(22) S. Winstein, *et al.*, *J. Amer. Chem. Soc.*, **76**, 2597 (1954).

(23) (a) Carbon tetrachloride solution; (b) deuteriochloroform for pmr, chloroform for ir.

(24) D. H. Barton, R. E. O'Brien, and S. Sternhell, *J. Chem. Soc.*, 470 (1962).

(25) These two absorptions actually constitute a AB pattern.

(26) Analysis believed to be low due to presence of ~4% **5**.

(27) The vinyl tosylate was found to decompose and rearrange whenever eluted through a silica gel column, the extent of which depended on the eluent and time spent on the column. The rearrangement yielded varying amounts of **1** and **5**.

(28) Pentane alone had been used previously.[3] Since there was some indication[11] that cyclopropyl ketones were not effectively measured under the previous conditions, it was hoped that the ether would be more effective. Since the present results agree quite well with the previous ones,[3] we conclude indeed that our percentages of ketones are accurate as well as precise.

(29) The identification of the first component as *cis*-acetylene and the second component as *trans*-acetylene as reported in ref 3 is now believed to have been in error. We have found that treatment of 90% *trans*-1-(2-methylcyclopropyl)-1-iodoethylene yields 90% of this first component acetylene. This would indicate that the first component acetylene should be trans and not cis, as reported previously.

(30) A listing of this program, which will be supplied on request, appears in the Ph.D. thesis of T.V.L., University of Cincinnati, 1974.

Stable Carbocations. CLXXX.[1] ^{13}C and ^{1}H Nuclear Magnetic Resonance Spectroscopic Study of Phenyl-, Methyl-, and Cyclopropyl-Substituted Alkenyl (Allyl) Cations. Further Studies of the Trend of Charge Distribution and the Relative Delocalization Afforded by Phenyl, Methyl, and Cyclopropyl Groups

George A. Olah* and Robert J. Spear[2]

Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106.

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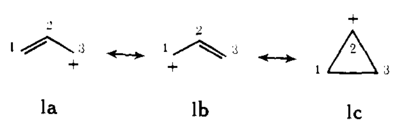
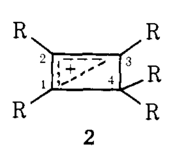
Abstract: Two series of methyl-, cyclopropyl-, and phenyl-substituted alkenyl (allyl) cations have been studied by ^{13}C NMR and ^{1}H NMR spectroscopy under stable-ion conditions. The 1,3-substituted alkenyl cations (**3a–f**) exclusively adopt the trans,trans conformation and exhibit strong charge delocalization between C_1 and C_3, whereas the charge in the 1,1-substituted alkenyl cations (**4a, 4b,** and **4d–f**) is substantially higher at C_1, the tertiary carbon. 1,3 overlap does not appear to contribute significantly to the total ion structure. In **3a–f,** the relative charge delocalization afforded by the substituents is cPr $\gtrsim$ Ph $\gg$ CH_3. It is suggested that the steric crowding inherent in tertiary carbenium ions and the subsequent disruption of resonance stabilization may lead to a different relative order for change delocalization in tertiary carbenium ions. A neighboring-group deshielding of carbenium ion centers by cyclopropyl groups was detected in addition to the normal α-substituent effect and opposing the shielding from charge delocalization, and this must be taken into consideration when comparing charge delocalization trends in carbocations.

Alkenyl cations (often called allyl cations) are the simplest conjugatively stabilized carbocations and have been the subject of many theoretical and experimental studies. The generation of alkenyl cations under stable-ion conditions can be achieved by a wide range of experimental procedures, including ionization of allylic alcohols and halides, ionization of cyclopropyl halides and alcohols, and hydride abstraction from alkenes. The earlier literature (to late 1965) on alkenyl cations generated under stable-ion conditions has been reviewed by Deno.[3]

The distribution of charge in alkenyl cations has been a subject of some controversy, particularly regarding the importance of 1,3 overlap (**1c**) relative to the two classical resonance structures **1a** and **1b**.[4,5] Recent molecular-orbital calculations have suggested that 1,3 overlap is not significant for acyclic alkenyl cations.[6] There is convincing experimental evidence that cyclobutenyl cations (**2**), where the proximity of C_1 and C_3 permits greater overlap between the π orbitals on these carbon atoms, have strong 1,3 overlap.[4] Our recent observation of the parent cyclobutenyl cation (**2**, R = H) indicates very strong 1,3 overlap in this species resulting in comparable charge density at C_1, C_2, and C_3 and thus the truly "homocyclopropenyl cation" nature of this ion.[7] The charge distribution will clearly be dependent upon the substituents at C_1, C_2, and C_3, and the relative delocalization afforded by the substituents should give additional insight into charge distributions in these systems.



1a **1b** **1c**



2

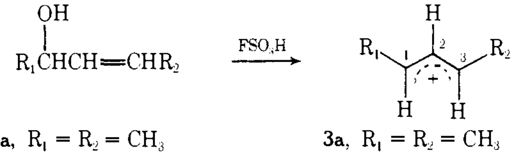
The factors which affect carbon-13 chemical shifts are currently being critically examined in many laboratories, including ours, and at the present time, it appears that although carbon-13 chemical shifts cannot be directly equated with charge densities, they do reflect the trend of charge densities at carbon atoms of similar hybridization and substitution.[1,8] Proton chemical shifts, which indirectly reflect the charge density at the carbon to which the proton is attached, are useful indications of charge distribution in carbocations, but the dependence of ^{1}H NMR shifts on a number of additional factors which are of comparable magnitude to the charge dependence can lead only to qualitative results. Although these same additional factors affect ^{13}C NMR shifts, they are of small magnitude relative to the total chemical shifts involved. Carbon chemical shifts therefore appear to be the most reliable tool for studies of charge distribution in carbocations.

Although the ^{1}H NMR spectra of a large number of alkenyl[3,9,10] and cycloalkenyl[3,4a,5,10] cations have been reported, the ^{13}C NMR shifts of only a few alkenyl[4b] and cycloalkenyl[5,11] cations have been published. In addition, the vast majority of carbocations of these types which have been studied by ^{1}H NMR or ^{13}C NMR spectroscopy have exclusive alkyl substitution. The 3-phenyl-2-pentenyl cation[4b] is the sole exception for alkenyl cations, while the ^{1}H NMR[5,11,12] and ^{13}C NMR[5,11] spectra of several cycloalkenyl cations which have phenyl substitution on the carbocationic fragment have been reported. In earlier work, Deno and coworkers had reported equilibrium and uv spectral data for some cycloalkenyl cations with either phenyl or cyclopropyl substitution.[3,12] It was concluded from this data that cyclopropyl groups gave considerable stability, while phenyl groups destabilized the cations relative to alkyl substituents.[3,12] At the same time, it must be recognized that these measurements always concern only energy differences between covalent precursors and their related ions. If there is, for example, release of strain going from the covalent precursor to the less strained ion, ion stabilities could be overestimated; this applies equally to solvolytic rate enhancements.

