

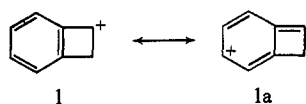
Stable Benzocyclobutenyl Cations<sup>1</sup>

Harold Hart and James A. Hartlage

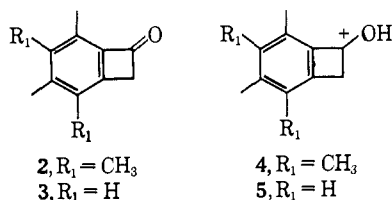
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**Abstract:** Several 1-arylbenzocyclobutenols or their derivatives (6–10, 15) containing different substituents in the aryl and benzo rings were synthesized and converted to the corresponding carbonium ions in sulfuric acid. The ions underwent no structural changes in strong acid and were converted into the starting materials on solvolysis. The extent to which charge in the cations is delocalized to the benzo ring was investigated. The nmr chemical shifts of substituents in the benzo ring showed that (a) substituents in *all* positions are deshielded in the cation relative to their shifts in its covalent precursor, (b) charge is delocalized more to the benzo ring than to the 1-aryl ring, and (c) delocalization is greater to *ortho* and *para* positions than to *meta* positions, suggesting a resonance effect despite the possible strain in benzylic structures (*i.e.*, 1a). The  $pK_R$ 's of the carbonium ions ranged from  $-5$  to  $-11$ ; substituent effects on the  $pK_R$ 's were best correlated by a Hammett plot which included a term due to appreciable 1,3- $\pi$  interaction across the four-membered ring (*i.e.*, 1c–e). Benzocyclobutenols with a 1-alkyl substituent also formed carbonium ions in sulfuric acid, but these rapidly underwent further structural changes.

Benzocyclobutenyl cations have not been extensively investigated. Cava and Napier<sup>2</sup> observed that unlike benzyl bromide, 1-bromobenzocyclobutene is not a lachrymator, nor is the bromine easily displaced by various anions. 1,2-Dibromobenzocyclobutene was also inert to  $S_N1$  conditions, no hydrolysis occurring in refluxing aqueous alcohol.<sup>3</sup> These observations were interpreted to mean that negative strain energy resulting from having a double bond *exo* to the aromatic ring and included in a four-membered ring in canonical forms such as 1a cancels the expected benzylic resonance energy. No kinetic measurements on precursors of 1 which would bear on this question have been reported.



We recently observed that there is nothing inherently wrong with structures such as 1. Benzocyclobutenones 2 and 3 were readily protonated to the corresponding hydroxycarbonium ions 4 and 5, both of which were stable; the ketones were recovered quantitatively on dilution.<sup>4</sup>

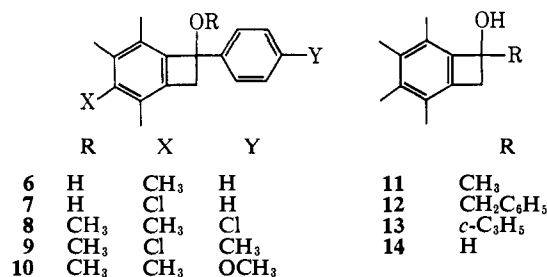


The present paper describes the synthesis of several stable tertiary benzocyclobutenyl cations by ionization of the corresponding carbinols or their methyl ethers in strong acid. Measurement of their nmr spectra and  $pK_R$ 's as a function of substituent changes in the aromatic rings gives information about the extent to which positive charge is delocalized *via* structures such

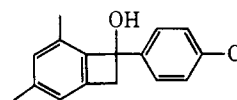
as 1a. Evidence is also presented for 1,3- $\pi$  interaction across the four-membered ring.

## Results

Compounds 6–13 were synthesized by reaction of the appropriate aryl or alkyl Grignard reagent with the corresponding benzocyclobutenone<sup>4</sup> and 14 was prepared



pared by reduction of the corresponding ketone. Compound 15 was prepared from 3 and *p*-chlorophenyl-



15

magnesium bromide. In some cases (8–10) methyl ethers were prepared because the corresponding carbonium ions could not be obtained pure and crystalline.

Compounds 6–10 gave intensely colored, stable solutions in 96% sulfuric acid whose electronic and nmr spectra were consistent with the formation of the corresponding carbonium ions.<sup>5</sup> Hydrolysis or methanolysis of the acid solutions gave the starting alcohols or methyl ethers in high yield, showing that no structural rearrangements or polymerization had occurred. The  $pK_R$ 's of the carbonium ions were determined by measuring changes in the visible spectra as a function of acid strength.<sup>6,7</sup> The visible spectra,  $pK_R$ 's, and nmr spectra are summarized in Tables I and II.

(1) We are indebted to the National Science Foundation for their generous financial support of this work.

(2) M. P. Cava and D. R. Napier, *J. Am. Chem. Soc.*, **80**, 2255 (1958).

(3) M. P. Cava and D. R. Napier, *ibid.*, **79**, 1701 (1957).

(4) H. Hart, J. A. Hartlage, R. W. Fish, and R. R. Rafos, *J. Org. Chem.*, **31**, 2244 (1966).

(5) For convenience, the ions will be designated by the same formula number, but with a + superscript; ion 6<sup>+</sup> derived from 6, etc.

