirring. The mixture was stirred for 1 hr, allowed to come to room temperature, and then poured into ice and HCl. The unreacted anisole was steam distilled off. The residue was taken up with ether, washed with dilute NaOH, then water. The organic layer was dried over $MgSO_4$. Solvent was evaporated and the residue was chromatographed on activity I Woelm alumina. The 50% ether–pentane eluent crystallized upon standing. This was recrystallized from ether–pentane, mp 70.5–71.5°, 2.61 g, 33% yield.

Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.60; H, 6.80.

The compounds **3**, **6**, and **7** were prepared similarly, mp 89–90° and bp 137° (0.06 mm) and 142–145° (0.02 mm) [lit.[18] mp 90.5°, bp 172–174° (3 mm) and 142–144° (0.02 mm), respectively]. The *p*-chloro compound **4** was prepared similarly, mp 123–124° (lit.[19] mp 125°). The mesityl compound was prepared by using anisoyl chloride and mesitylene, mp 77–78° (lit.[20] mp 78°). Deuteriosulfuric acid was obtained from Merck Sharpe and Dohme of Canada and was used as received. Titration disclosed that this acid was 35.8 *N*.

The nmr spectra were taken on a Varian A-60 instrument at normal probe temperature. Ultraviolet spectra were run on a Beckman DK-2 instrument. The position of the maxima should only be considered accurate to ±3 mμ. The spectrum of **3** in 96% H_2SO_4 was constant over a 4-day period. Rates of exchange were studied by dissolving approximately 120 mg of substrate in 1 ml of D_2SO_4 plus *ca.* 10 mg of tetramethylammonium bromide which was used as an internal standard taken as 191 cps. The extent of deuteration was determined by integration. The ratios of a given peak area *vs.* peak area of standard were determined (this ratio was called a). Plots were made of ln $(a_0 - a_\infty)/(a_t - a_\infty)$ *vs.* time and the half-lives were determined graphically. Rate tubes were sealed with Pliofilm and placed in a constant-temperature bath at 30.01° between points.

Registry No.—Ion **2**, 10487-81-7; ion **3**, 10487-82-8; ion **4**, 10487-83-9; ion **5**, 10472-80-7; ion **6**, 10472-81-8; ion **7**, 10472-82-9; ion **8**, 10487-84-0; ketone **8**, 10472-83-0; ion **9**, 10472-84-1; ion **10**, 10472-85-2.

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(16) W. D. Cohen, *Rec. Trav. Chim.*, **38**, 121 (1919).

(17) H. Staudinger and N. Kon, *Ann. Chem. Liebig's*, **384**, 101 (1911).

(18) N. Sugiama and S. Baba, *Nippon Kagabu Zasshi*, **84**, 936 (1963).

(19) P. P. Peterson, *Am. Chem. J.*, **46**, 339 (1911).

(20) R. C. Fuson and R. Gaertner, *J. Org. Chem.*, **13**, 496 (1948).