We have recently reported[13] the ^{13}C NMR spectra of a series of carbenium ions $R_1R_2R_3C^+$, where R_1, R_2, and R_3 were hydrogen, methyl, cyclopropyl, phenyl, and hydroxyl groups. It was concluded, largely from the ^{13}C NMR data for these ions, that the degree of charge delocalization afforded by the substituents was Ph > cPr ≫ CH_3, in contrast with Deno's results.[3,12] We have pointed out, however, that this sequence may differ in other systems.[13] We report now, as part of our continuing work, a study using ^{1}H NMR and ^{13}C NMR spectroscopy of a number of alkenyl cations with methyl, phenyl, and cyclopropyl substituents on the carbocationic fragment. The results are discussed in relation to charge distribution in these ions and the relative charge delocalization afforded by the substituents.

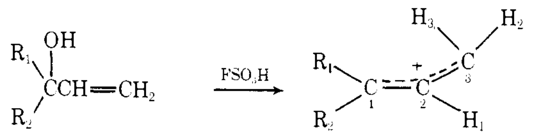
Results

We have prepared the alkenyl cations **3a–f**, **4a**, **4b**, and **4d–f** under stable-ion conditions. **3a–f**, **4b**, and **4d–f** were prepared by ionization of the allylic alcohols **5a–f**, **6b**, and **6d–f**, respectively, using FSO_3H-SO_2 at −78° (**5e**, **5f**, and **6a–f**) or FSO_3H-SO_2ClF at −120° (**5a–d**, **6b**). Under these conditions, polymer formation was negligible in all cases. **3d–f**, **2d**, and **2f** were stable to −15°, while **3b**, **3c**, **4b**, and **4e** decomposed at temperatures above −40°, and **3a** was not stable above −60°. The preparation of **3a** has been reported previously from 2,4-pentanediol in FSO_3H-SbF_5-SO_2,[14a] penta-2,3-diene in FSO_3H-SbF_5-SO_2[14b] and 1-chloro-2,3-dimethylcyclopropane in SbF_5-SO_2ClF.[14c]



5a, $R_1 = R_2 = CH_3$
b, R_1 = cPr; $R_2 = CH_3$
c, R_1 = Ph; $R_2 = CH_3$
d, $R_1 = R_2$ = cPr
e, R_1 = cPr; R_2 = Ph
f, $R_1 = R_2$ = Ph

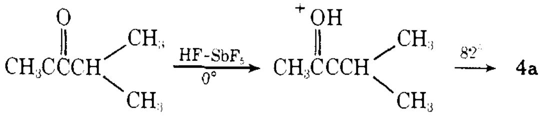
3a, $R_1 = R_2 = CH_3$
b, $R_1 = CH_3$; R_2 = cPr
c, $R_1 = CH_3$; R_2 = Ph
d, $R_1 = R_2$ = cPr
e, R_1 = cPr; R_2 = Ph
f, $R_1 = R_2$ = Ph



6a, $R_1 = R_2 = CH_3$
b, $R_1 = CH_3$; R_2 = cPr
c, $R_1 = CH_3$; R_2 = Ph
d, $R_1 = R_2$ = cPr
e, R_1 = cPr; R_2 = Ph
f, $R_1 = R_2$ = Ph

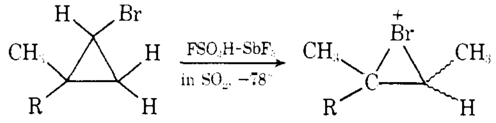
4a, $R_1 = R_2 = CH_3$
b, $R_1 = CH_3$; R_2 = cPr
c, $R_1 = CH_3$; R_2 = Ph
d, $R_1 = R_2$ = cPr
e, R_1 = cPr; R_2 = Ph
f, $R_1 = R_2$ = Ph

Attempted ionization of **6a** and **6c** under a variety of conditions yielded only polymeric materials. The preparation of **4a** has been reported previously from 3-methyl-2-butanone (**7a**) and HF-SbF_5[10] and from 3-chloro-2-methylbut-1-ene and SbF_5 using the "molecular beam" technique.[15] In our hands, heating **7a** in HF-SbF_5 at 82° as described[10] proceeded extremely slowly to about 50% conversion to **4a**, but any attempt to increase this significantly resulted in complete polymerization.



7a **7b**

The preparation of **4a** and **4c** from 1-bromo-2,2-dimethylcyclopropane (**8a**) and 1-bromo-2-methyl-2-phenylcyclopropane (**8b**), respectively, was attempted, using the procedure described for other cyclopropyl halides.[9] Under these conditions, **8a** and **8b** initially yielded the bromonium ions **9a** [^{1}H NMR δ 2.45 (3 H, d, J = 6.5 Hz, C_2CH_3), 2.92 (6 H, s, 2 × C_1CH_3), 6.41 (1 H, q, H-2)] and **9b** [^{1}H NMR δ 2.70 (3 H, d, J = 6.5 Hz, C_2CH_3), 3.46 (3 H, s, C_1CH_3), 7.11 (1 H, q, H-2), 8.0–8.5 (5 H, m, Ph)]. When the temperature was raised, **9b** yielded only polymeric products, whereas **9a** could be heated at −10° for 10 min without decomposition.

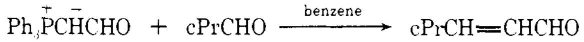


8a, R = CH_3
b, R = Ph

9a, R = CH_3
b, R = Ph

Ionization of 3-chloro-3-phenyl-1-butene under a variety of conditions also yielded only polymeric materials, and thus all attempts to prepare **4c** were unsuccessful. This most probably is due to the ion, when formed, reacting with unionized precursor and not to any instability of the ion.[16] **4a** was prepared from **7a** as described;[10] the absorptions (^{13}C NMR and ^{1}H NMR) due to **7b** were readily differentiated from those due to **4a**.