(6) N. C. Deno, J. J. Jaruzelski, and A. Schriesheim, *J. Am. Chem. Soc.*, **77**, 3044 (1955).

(7) The spectra of ions 6<sup>+</sup>–10<sup>+</sup> and 15<sup>+</sup> did not change with time in 96% sulfuric acid, but in acid solutions of such a concentration that

**Table I.** Electronic Spectra and Ionization Constants of Substituted Benzocyclobutenyls Cations

Carbonium ion source	$\lambda_{\max}$ , <sup>a</sup> m $\mu$	$\epsilon$	$pK_R$ <sup>+b</sup>
6	435	25,900	-7.95
	310	6100	
7	444	54,200	-10.59
	304	6080	
8	453	48,200	-8.66
	324	5750	
9	458	67,400	-9.30
	323	4500	
10	471	76,400	-5.09
	324	5750	
15	450	47,400	-9.40
	310	4050	
11 <sup>c</sup>	422	3790	-16.63
	353	5550	
12 <sup>c</sup>	452	8210	-17.23
	348	4000	
13 <sup>c,e</sup>	425	3730	-13.24 <sup>d</sup>
	368	11,900	
14 <sup>c,e</sup>	560	6860	-14.77 <sup>d</sup>
	344	5490	

<sup>a</sup> In 96% sulfuric acid. <sup>b</sup> Experimental details are given in Table III; except where noted, these have been calculated according to eq 1. <sup>c</sup> These spectra change with time and have been extrapolated to  $t = 0$ ; see ref 8. <sup>d</sup> These were calculated according to eq 2; see Discussion in text. <sup>e</sup> The ions which give rise to the reported spectra probably have rearranged structures; see text.

**Table II.** Nmr Spectral Data<sup>a</sup> of 1-Arylbencocyclobutenyl Cations

Compound	Carbon tetrachloride				Sulfuric acid			
	Aryl methyls	Methylene	Aryl	Other	Aryl methyls	Methylene	Aryl	Other
6	8.14, 7.92, 7.87 (3) (6) (3)	6.80 (2, br)	2.67-3.07 (5, m)	7.28 (OH)	7.72, 7.63, 7.47, 7.30 (3) (3) (3) (3)	5.55-5.75 (2)	1.47-2.45 (5, m)	
6, R = CH <sub>3</sub>	7.97, 7.89, 7.82 (3) (3) (6)	6.46, 6.88 (2, J = 13)	2.55-2.92 (5, m)	6.65 (OCH <sub>3</sub> )				
7	8.05, 7.82, 7.73 (3) (3) (3)	6.73 (2, br)	2.70-2.92 (5, m)	7.07 (OH)	7.62, 7.48, 7.22 (3) (3) (3)	5.47-5.67 (2)	1.50-2.38 (5, m)	
8	8.05, 7.78-7.93 (3) (9)	6.56, 7.04 (2, J = 13)	2.44 (4, s)	6.73 (OCH <sub>3</sub> )	7.73, 7.65, 7.45, 7.30 (3) (3) (3) (3)	5.58-5.75 (2)	1.80, 2.20 (4, J = 8)	
8 (chloride)	7.95, 7.78-7.90 (3) (9)	6.25, 6.55 (2, J = 13)	2.75, 2.88 (4, J = 8)					
9	7.95, 7.78, 7.70 (3) (3) (6)	6.53, 6.93 (2, J = 13)	2.87, 3.00 (4, J = 8)	6.73 (OCH <sub>3</sub> )	7.63, 7.50, 7.30, 7.25 (3) (3) (3) (3)	5.50-5.74 (2)	1.67, 2.27 (4, J = 8)	
10	8.00, 7.92-7.85 (3) (9)	6.65, 5.95 (2, J = 13)	2.88, 3.35 (4, J = 8.5)	6.75, 6.34 (OCH <sub>3</sub> )	7.81, 7.75, 7.65, 7.47 (3) (3) (3) (3)	5.88 (2)	1.75, 2.70 (4, J = 7)	5.93 (Ar-OCH <sub>3</sub> )
15	8.03, 7.70 (3) (3)	6.73 (2, br)	3.25, 2.87 (2, br) (4, s)	6.57 (OH)	7.35, 7.23 (3) (3)	5.75 (2)	2.67, 2.58, 1.75, 2.18 (1) (1) (4, J = 8)	

<sup>a</sup> Chemical shifts on the  $\tau$  scale; TMS reference in CCl<sub>4</sub>; Me<sub>4</sub>N<sup>+</sup>BF<sub>4</sub><sup>-</sup>,  $\tau$  6.87, used as reference in sulfuric acid.

Compounds without an aryl group at C-1 (*i.e.*, 11-14) also gave bright red solutions in concentrated sulfuric acid, indicating carbonium ion formation, but the spectra changed with time.<sup>8</sup> The structural changes which accompany these spectral changes have not been investigated; hydrolysis failed to give recovered carbinols. However, extrapolation to zero time gave

the compound was about 50% ionized, a gradual decrease in absorbance was noted. The shortest lived ion was 8<sup>+</sup>, with a  $t_{1/2}$  of 9 min in 59.43% sulfuric acid. Straight-line plots of absorbance vs. time were extrapolated to zero time to obtain the absorbances from which the ionization ratios and  $pK_R$ 's were calculated.

(8) When the 1-substituent was methyl or cyclopropyl, the absorbance decreased by about 40-50% in 1 hr but there was no shift in the  $\lambda_{\max}$ . With R = benzyl (12) the initial spectrum, obtained after 2.3 min, was as reported in Table I; however, the long wavelength band gradually shifted to 485 m $\mu$  ( $\epsilon$  6980) during 45 min, after which no further change was noted (12 hr). A similar shift, but in the opposite direction, was noted with 14; the initial  $\lambda_{\max}$  at 560 m $\mu$  shifted to 483 m $\mu$  ( $\epsilon$  12,300) in 48 min, then remained unchanged (12 hr).

absorbances which resulted in the reasonably constant  $pK_R$ + values reported in Table I. Their significance is discussed below.

## Discussion

**Nmr Spectra.**<sup>9</sup> The difference between the nmr spectra of 6-10 (Figure 1) and 15 in carbon tetrachloride and in sulfuric acid (Table II) clearly supports the conclusion that the corresponding carbonium ions are produced in the latter solvent. It also shows that considerable positive charge is delocalized to the benzo ring. For example, in 15<sup>+</sup>, both methyls (*ortho* and *para* to the carbonium ion center) are deshielded relative to their positions in 15. The methylene protons experience an even greater downfield shift (about 1 ppm), being directly attached to the ionization site. Even the aromatic protons *meta* to the carbonium carbon are deshielded by  $\sim 0.7$  ppm, showing that there is considerable positive charge on the *meta* carbon atoms of the benzo ring.

All four aromatic methyls in 6<sup>+</sup> are deshielded from their positions in 6 (see Figure 1), showing again that positive charge is delocalized to *all* positions of the benzo ring. Using 15<sup>+</sup> as a reference, the two lowest field aryl methyl peaks in 6<sup>+</sup> can be ascribed to the *ortho* and *para* methyls. The deshielding effect is

therefore selective, being stronger at *ortho/para* positions than at *meta* positions. This suggests that the mechanism for transmitting the effect is probably *via* contributions from resonance forms such as 1a, rather than a general inductive electron withdrawal by the carbonium carbon atom.

The remaining nmr spectra in Table II show features similar to those mentioned for 6<sup>+</sup> and 15<sup>+</sup>; the methylene protons are in each case shifted downfield about 1 ppm and the aryl methyls and hydrogens are also

(9) The nmr spectra of the un-ionized forms of 6-10 are consistent with their structures and will not be discussed in detail. They all show one allylic methyl separate and shielded with respect to the others (Figure 1). Since one of the aryl methyls in 15 also occurs at high field ( $\tau$  8.03), it seems likely that in all these compounds this peak may be assigned to the methyl *ortho* to the carbinol carbon, shielded by the adjacent aryl and/or oxygen function. In all cases the methylene protons of the four-membered ring appear either as a broad peak or a well-defined AB spectrum,  $J = 13$  Hz.

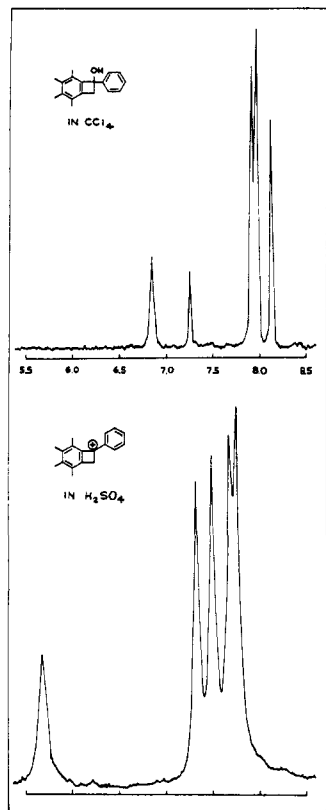


Figure 1. The nmr spectra of 1-phenyltetramethylcyclobuten-1-ol in carbon tetrachloride (top) and in 96% sulfuric acid ( $\tau$  scale).

deshielded. We conclude from the nmr spectra that in all cases positive charge is delocalized to the benzo ring, that the delocalization is selectively greater for *ortho/para* positions (probably *via* benzylic structures such as **1a**, etc.), and that a mechanism also exists for placing appreciable positive charge<sup>10</sup> in the *meta* positions. The latter will be discussed in more detail below.

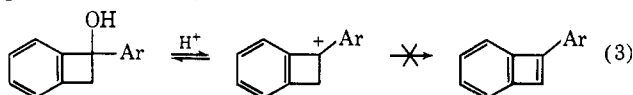
**$pK_{R^+}$  Measurements.** Except for **13** and **14**, all compounds studied gave constant  $pK_{R^+}$  values when calculated according to eq 1.<sup>6</sup> The data are in Table

$$pK_{R^+} = H_R - \log(C_{ROH}/C_{R^+}) \quad (1)$$

III. This correlation is noteworthy, since Deno, Groves, and Saines<sup>11</sup> found protonation of diarylalkenes to deviate widely from eq 1, which is used for arylmethanols which are structurally prevented from dehydrating to alkenes. In general, compounds which are structurally able to eliminate to alkenes do so and the equilibrium in various concentrations of sulfuric acid is best expressed by eq 2. The correlation of

$$pK_{R^+}' = H_R - \log(C_{ol}/C_{R^+}) - \log a_{H_2O} \quad (2)$$

$pK_{R^+}$ 's with eq 1 rather than eq 2 shows that equilibration of benzocyclobutenyl cations with the corresponding benzocyclobutadienes (eq 3) is unimportant.