The preparation of **5b**, **5d**, **5e**, and **6d** had not previously been described. **5b**, **5d**, and **5e** were readily prepared by the reaction of cyclopropylmagnesium bromide on 2-butenal, 3-cyclopropylpropenal (**10**, from formylmethylenetriphenylphosphorane and cyclopropylcarboxaldehyde, shown below) and 3-phenylpropenal, respectively, and all were isolated in high yield. **6d** was prepared by the reaction of vinylmagnesium chloride with dicyclopropyl ketone. The full details are given in the Experimental Section.



$$Ph_3\overset{+}{P}\overset{-}{C}HCHO + cPrCHO \xrightarrow[\text{reflux, 24 hr}]{\text{benzene}} \underset{\textbf{10}}{cPrCH{=}CHCHO}$$

The ^{13}C NMR and ^{1}H NMR parameters for **3a–f**, **4a**, **4b**, and **4d–f** are given in Tables I and II, respectively; the parameters for **6a–f** are also included for comparison. The assignment of the proton resonances in **3a–f**, **4a**, **4b**, and **4d–f** is straightforward. The majority of the carbon-13 resonances are also readily assigned by consideration of the off-resonance and proton-coupled spectra. The assignment of C_1 and C_3 in **3b**, **3c**, and **3e** is not obvious, and it was initially anticipated that the determination of specific long-range

Table I. ^{13}C NMR Data[a] for the 1,3-Substituted Alkenyl Carbenium Ions (3a–f), the 1,1-Substituted Alkenyl Carbenium Ions (4a, 4b, 4d–f), and Precursor Alcohols 6a–f

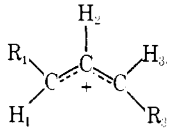
Compd	Alkenyl			Cyclopropyl		Aromatic				Methyl
	C_1	C_2	C_3	C_α	C_β	C_{ipso}	C_{ortho}	C_{meta}	C_{para}	CH_3
3a[b]	231.3	147.0	231.3							29.8
3b[c]	194.7 $^1J = 164.4$	139.4 $^1J = 167.5$	227.0 $^1J = 159.1$	45.8 $^1J = 180.5$	42.2 $^1J = 174.3$					24.0
3c[c]	205.1 $^1J = 160.5$	136.5 [l]	196.9 $^1J = 160.6$			135.1	148.0, 137.0	132.2, 132.0	149.9	26.7
3d[c]	211.3 $^1J = 160.7$	135.6 $^1J = 167.7$	211.3 $^1J = 160.7$	32.9 $^1J = 177.3$	23.4 $^1J = 171.6$					
3e[e]	218.1 $^1J = 162.1$	132.0 [l]	181.2 $^1J = 166.8$	40.4 $^1J = 179.2$	35.1 $^1J = 173.0$	132.6	137.2, 132.6	131.0, 130.4	141.8	
3f[e]	186.8 $^1J = 162.7$	129.3 $^1J = 166.3$	186.8 $^1J = 162.7$			135.3	143.3, 133.5	131.6, 131.3	144.7	
4a[f]	268.2	146.7	174.0							19.3
6a[g,j]	73.6 (194.6)	147.0 (−0.3)	112.5 (61.5)							29.4 (−10.1)
4b[d]	249.6	141.8 $^1J = 166.6$	150.3 $^1J = 168.2$	54.0 $^1J = 176.3$	49.9 $^1J = 175.6$					19.6
6b[h,j]	74.3 (175.3)	143.8 (−2.0)	113.7 (36.6)	21.9 (32.1)	1.8, 1.6 (48.1, 48.3)					26.9 (−7.3)
6c[i,k]	75.4	144.1	112.5			146.6	128.6	125.5	127.2	28.2
4d[e]	276.4	132.7 $^1J = 158.8$	148.5 $^1J = 167.2$	34.2 $^1J = 178.5$	34.2 $^1J = 172.2$					
6d[g,j]	76.1 (200.3)	140.0 (−7.3)	115.2 (33.3)	19.6 (14.6)	0.9, 1.3 (32.9, 33.3)					
4e[e]	234.6	133.8	157.7	42.0	43.9	140.2	135.8	130.4	142.5	
6e[i,j]	77.9 (156.7)	142.2 (−8.4)	115.2 (42.5)	22.0 (20.0)	3.2, 1.6 (40.8, 42.2)	146.7 (−6.5)	129.4 (6.4)	127.3 (3.1)	128.5 (14.0)	
4f[e]	227.0	136.2	149.5			142.2	141.3	132.0	147.8	
6f[h,j]	79.9 (147.3)	143.2 (−7.0)	114.4 (35.1)			146.3 (−4.1)	127.4 (13.9)	128.8 (3.2)	127.9 (19.9)	

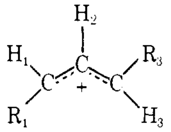
[a] Chemical shifts are in parts per million external (capillary) TMS, coupling constants are in hertz. [b–d] In FSO_3H-SO_2ClF solution at −70, −80, and −60°, respectively. [e] In FSO_3H-SO_2 solution at −60°. [f] In $HF-SbF_5$ (1 : 1) solution at 37°. [g–i] In SO_2 solution at −60, −30, and −40°, respectively. [j] Numbers in brackets refer to $\delta_{ion} - \delta_{alcohol}$. [k] 4c could not be observed under stable ion conditions. [l] ^1J could not be determined due to overlap with neighboring signals.

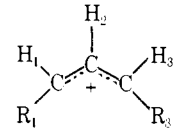
($^2J_{CH}$ or $^3J_{CH}$) couplings might differentiate these carbons. However, the proton-coupled C_1, C_3, and C_2 resonances show only the large $^1J_{CH}$ couplings with no clearly resolved fine structure but it was noticed that the proton-coupled C_1 = C_3 resonance in **3a**, the δ 194.7 resonance in **3b**, and the δ 205.1 resonance in **3c** were much broader (width at half-height ($W_{1/2}$) $\simeq$ 25 Hz for each doublet peak) than the other C_1, C_3, and C_2 resonances in **3b–f**, where $W_{1/2}$ was $\simeq$15 Hz. This is consistent with all the long-range couplings being small (<4 Hz), and the methyl-substituted carbons, having more geminal protons, are broader because of the larger number of couplings; these broader resonances are assigned to C_1 in **3b** and **3c**. The proton-coupled resonances assigned to C_1, C_2, and C_3 in **3b** and C_1 and C_3 in **3c** (C_2 is obscured by the aromatic carbon resonances) are shown in Figures 1a and 1b, respectively.