(10) Perhaps about 0.07 unit, using the 0.7-ppm shift of the benzo protons and a proportionality constant of 10 ppm/unit charge; G. Fraenkel, R. E. Carter, A. M. McLachlan, and J. H. Richards, *J. Am. Chem. Soc.*, **82**, 5846 (1960).

(11) N. C. Deno, P. T. Groves, and G. Saines, *J. Am. Chem. Soc.*, **81**, 5790 (1959).

Table III. Ionization Constant Data for Benzocyclobutenyl Cations

Compd	H <sub>2</sub> SO <sub>4</sub> , %	Log (C <sub>R</sub> <sup>+</sup> /C <sub>ROH</sub> )	H <sub>R</sub>	pK <sub>R</sub> <sup>+</sup>
6	62.64	1.48	-9.35	-7.87
	58.51	0.26	-8.22	-7.96
	56.23	-0.24	-7.73	-7.97
	55.12	-0.46	-7.49	-7.95
	53.81	-0.95	-7.06	-8.01
			Av	-7.95
7	67.63	0.31	-10.88	-10.57
	66.71	0.01	-10.59	-10.58
	66.27	-0.16	-10.45	-10.61
	65.27	-0.46	-10.15	-10.61
			Av	-10.59
8	62.72	0.70	-9.38	-8.68
	61.40	0.32	-9.00	-8.68
	59.80	-0.07	-8.57	-8.64
	58.58	-0.42	-8.21	-8.63
			Av	-8.66
9	64.77	0.67	-9.99	-9.32
	62.95	0.10	-9.44	-9.34
	61.75	-0.22	-9.09	-9.31
	59.80	-0.65	-8.56	-9.21
			Av	-9.30
10	48.87	1.08	-6.17	-5.09
	45.08	0.36	-5.43	-5.07
	44.22	0.17	-5.27	-5.10
	42.19	-0.20	-4.90	-5.10
			Av	-5.09
11	86.3	0.59	-17.30	-16.71
	85.1	0.32	-16.95	-16.63
	84.2	0.06	-16.64	-16.58
	82.6	-0.49	-16.13	-16.62
			Av	-16.63
12	87.8	0.47	-17.76	-17.29
	85.9	0.02	-17.18	-17.16
	85.0	-0.41	-16.90	-17.31
	84.2	-0.53	-16.64	-17.17
			Av	-17.23
13 <sup>a</sup>	84.2	0.34	-16.64	-16.30
	82.0	0.03	-15.94	-15.91
	79.8	-0.26	-15.21	-15.47
	77.9	-0.42	-14.56	-14.98
			Av	-15.66
14 <sup>a</sup>	93.1	0.56	-19.29	-18.73
	90.4	0.15	-18.53	-18.38
	87.8	-0.42	-17.76	-18.18
	86.6	-0.56	-17.39	-17.95
	84.2	-0.98	-16.64	-17.62
				-17.48
			Av	-18.06
15	64.77	0.55	-9.99	-9.44
	62.95	-0.03	-9.44	-9.47
	61.75	-0.33	-9.09	-9.42
	59.80	-0.68	-8.56	-9.24
			Av	-9.40

<sup>a</sup> See also Table IV.

In confirmation of this conclusion, the nmr spectrum of **6**<sup>+</sup> showed no change in the area of the methylene proton peak on standing in 70% D<sub>2</sub>SO<sub>4</sub>-30% D<sub>2</sub>O for 24 hr.

Compounds **13** and **14** were exceptions to this correlation; the data in Table III show that  $pK_{R^+}$  calculated according to eq 1 for these compounds varied continuously with the per cent of  $H_2SO_4$  and that the color change occurred over a rather wide acidity range. These compounds gave reasonably constant  $pK_{R^+}$  values when calculated according to eq 2 (see Table IV). This implies that alkenes may be formed, *via* ring opening (for **13**)<sup>12</sup> or dimerization (for **14**) reactions.

Table IV. Ionizations According to Eq 2

Compd	H <sub>2</sub> SO <sub>4</sub> , %	$a_{H_2O}$	$H_R - a_{H_2O}$	$pK_{R^+}$
<b>13</b>	84.2	-2.85	-13.79	-13.45
	82.0	-2.55	-13.39	-13.36
	79.8	-2.25	-12.96	-13.22
	77.9	-2.05	-12.51	-12.93
			Av	-13.24
<b>14</b>	93.1	-4.09	-15.20	-14.64
	90.4	-3.68	-14.85	-14.70
	87.8	-3.32	-14.44	-14.86
	86.6	-3.15	-14.24	-14.80
	84.2	-2.85	-13.79	-14.77
	82.0	-2.55	-13.39	-14.83
		Av	-14.77	

Discussion of the  $pK_{R^+}$  values will be restricted to compounds **6–10** and **15**, since only in these cases it is certain that the carbonium ions have structures which correspond to simple ionization of their carbinol (or methyl ether) precursors.