Discussion

The ^1H NMR and ^{13}C NMR spectra of the 1,3-substituted carbenium ions **3a–f** provide new and interesting information. It was previously concluded[14a,c] that since the ^1H NMR spectrum was temperature independent and indicated a symmetrical ion, **3a** exclusively adopted the trans,trans conformation (with respect to H_1,H_2 and H_2,H_3, Table II). The ^1H NMR spectra for **3a–f** are consistent with this conclusion since, with the exception of **3f**, all have very large $J_{1,2}$ and $J_{2,3}$ values, consistent with transoid vicinal protons. The negligible $J_{1,3}$ values in **3b, 3c**, and **3e** also support this conclusion since $J_{1,3}$ would be predicted to be negligible in the trans,trans conformation but substantial (2–3 Hz) in **IIc**.[17] The symmetry of the ^1H NMR spectra of **3d** and **3f** rules out **IIa** and **IIb**, and the temperature independence of the H_1, H_2, and H_3 resonances in **3a–f** defines the conformation of these ions as trans,trans.


IIa


IIb


IIc

The barrier to rotation about the C_1–C_2 and C_2–C_3 bonds has previously been shown to be substantial in a number of alkylated alkenyl cations.[14a,c,18] The ^1H NMR spectra of **3f** and **3g** are characterized by two ortho proton resonances (Table II), and the ^{13}C NMR spectra show both nonequivalent ortho and meta carbons (Table I), indicating hindered rotation about the C_1–Ph and C_3–Ph bonds. When the temperature is slowly raised, the ortho proton resonances in **3f** and **3g** slowly coalesce, and at −20° only one resonance is observed. The H_1, H_2, and H_3 resonances are, however, temperature independent, indicative of the high C_1–C_2 and C_2–C_3 rotational barriers. We have not, as yet, determined the temperature dependence of the carbon-13 spectra.

As discussed in the introductory section, alkenyl cations can be considered as resonance hybrids of **1a–c**. The nature of the substituents at C_1 and C_3 will clearly influence the relative contributions from **1a** and **1b**, and this can be seen in the C_1 and C_3 shifts (Table I) of **3a–f** and **4a, 4b**, and **4d–f.** In the 1,3-substituted ions, the downfield shifts indicate that there is extensive charge delocalization between C_1 and C_3, with the differences in these two chemical shifts reflecting differences in charge delocalizing capabilities and other substituent influences of the phenyl, methyl, and cyclopropyl groups. In contrast, the charge in the 1,1-substi-

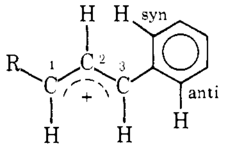
Table II. ^1H NMR Data[a,b] for the 1,3-Substituted Alkenyl Carbenium Ions (3a–f), the 1,1-Substituted Alkenyl Carbenium Ions 4a, 4b, and 4d–f, and Precursor Alcohols 6a–f

Compd	Alkenyl protons H_1	Alkenyl protons H_2	Alkenyl protons H_3	Cyclopropyl[c] H_α	Cyclopropyl[c] H_β	Aromatic	Methyl
3a[d]	9.83 m	8.05 t $J_{1,2} = J_{2,3} = 14.0$	9.83 m				3.12 d $J_{1,CH_3} = 5.5$
3b[e]	8.65 dq $J_{1,2} = 14.5$ $J_{1,CH_3} = 7.0$	7.29 dd $J_{1,2} = 14.5$ $J_{2,3} = 11.5$	8.96 t $J_{2,3} = J_{\alpha,3} = 11.5$	3.60	3.20, 3.46		2.78 d $J_{1,CH_3} = 7.0$
3c[e]	8.89 dq $J_{1,2} = 14.0$ $J_{1,CH_3} = 7.5$	8.39 t (broadened)	9.14 d $J_{2,3} = 13.8$			H_{ortho} 8.10 H_{meta} 7.68 H_{para} 7.83	2.59 d $J_{1,CH_3} = 7.5$
3d[e]	7.92[i]	7.92[i]	7.92[i]	2.70	2.14, 2.43		
3e[f]	8.60 dd $J_{1,\alpha} = 3.3$ $J_{1,2} = 15.5$	7.23 t $J_{1,2} = J_{2,3} = 15.5$	8.66 d $J_{2,3} = 15.5$	2.55	2.05 2.83	H_{ortho} 8.09, 8.39 H_{meta} 7.62 H_{para} 7.70	
3f[f]	8.76 d $J_{1,2} = 9.5$	8.52 t $J_{1,2} = J_{2,3} = 9.5$	8.76 d $J_{1,2} = 9.5$			H_{ortho} 7.95, 8.26 H_{meta} 7.50 H_{para} 7.70	
4a[g]	8.40	8.05[i]	8.05[i]				3.55
6a[h]	5.98	4.95	5.18				1.22
4b[d]	7.99 dd $J_{1,2} = 10.5$	7.20 d $J_{2,3} < 1$	7.42 d $J_{1,3} = 15.5$	3.7	3.6		2.74
6b[h]	5.98	5.20	5.36	1.20	0.55		1.40
6c[h]	5.96	4.98	5.08			7.2 m	1.36
4d[f]	7.20 dd $J_{1,2} = 4.0$	6.65 d $J_{2,3} < 1$	6.58 d $J_{1,3} = 14.0$	2.70	2.4		
6d[h]	5.85 dd	5.14 dd	5.33 dd	1.00	0.35		
4e[f]	6.42 dd $J_{1,2} = 6.0$	7.01 d $J_{2,3} < 1$	7.06 d $J_{1,3} = 12.5$	3.16	3.00	7.6–8.1, m	
6e[h]	5.66	4.96	5.15	1.05	0.25	7.2 m	
4f[f]	[j]	[j]	[j]			7.7–8.5, m	
6f[h]	6.23	5.00	5.05			7.10	

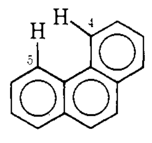
[a] Chemical shifts are in parts per million external (capillary) TMS, coupling constants are in hertz. [b] Multiplicities are given as d = doublet, t = triplet, q = quartet, m = multiplet, etc. [c] The cyclopropyl chemical shifts represent the center of the multiplets. [d,e] In FSO_3H-SO_2ClF solution at −80 and −60°, respectively. [f] In FSO_3H-SO_2 solution at −60°. [g] In $HF-SbF_5$ solution at 37°. [h] In SO_2 solution at −40°. [i] Approximate chemical shifts, tightly coupled system. [j] Obscured by the aromatic absorptions.

tuted cations resides substantially at the tertiary C_1 carbon relative to the primary C_3 carbon; $\Delta\delta$ C_1,C_3 = 76.9 (**4e**) to 127.9 (**4d**). Variations in the C_1 and C_3 shifts again largely reflect additional substituent influences.