Substituent changes in the "benzo" ring have a larger effect on the  $pK_{R^+}$  than do comparable changes in the C-1 aryl ring. For example, interchange of a *p*-Cl and *p*-CH<sub>3</sub> in the two rings (compare **8** and **9**) results in a  $\delta_{pK}$  of 0.63 unit, the unfavorable effect of the Cl substituent being felt appreciably more when it is in the "benzo" ring than when it is in the "aryl" ring. If an ordinary Hammett relationship were operative, one might have expected **8** and **9** to have identical  $pK_{R^+}$  values.

If substituent changes are confined to a single ring, the Hammett equation holds very well, using  $\sigma^+$  constants. Although the number of substituents is unfortunately small, the closeness of the correlation coefficients to unity encourages confidence in this treatment of the data. A Hammett plot for compounds **6**, **8**, and **10**, which differ only in the C-1 aryl ring, is shown in Figure 2. The equation  $pK_{R^+} = -8.11 - 3.90\sigma^+$  holds with a correlation coefficient of 0.998. Furthermore, if one assumes the same  $\rho$  value (-3.90) for compounds **7** and **9**, which also differ only in the C-1 aryl group, then a  $\delta_{pK_{R^+}}$  for **7** and **9** of 1.21 units is calculated, in rather good agreement with the observed difference of 1.29 units. Thus *para* substituents in the C-1 aryl group seem to follow the usual  $\sigma_p^+$  constants rather well.<sup>13</sup> However, if one uses the same  $\rho$  to

(12) Measurements on **13** were particularly difficult to obtain. There was a very rapid decrease in the absorptivity during the first 3 min after solutions were mixed; this was followed by a much slower decrease (about 50%) during the next hour. There was, however, no shift in the position of  $\lambda_{max}$ . Data are calculated from extrapolations to zero time.

(13) All  $\sigma^+$  values used in this paper are found in R. O. C. Norman and R. Taylor, "Electrophilic Substitution in Benzenoid Compounds," Elsevier Publishing Co., Amsterdam, 1965, p 287, Table 58.

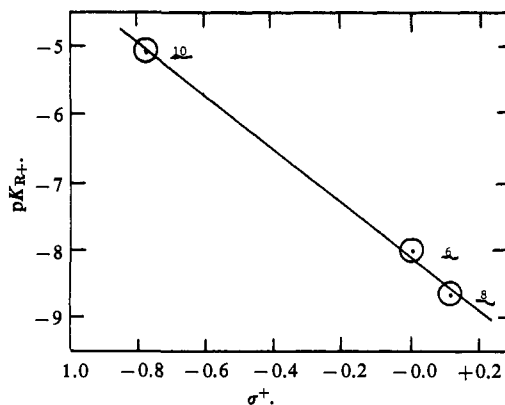
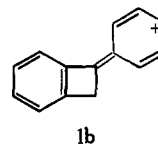


Figure 2. Hammett plot of  $pK_{R^+}$  vs.  $\sigma^+$  for substituents in the C-1 aryl ring.

predict the  $pK_{R^+}$  difference between **8** and **15**, the calculated  $\delta$  (0.51 unit) falls appreciably short of the observed  $\delta$  of 0.74  $pK$  unit. The two "meta" methyl groups in **8** stabilize the corresponding carbonium ion more than would have been predicted using  $\sigma_m^+$  for the methyl groups. Once more, substituent effects seem to be more significant in the "benzo" ring than in the C-1 aryl ring.

Taking the nmr and  $pK_{R^+}$  data together, then, one concludes that structures such as **1a**, despite the strain of having a double bond in the four-membered ring, are preferred to structures such as **1b**. Possible



factors are that **1b** includes a double bond exocyclic to the four-membered ring and also requires complete coplanarity of the cation, with consequent decrease in degrees of freedom and possible unfavorable steric interactions.

In Figure 3 the  $pK_{R^+}$  values of **6–10** are plotted against the sum of  $\sigma_p^+$  values for substituents X and Y. The best straight line through the points has  $\rho = -4.49$ , the rather good correlation coefficient of 0.985, and a variance of 0.123. A simple assumption, however, which takes into account the fact that substituent effects are felt at the carbonium carbon more strongly from the "benzo" than from the C-1 aryl ring, improves the quality of this fit tremendously.

The possibility of 1,3- $\pi$  interaction across a cyclobutane ring has frequently been considered.<sup>14</sup> Perhaps the most striking evidence for 1,3- $\pi$  interaction is the ultraviolet absorption spectrum of the pentamethylcyclobutenyl cation,<sup>14g</sup> which has a  $\lambda_{max}$  at 245  $m\mu$ . Comparison with the spectra of allylic ( $\lambda_{max} \approx 300 m\mu$ ) and cyclopropenyl ( $\lambda_{max} < 185 m\mu$ ) cations suggests that the HMO 1,3- $\pi$  resonance integral is about  $0.33\beta$ . Nmr chemical shifts of the methyl groups reinforced this view.

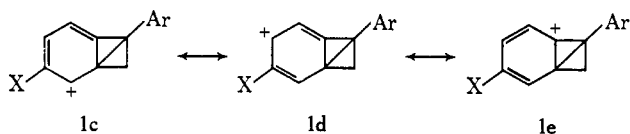
(14) (a) E. F. Silversmith and J. D. Roberts, *J. Am. Chem. Soc.*, **80**, 4083 (1958); (b) F. F. Caserio, Jr., S. H. Parker, R. Piccolini, and J. D. Roberts, *ibid.*, **80**, 5507 (1958); (c) F. F. Caserio, Jr., and J. D. Roberts, *ibid.*, **80**, 5837 (1958); (d) E. J. Smutny, M. C. Caserio, and J. D. Roberts, *ibid.*, **82**, 1793 (1960); (e) E. A. LaLancette and R. E. Benson, *ibid.*, **83**, 4867 (1961); (f) E. F. Kiefer and J. D. Roberts, *ibid.*, **84**, 784 (1962); (g) T. J. Katz and E. H. Gold, *ibid.*, **86**, 1600 (1964).

Table V. Preparation and Properties of the Carbonium Ion Precursors

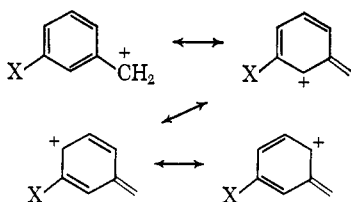
Compd	Mg, g (g-atom)	RBr, g (mole)	Ketone, g (mole)	Solvent, ml	Conditions	Yield, %	Mp, °C (recrystn solvent) <sup>b</sup>	Calcd, % C H	Found, <sup>c</sup> % C H
6	1.20 (0.05)	7.06 (0.045)	2.00 (0.0115)	THF, 35	Ref, 4 hr	35.5	89–90 (PE)	85.67 7.99	85.34 7.90
7	0.24 (0.01)	1.57 (0.01)	1.00 (0.00515)	THF, 25	Ref, 3 hr	74	101–102 (PE)	74.85 6.28	74.71 6.32
8	1.00 (0.04)	3.83 (0.02)	2.00 (0.0115)	THF, 25	Ref, 3 hr	18.3	69–70 (M)	75.86 7.04	75.62 7.04
9	0.36 (0.015)	2.22 (0.013)	2.00 (0.0103)	THF, 40	Ref, 5 hr	7	78–79 (M)	75.86 7.04	75.83 6.94
10	1.00 (0.04)	5.61 (0.03)	2.00 (0.0115)	THF, 25	Ref, 3 hr	10	84–85 (M)	81.04 8.16	81.00 8.14
11	0.48 (0.02)	2.13 (0.015) <sup>d</sup>	1.00 (0.0057)	E, 35	Rt, 4 hr	65.5	90–91 (PE)	82.06 9.54	82.04 9.58
12	1.20 (0.05)	7.69 (0.045)	2.00 (0.0115)	THF, 40	Ref, 4 hr	39	83–83.5 (PE)	85.67 8.33	85.68 8.11
13	0.36 (0.015)	1.04 (0.0086)	1.50 (0.0086)	E, 15	Rt, 1 hr	21	66–67 (PE)	83.28 9.32	83.22 9.24
15	0.60 (0.025)	3.83 (0.02)	2.00 (0.0137)	E, 30	Rt, 2 hr	<i>e</i>	<i>f</i>	74.27 5.84	74.16 5.72

<sup>a</sup> THF = tetrahydrofuran, E = anhydrous ether; the volume includes solvent used to prepare the Grignard reagent and solvent used to dissolve the ketone. <sup>b</sup> PE = 60–90° petroleum ether, M = methanol. <sup>c</sup> Spang Microanalytical Laboratory, Ann Arbor, Mich. <sup>d</sup> Methyl iodide. <sup>e</sup> Not determined, but about 50%. <sup>f</sup> The compound was an oil, purified by chromatography on Fisher S 157 28–200 mesh silica gel, using 75% petroleum ether–25% anhydrous ether as eluent.

A similar effect, if important in benzocyclobutenyl cations, could be represented by structures 1c–1e. This effect would be felt by substituents in the “benzo”



ring, but not in the C-1 aryl ring. The effect is approximated by that of a benzyl cation with a *meta*-X substituent and might be incorporated into the Hammett



plot (Figure 3) by including some fraction of  $\sigma_m^+$  for substituent X. Since the magnitude of 1,3- $\pi$  interaction appears to be about  $0.33\beta$ , we plotted  $pK_R^+$

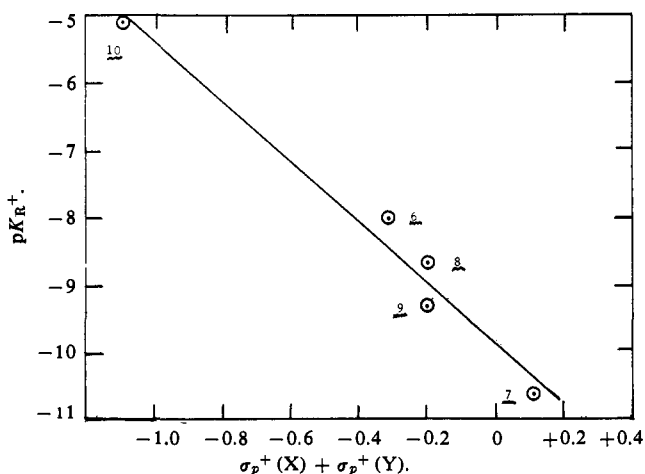


Figure 3. Hammett plot using the sum of  $\sigma_p^+$  for substituents in each ring.

against the sum  $\sigma_p^+(X) + 0.33\sigma_m^+(X) + \sigma_p^+(Y)$ , as shown in Figure 4.<sup>15</sup> The improvement in fit is striking.