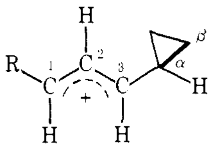
It would be expected that the absence of substituents at C_1 and C_3 which can conjugatively delocalize positive charge (or their presence at C_2) should enhance the contribution of **1c**. In **3a–f**, the successive replacement, at C_1 and C_3, of cyclopropyl and phenyl groups by methyl groups should therefore place more charge at C_2 (i.e., increase **1c**) and thereby deshield C_2. Comparison of the ^{13}C NMR data for **3a–f** indicates that relative deshielding does occur. However, an additional factor must be considered since the ortho carbons in the phenyl groups and the β carbons in the cyclopropyl groups, attached to C_1 and C_3, are γ substituents with respect to C_2 (CH_3 is only a β substituent), and the presence of a γ substituent is well known to produce shielding of carbon resonances, most probably by a through-space mechanism.[19] Ion **12**, shown above, is clearly analogous, in this regard, to phenanthrene (**13**) where C_4 and C_5 are mutually shielding. This strong mutual shielding can be seen in the C_{ortho} shifts for **3c**, **3e**, and **3f** (Table I) where one carbon resonates at normal field, i.e., slightly more shielded than C_{para}; while the other ortho carbon is only slightly less shielded than the meta carbons; $\Delta\delta_{ortho}$ = 11.0 (**3c**), 4.6 (**3e**), and 9.8 (**3f**). The shielded ortho carbon is therefore assigned as $C_{ortho,syn}$ (cf. **12**). The cyclopropyl group could adopt either the syn (**14a**) or anti (**14b**) conformation, but it is not possible to decide, either from the ^{13}C NMR or ^1H NMR (e.g., J_{H_1,H_α}) data, the relative proportions of the conformers. Since C_2 is shielded in **3b**, **3d**, and **3e** relative to **3a**, it can be concluded that the proportion of the syn conformer, where the β carbons of the cyclopropyl group are γ substituents to C_2, is significant.



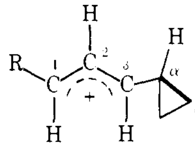
12



13



14a



14b

It can reasonably be assumed that the α- and β-substituent effects (and any other longer range effects) should be approximately equal for $C_{ortho,anti}$ and $C_{ortho,syn}$, hence the difference $\Delta\delta_{ortho}$ in **3c**, **3e**, and **3f** should closely approximate the shielding of C_2 by $C_{ortho,syn}$, i.e., the γ-substituent effect. Although the analogous shielding of C_2 by C_β of the cyclopropyl group is not known, it would be expected to be comparable to that due to the phenyl group. The C_2 shifts in **3b–f** can thus be corrected for the γ-substituent effect, yielding a value of 145–150 ppm which is comparable to the 147.0 ppm shift observed for C_2 in **3a**.

In the 1,1-substituted alkenyl cations, the same trend in

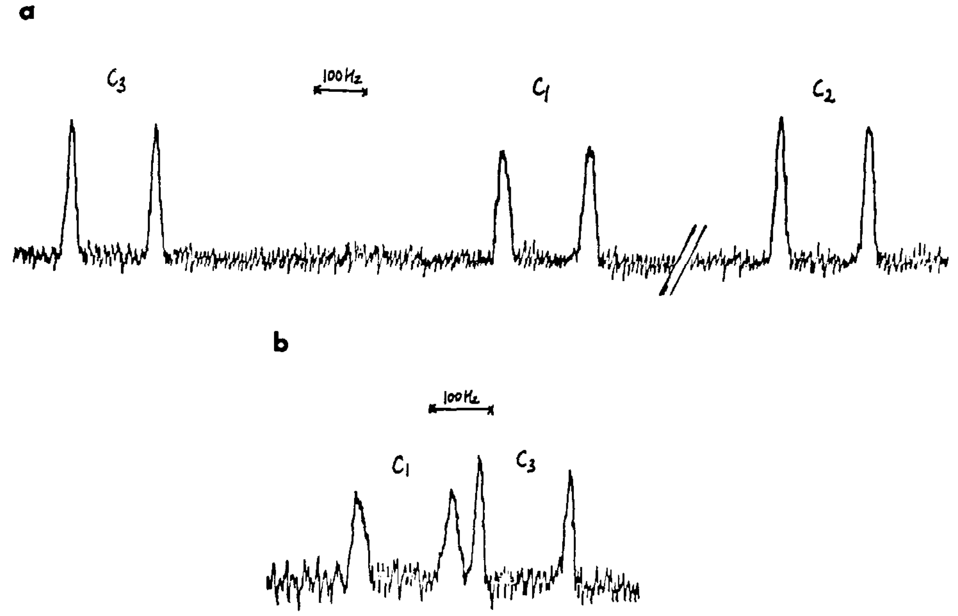


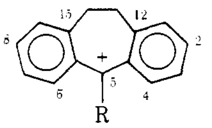
Figure 1. (a) A portion of the proton-coupled ^{13}C NMR spectrum of the 3-cyclopropyl-2-butenyl cation (**3b**). The portions shown are those assigned to C_1, C_2, and C_3. (b) A portion of the proton-coupled ^{13}C NMR spectrum of the 3-phenyl-2-butenyl cation (**3c**). The portions shown are those assigned to C_1 and C_3; C_2 is obscured by overlapping aromatic carbon resonances.

the C_2 shift can be seen (cf. **3a–f**). However, it was concluded that the change is largely localized at C_1, i.e., **1b** predominates over **1a,** and thus **1c** should not be expected to contribute significantly either. The shielding of C_2 in **4b** and **4d–f** relative to **4a** is again most probably attributable to γ-substituent effects.