(15) There is precedence for using more than one  $\sigma^+$  constant to define the total effect of a substituent in carbonium ion reactions; see, for example, H. Tanida, T. Tsuji, and H. Ishotobi, *J. Am. Chem. Soc.*, **86**, 4904 (1964).

The best straight line through the points has  $\rho = -4.05$ , with a correlation coefficient of 0.999 and a variance of 0.0139, barely one-tenth that of the line in Figure 3. A slightly better fit is obtained if one uses  $0.40\sigma_m^+(X)$  (variance 0.010) but any further increase in the coefficient of  $\sigma_m^+(X)$  has a deleterious effect on the fit.

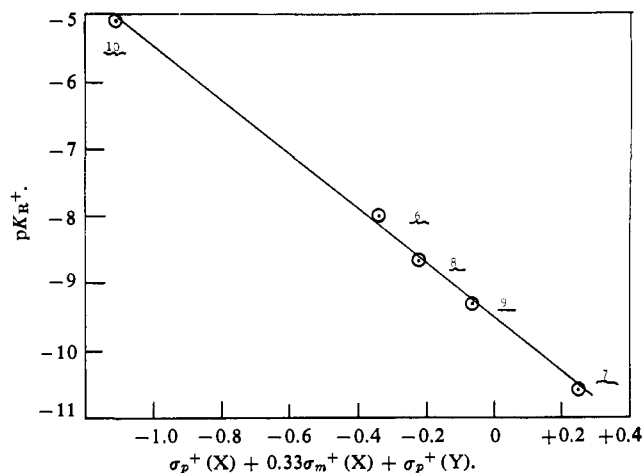


Figure 4. Hammett plot which includes 1,3- $\pi$  interaction.

We conclude that both the  $pK_R^+$  measurements and the nmr chemical shifts provide evidence for (a) a resonance mechanism (*i.e.*, 1a) and (b) 1,3- $\pi$  interaction (*i.e.*, 1c–e) as means by which charge may be delocalized in benzocyclobutenyl cations.

### Experimental Section

**Syntheses.** The required benzocyclobutenols or their methyl ethers were synthesized by adding the benzocyclobutenone to a solution of the appropriate Grignard reagent (excess) in either tetrahydrofuran or ether. The procedures were standard and require no elaboration. Work-up was by hydrolysis with dilute hydrochloric acid and the compounds were purified mainly by recrystallization, but sometimes by column chromatography on Alcoa 20F alumina, using petroleum ether (bp 30–60°) as the eluent. The essential details are given in Table V. The nmr spectra are summarized in Table II.

**Solvolysis of the Carbonium Ions.** Solution of 0.10 g of 6 in 0.5 ml of concentrated sulfuric acid gave the familiar deep red color of the carbonium ion  $6^+$ . After 10 min, the solution was hydrolyzed over approximately 5 g of ice. A white precipitate formed immediately; this was filtered and dried and gave 0.09 g (90%) of recovered 6, mp 88–89°, which had an infrared spectrum identical with that of the starting material. Similar treatment of 7 and 15 allowed 88 and 77% recovery of the carbinols, on hydrolysis of the carbonium ions. In the case of 8, 9, and 10, the carbonium

ion solutions were poured into cold methanol, rather than ice. The methyl ethers were recovered in 80, 89, and 76% yields, respectively.

Solutions of 11–14 in sulfuric acid were hydrolyzed using the "rapid dispersal" technique.<sup>16</sup> In no case was the starting carbinol

(16) N. C. Deno, H. G. Richey, Jr., N. Friedman, J. D. Hodge, J. J. Houser, and C. U. Pittman, Jr., *J. Am. Chem. Soc.*, **85**, 2991 (1963).

recovered; the products from these experiments have not been characterized.

**Spectra and  $pK_R$  + Measurement.** Spectra were measured at 25° using a Beckman DB spectrophotometer equipped with a Sargent recorder. Stock solutions in anhydrous methanol were prepared of such concentration that 0.100-ml aliquots in 10.00 ml of sulfuric acid gave measurable spectra. The sulfuric acid concentrations were determined by titration of weighed samples with standard base.