The ^{13}C NMR shifts in the alkenyl cations can thus be explained without invoking significant 1,3-orbital overlap. It would appear that 1,3 overlap does not contribute significantly to the total ion structure of alkenyl cations unless the cationic fragment is contained in a cyclobutane ring.[4,7]

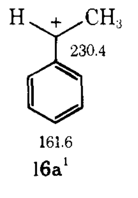
The presence of methyl, phenyl, and cyclopropyl groups in **3a–f** gives rise to distinct chemical shift changes, particularly at C_1 and C_3. The $C_1 = C_3$ resonances in the symmetrical ions **3a** (δ 231.3), **3d** (δ 211.3), and **3f** (δ 186.8) are clearly analogous to the results seen previously in the carbenium ions[13] where the substitution of CH_3 by cPr, and cPr by Ph, results in shielding of the carbenium center. In contrast, comparison of the C_1 and C_3 resonances in the unsymmetrical ions **3b, 3c,** and **3e** (Table I) gives a different picture; C_1 in **3b** (δ 194.7) and **3c** (δ 205.1) can be compared with that in **3a** (δ 231.3), and this suggests that the cyclopropyl group at C_3 delocalizes more charge away from C_1 than does a phenyl group. In addition, the problem of neighboring-group effects is minimized since a change in the chemical shift of C_1 is observed, while the substituent changes are occurring at C_3 which is effectively screened from C_1. Comparison of the cyclopropyl-substituted carbons (C_3 in **3b** and C_1 in **3d** and **3e,** Table I), the phenyl-substituted carbons (C_3 in **3c, 3e,** and **3f,** Table I), or the methyl resonances in **3a–c** shows the same trends.[20] The para carbon resonances in **3c** (δ 149.9), **3e** (δ 141.8), and **3f** (δ 144.7) also demonstrate that the relative order of charge delocalization in the system is cPr $\gtrsim$ Ph $\gg$ CH_3, as do the ortho carbon resonances.

A rationalization of the results for **3a, 3d,** and **3f** and the trend of deshielding of the carbenium carbon when cPr replaces Ph, with the conclusions reached concerning the relative order of charge delocalization, requires that a phenyl group gives rise to a smaller substituent deshielding, i.e., α-substituent effect, than cyclopropyl or methyl groups, in addition to the charge factor. Evidence for this conclusion can be found in the results for the dibenzocycloheptadienyl cations **15a–d**[21] where it was shown that the α effect (i.e., substituent effect) of a methyl or cyclopropyl group at a carbenium ion center is deshielding by about 22 ppm relative to hydrogen, while a phenyl group deshields by about 10 ppm.

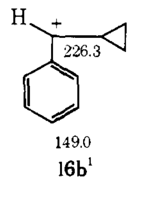


15a, R = H; δC_5 = 195.6
b, R = CH_3; δC_5 = 218.3
c, R = cPr; δC_5 = 217.0
d, R = Ph; δC_5 = 205.1

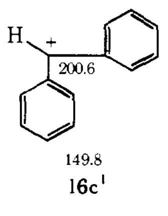
Although the differences in the carbenium ion shifts for the phenyl and cyclopropyl substituted carbenium ion centers can, in part, be explained by differing neighboring α-substituent effects, it must be recognized that in **3a–f,** the phenyl and cyclopropyl groups most probably adopt the conformation giving optimum orbital overlap with the carbenium carbon p orbital, as opposed to **15a–d,** and the α effect of these groups may, in addition, be dependent upon the conformation of the substituent. By comparison of the carbon resonances in **3a–f** with some secondary carbenium ions (**16a–c**),[1] the same trends are observed; the C_{para} shifts reflect the same order of charge delocalization observed in **3a–f** with the difference between cPr and Ph being very much smaller than CH_3, and the relative carbenium carbon shifts are analogous. The large differences in the C_{para} shifts in **16a** and **16b,** and C^+ shifts in **16b** and **16c,** coupled with the small differences in the C^+ shifts for **16a** and **16b,** and the C_{para} shifts for **16b** and **16c,** strongly indicate that



16a[1]



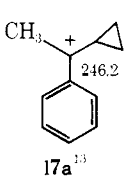
16b[1]



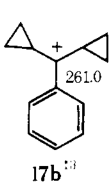
16c[1]

the cyclopropyl group is causing a large neighboring-group deshielding, while the phenyl and cyclopropyl groups delocalize comparable charge.

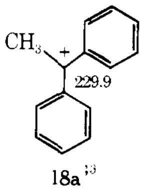
The 1,1-substituted alkenyl cations **4a, 4b,** and **4d–f** follow comparable trends to **3a–f.** The C_1 resonances for **4b** (δ 249.6) and **4d** (δ 276.4) are unexpected, because replacement of a CH_3 by a cPr produces a *deshielding* of 27.2 ppm. Two similar but smaller effects were noted in the previous carbenium ion studies (**17a, 17b** and **18a, 18b**).[13] The understanding of tertiary carbenium ions can be more complicated than that of secondary ions, because steric constraints permit only two of the three groups at C_1 to simultaneously delocalize the charge, and this gives rise to situations such as **18a** and **4f** (Table I) where the two phenyl groups are magnetically equivalent, **18b** which has nonequivalent phenyl groups, while the three phenyl groups in the triphenyl carbenium ion are magnetically equivalent. We recognize that the explanation suggested previously[13] for the nonequivalence of the two phenyl groups in **18b**, i.e., that the cyclopropyl group causes a significant shielding of the phenyl group lying in its face in the bisected conformation cannot explain these effects, and a more probable rationale is that the two phenyl groups in **18b** have a different degree of planarity.



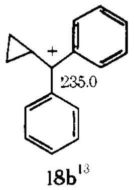
17a[13]



17b[13]



18a[13]



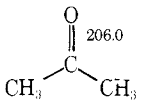
18b[13]

The tertiary carbenium ions thus may be characterized by the substituents adopting a conformation which is a balance between the optimum geometry for conjugative delocalization and steric interactions. Steric crowding may therefore become a significant factor with respect to competitive charge delocalization in tertiary carbenium ions, and any comparison with secondary systems (i.e., **3a–f, 16a–c**) must be made with extreme caution.

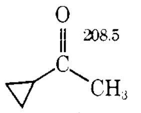
Indeed, steric factors are probably of major importance in competitive charge delocalization in carbenium ions. Delocalization of charge into a phenyl ring will be favored, because a large conjugated system is formed, although the aromatic resonance energy must, in part, be overcome, while conjugation employing the bent σ bonds of the cyclopropyl group will produce a smaller conjugated system but will probably release some strain in the small ring. However, comparing **12** with **14a** and **14b,** there will be greater steric interaction in **12,** and this may be the factor which favors delocalization by the bent σ bonds of the cyclopropyl group. A similar argument can be made for delocalization by a vinyl group, and the relative order of Ph, cPr, and $-CH{=}CH_2$ delocalization could presumably change within systems of different steric crowding.

We therefore conclude that *the relative order of charge delocalization in substituted secondary carbenium ions is* $cPr \gtrsim Ph \gg CH_3$, *and that the cyclopropyl group induces a significant neighboring-group deshielding of the carbenium ion center.* In order that the delocalization trends can be rationalized with the C_1 and C_3 shifts in **3a–f** and the results for **16a–c,** a neighboring-group deshielding, opposing the shielding from conjugative delocalization, of up to 30 ppm must be induced by the cyclopropyl group.