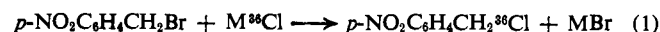
## The Effect of Ion Pairing on the Nucleophilic Reactivity of Anionic Nucleophiles. II. The Reaction of *p*-Nitrobenzyl Bromide with Chloride Ion in Liquid Sulfur Dioxide Solution at 0.00°<sup>1</sup>

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**Abstract:** Reaction kinetics were studied with the aid of <sup>36</sup>Cl. Relevant ion-pair dissociation constants,  $K_d$ , were determined by application of Shedlovsky's computational procedure to electrical conductance data. Gross second-order specific rates determined over a more than tenfold range of initial ionophore concentration were correlated by means of Acree's equation:  $k_2 = \alpha k_i + (1 - \alpha)k_p$ , where  $k_i$  and  $k_p$ , respectively represent the specific rates of the free ion and paired ion and  $\alpha$  is the degree of dissociation of the ionophoric nucleophile. Values of  $K_d$  and  $\alpha$  were obtained for each ionophore using several values of the Debye-Hückel distance parameter,  $a_{DH}$ , to calculate mean ionic activity coefficients. It was found that, although  $k_p$  values are sensitive to the choice of  $a_{DH}$ , the major conclusions of this work do not depend on this choice so long as  $a_{DH}$  is not taken as zero. Values of  $k_i$  and  $k_p$  (in units of  $10^{-5} M^{-1} \text{sec}^{-1}$ ) obtained with  $a_{DH}$  taken equal to the sum of ionic radii are, respectively, for RbCl,  $2.69 \pm 0.14$  and  $0.076 \pm 0.042$ ; for  $(\text{CH}_3)_4\text{NCl}$ ,  $2.92 \pm 0.25$  and  $0.47 \pm 0.38$ ; for  $(\text{C}_2\text{H}_5)_4\text{NCl}$ ,  $3.17 \pm 0.01$  and  $1.61 \pm 0.04$ . The value of  $k_p$  for KCl estimated from a single experiment with the aid of the average of  $k_i$  for the other three ionophores is  $0.03 \times 10^{-5} \text{sec}^{-1}$ . The present results and previous data<sup>3</sup> for bromide ion together show a regular increase of  $k_i/k_p$  with increase in  $1/K_d$  and a regular increase of  $(\Delta F_p^* - \Delta F_i^*)/\Delta F_d^\circ$  with increase in  $\Delta F_d^\circ$ . The mean value of  $k_i^{\text{Br}^-}/k_i^{\text{Cl}^-}$  is 2.52 for  $a_{DH} = r_+ + r_-$ . This sequence is the same as that observed in water and other protic solvents and opposite to that observed in acetone and dimethylformamide.

The background of this contribution is presented<sup>3</sup> in the first paper of this series. The objective of the second paper is to compare critically the effect of ion pairing on the nucleophilic reactivity of chloride ion in liquid  $\text{SO}_2$  solution with the analogous effect for bromide ion and to compare the nucleophilicities of the two halide ions when unencumbered by counterions. These comparisons are based on the reactions of both nucleophiles with the same substrate, *p*-nitrobenzyl bromide, PNBB. Thus, eq 1 represents the reaction investigated in this research.



### Experimental Section

**Preparation of Solutions, Sampling, Quenching, and Separation of Products.** These were performed as described previously<sup>3</sup> for reaction of ionophoric bromides at 0°. Sulfur dioxide was Virginia Smelting Co., Extra Dry grade. The completeness of separation

was judged to be satisfactory for RbCl and  $(\text{CH}_3)_4\text{NCl}$  on the basis of values of initial exchange which fell below 2% in almost all cases. Initial exchange was 20.7% in the single run carried out with KCl (concentration,  $8.25 \times 10^{-4} M$ ). The reason for this is not apparent. A single blank separation carried out with  $10^{-3} M (\text{C}_2\text{H}_5)_4\text{NCl}$  in the absence of *p*-nitrobenzyl bromide indicated that its concentration in toluene was about 9% of its concentration in water at room temperature. Initial exchange values confirmed this assessment. Because reactions were carried to relatively low conversions, 16% (in addition to initial exchange) or less in the case of  $(\text{C}_2\text{H}_5)_4\text{NCl}$ , no significant error was introduced by imperfect separation.

**Counting.** Proportional counting of solid mercurous chloride-364 was used to monitor the progress of the reaction. A thin ( $<125 \mu\text{g cm}^{-2}$ ) window flow counter, operated at a flow rate of 105 cc/min of P-10 gas, was used in conjunction with a Model SC-101 manual sample changer, a Model P-30 proportional preamplifier, and a Model SC-72 scaler, all Tracerlab products. The counter was operated at 2300 v, and the scaler at a sensitivity of 0.05 v. Sample dimensions, mounting technique, and counting geometry were constant throughout. Dead time error was negligible and statistical error in counts after correction for background less than 1.5%. Sample thicknesses were  $\sim 10 \text{mg/cm}^2$ .

The total aqueous extract<sup>3</sup> was evaporated to about 20 ml under reduced pressure and an amount of aqueous inactive KBr added sufficient to provide, *in toto*, the same mass of mercurous halide as that provided by the aliquots of the toluene extract employed for radioassay. (Throughout this work, *p*-nitrobenzyl bromide was

(1) Research supported by the National Science Foundation under Grants G 11315 and GP 4023.

(2) Based in part on a dissertation submitted by M. S. P. in partial fulfillment of the requirements for the Ph.D. degree granted by Boston University in June 1966. Cf., N. N. Lichtin and M. S. Puar, Abstracts, 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., April 1966, p 87K, for a preliminary communication.

(3) N. N. Lichtin and K. N. Rao, *J. Am. Chem. Soc.*, **83**, 2417 (1961).

(4) M. Kahn, A. J. Freedman, R. D. Feltham, and N. L. Lark, *Nucleonics*, **13** (5), 58 (1955).