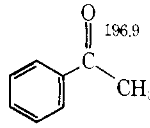
The magnitude of this effect in ionic species is unexpected since there is no unusual effect upon saturated carbons (e.g., compare C_1 in **6a–f,** Table I) or aromatic hydrocarbons,[13] but the effect is possibly operative in the ^{13}C NMR shifts for the carbonyl carbon atoms in 2-propanone (**19a**), cyclopropylmethyl ketone (**19b**), and acetophenone (**19c**) since it would be expected that **19b** and **19c** would both be more shielded than **19a** because of charge delocalization.



19a[13]



19b[13]



19c[13]

It would seem that this neighboring-group effect must be strongly dependent upon the orientation of the cyclopropyl group since it is apparently only observed concurrent with conjugative electron donation and on the total charge at the carbenium center which is being stabilized. The shielding constant for an atom is generally assumed[22] to be composed of a paramagnetic term (σ_p) which is dominated by charge polarization with lesser contributions from bond order and average excitation energy, a diamagnetic term (σ_d), and a term reflecting neighboring-group effects (σ^1).[23] For carbon atoms, the paramagnetic term is usually considered to be much more significant than the ΔE and σ_d factors, but recent work suggests that variations in these latter two parameters may be important for some types of carbon atoms,[24-26] and this possibility certainly cannot be excluded. We are continuing experimental and theoretical studies of other model systems to further deduce the nature of neighboring-group effects, i.e., α-substituent effects and additional factors in carbocations.

Conclusion

The ^{13}C NMR spectra of a series of 1,3-substituted alkenyl cations (**3a–f**) and 1,1-substituted alkenyl cations (**4a, 4b,** and **4d–f**) have demonstrated extensive charge delocalization between C_1 and C_3 in **3a–f** but substantial localization of charge at C_1, the tertiary carbon, in **4a, 4b,** and **4d–f.** 1,3-Orbital overlap does not appear to contribute significantly to the total resonance structure of these ions. The ^{1}H NMR spectra indicate that **3a–f** exclusively adopt the trans,trans conformation.

The additional charge delocalization afforded by the substituents at C_1 and C_3 in **3a–f** is in the relative order $CH_3 \ll Ph \lesssim cPr$. The relative order of charge delocalization deduced from preceding carbenium ion studies,[13] i.e., phenyl delocalizes charge better than cyclopropyl by a significant factor, should therefore be reconsidered since the large neighboring-group deshielding by the cyclopropyl group was not fully realized. However, the carbenium ions which were studied were mainly tertiary, and comparison of results from secondary systems (e.g., **3a–f**) with tertiary systems (e.g., **4a, 4b,** and **4d–f**), where steric crowding will be significantly greater, should be made with caution. Further, the additivity of these neighboring-group effects cannot be assessed.

Phenyl, vinyl, and cyclopropyl groups in all probability can show comparable ability to conjugatively delocalize positive charge, and steric interactions within a particular system may determine the relative order. Cyclopropyl-substituted carbenium ions are comparable to phenyl-substituted carbenium ions in their stability, and the large rate enhancements observed in some solvolytic reactions proceeding through the former ions are probably caused by release of strain in reaching the carbocationic transition state and not by large energy differences between the former and latter ions.

The significant neighboring-group effect of a cyclopropyl group on a carbenium ion center appears to be dependent upon both the orientation of the cyclopropyl group and the charge being stabilized. As emphasized before, the chemical shifts of carbenium ion centers cannot be directly related with charge differences, while relative comparisons can only be made with certainty if no substituents are changed at the center. The change of CH_3 by cPr by Ph will introduce significant neighboring-group differences as will other groups with differing size and bonding nature. However ^{13}C NMR studies, even with these restrictions, remain the optimum tool for studying not only the structure but the charge distribution in carbocations. We are continuing our studies on neighboring-group effects in carbocations to increase our knowledge and understanding of the factors which affect these systems.

Experimental Section

Pent-3-en-2-ol (**5a**), 2-methylbut-3-en-2-ol (**6a**), 1-cyclopropyl-1-phenylprop-2-en-1-ol (**6e**), and 3-methyl-2-butanone (**7a**) were commercial samples. Vinylmagnesium chloride was commercially obtained as an approximately 2 *M* solution in THF. 1-Phenylbut-2-en-1-ol (**5c**),[27] 1,3-diphenylprop-2-en-1-ol (**5f**),[28] 1,1-dibromo-2,2-dimethylcyclopropane,[29] and 1-bromo-2,2-dimethylcyclopropane (**8a**)[30] were prepared as described in the literature.

1-Cyclopropylbut-2-en-1-ol (5b). A solution of 2-butenal (12.2 g) in THF (50 ml) was added dropwise, with stirring, to an ice-cooled solution of cyclopropylmagnesium bromide [from magnesium (6 g) and cyclopropyl bromide (36 g) in THF (150 ml)]. After complete addition, the reaction was stirred overnight and worked up by the addition of water. The mixture was filtered, and the combined organic layers after ether extraction were washed with water, 10% sodium bisulfite solution, saturated aqueous bicarbonate, and brine. Removal of solvent yielded a yellow oil which upon distillation gave **5b** as a colorless liquid (10.2 g): bp 60-61° (5 mm); ν_{max} (liquid film) 3420 (broad), 3090, 1660, 1445, 1375, 825 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.5-0.8 (4 H, m, H_β-cyclopropyl), 1.58 (1 H, dd, J = 4.0, 6.5 Hz, H_α-cyclopropyl), 2.00 (3 H, d, J = 4.0 Hz, CH_3), 2.96 (1 H, broad s, OH), 3.76 (1 H, dd, J = 4.0, 7.5 Hz, H_1), 5.77 (1 H, dd, J = 17.0, 7.5 Hz, H_2), and 6.15 (1 H, dq, J = 17.0, 4.0 Hz, H_3).

Anal. Calcd for $C_7H_{12}O$: C, 75.0; H, 10.8. Found: C, 75.0; H, 10.7.

1,3-Dicyclopropylprop-2-en-1-ol (5d). A solution of cyclopropylcarboxaldehyde (6.0 g, prepared from cyclopropylcarbinol as described by Trahanovsky)[31] and formylmethylenetriphenylphosphorane (9.8 g, prepared as described by Trippett and Walker)[32] in benzene (80 ml) was refluxed for 24 hr. The benzene was removed by distillation and the residue was diluted with pentane, filtered, and distilled to give **3-cyclopropylpropenal** (**10**) as a slightly yellow oil (2.6 g): bp 70-71° (20 mm); ν_{max} (liquid film) 1679, 1632, 1180, 1120, 958 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.71, 1.05 (2 × 2 H, m, H_β-cyclopropyl), 1.66 (1 H, m, H_α-cyclopropyl), 6.20 (2 H, m, H_2, H_3), 9.38 (1 H, m, CHO).

A solution of **10** (2.1 g) in THF (20 ml) was added dropwise, with stirring, to an ice-cooled solution of cyclopropylmagnesium bromide [from magnesium (1 g) and cyclopropyl bromide (6 g)] in THF (25 ml). After stirring overnight, work-up as described for **5b** followed by distillation gave **5d** as a colorless oil (1.8 g): bp 92-94° (5 mm); ν_{max} (liquid film) 3360 (broad), 3093, 1664, 875, 828 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.2-1.6 (10 H, m, H-cyclopropyl), 2.65 (1 H, broad s, OH), 3.42 (1 H, t, J = 6.0 Hz, H_1), 5.18 (1 H, dd, J = 17.5, 7.0 Hz, H_3) and 5.64 (1 H, dd, J = 17.5, 6.0 Hz, H_2).

Anal. Calcd for $C_9H_{14}O$: C, 78.2; H, 10.2. Found: C, 78.1; H, 10.3.

1-Cyclopropyl-3-phenylprop-2-en-1-ol (5e). A solution of 3-phenylpropenal (12.5 g) in THF (50 ml) was added dropwise, with stirring, to an ice-cooled solution of cyclopropylmagnesium bromide [from magnesium (3 g) and cyclopropyl bromide (18 g)] in THF (75 ml). The reaction was stirred overnight and worked up as described for **5b** to give **5e** as a colorless oil (8.2 g): bp 140-141° (2 mm); ν_{max} (liquid film) 3420 (broad), 3080, 1670, 1642, 1607, 1578, 1499, 1452, 1390 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.43, 1.03 (2 H and 3 H, respectively, m, H-cyclopropyl), 2.72 (1 H, broad s, OH), 3.62 (1 H, dd, J = 5.3, 7.5 Hz, H_1), 6.20 (1 H, dd, J = 17.5, 5.3 Hz, H_2), 6.55 (1 H, d, J = 17.5 Hz, H_3), and 7.3 (5 H, m, phenyl).

Anal. Calcd for $C_{12}H_{14}O$: C, 82.7; H, 8.1. Found: C, 82.9; H, 8.0.

1,1-Dicyclopropylprop-2-en-1-ol (6d). Dicyclopropyl ketone (17.7 g, 0.16 mol) in THF (50 ml) was added to a solution of vinylmagnesium chloride (0.25 mol) in THF under nitrogen. After stirring overnight, the reaction was worked up by the addition of water, and the organic phase was separated and dried. Removal of solvent gave a yellow oil which upon distillation yielded **6d** as a colorless liquid (18.2 g): bp 123-125° (20 mm); ν_{max} (liquid film) 3460 (broad), 3098, 3012, 1635, 1410, 923 cm^{-1}; ^1H NMR spectrum is given in Table II.

Anal. Calcd for $C_9H_{14}O$: C, 78.2; H, 10.2. Found: C, 78.4; H, 10.4.

2-Cyclopropylbut-3-en-2-ol (6b). Cyclopropyl methyl ketone (8.4 g, 0.1 mol) was reacted with vinylmagnesium chloride (0.15 mol) as described for **6d**. Work-up gave **6b** as a colorless liquid (7.7 g), bp 40-41° (15 mm) (lit.[33] bp 137-138°).

2-Phenylbut-3-en-2-ol (6c). Acetophenone (12.0 g, 0.1 mol) was reacted with vinylmagnesium chloride (0.15 mol) as described for **6d**. Work-up gave **6c** as a colorless liquid (10.8 g), bp 76-78° (1.5 mm) [lit.[34] bp 73-74° (1 mm)].

1,1-Diphenylprop-2-en-1-ol (6f). Benzophenone (18.2 g, 0.1 mol) was reacted with vinylmagnesium chloride (0.15 mol) as described for **6d**. Work-up gave **6f** as a colorless liquid (14.8 g), bp 143-145° (1.8 mm) [lit.[35] bp 133.5-135° (1 mm)].

1,1-Dibromo-2-methyl-2-phenylcyclopropane (19). Potassium *tert*-butoxide (30 g) was added in small portions to a stirred solution of bromoform (50.5 g) and 2-phenylpropene (23.6 g) in *tert*-butanol (200 ml) over 6 hr. After stirring for an additional 2 hr, pentane and water were added, and the organic layer was separated when all the solid had dissolved. Removal of solvent and distillation gave **19** as a colorless oil (18.3 g), bp 106-110° (1.5 mm) [lit.[36] bp 94-100° (2 mm)].

1-Bromo-2-methyl-2-phenylcyclopropane (8b). 19 (17.0 g) was added dropwise, with stirring, to tri-*n*-butyltin hydride[37] (11.2 g), while the temperature was maintained below 30°. The solution was stirred for an additional 4 hr and then distilled to give **8b** as an approximately 2:1 mixture of isomers (10.2 g), bp 80-90° (1.5 mm): ^1H NMR ($CDCl_3$) δ 1.08, 1.26 (total 3 H, s, ratio 1:2, CH_3 in two isomers), 0.5-1.5 (total 2 H, m, $H_{3\alpha}$ and $H_{3\beta}$), 2.95 (total 1 H, two overlapping dd, H_2), and 7.05-7.15 (total 5 H, narrow m, phenyl).

Preparation of Ions (3a-f, 4b, and 4d-f). A dilute solution of the alcohol in SO_2 at −78° or SO_2ClF at −120° was added dropwise, with shaking, to an approximately 1:1 (by volume) solution of FSO_3H in SO_2 at −78° or FSO_3H in SO_2ClF at −120°. The generation of **3a**, **3b**, **3d**, and **4b** required extremely slow addition to avoid polymer formation. **4a** was prepared as described previously.[10]

Proton Magnetic Resonance Spectra. ^1H NMR spectra were obtained on a Varian Associates Model A56/60A spectrometer equipped with a variable-temperature probe. External TMS (capillary) was used as a reference for the carbenium ions and internal TMS for the alcohols **5a-f** and **6a-f**.

Carbon-13 Magnetic Resonance Spectra. The spectrometer used was a Varian Associates Model XL-100 equipped with a broadband decoupler and variable-temperature probe. The instrument and techniques used are described in more detail in ref 15. Chemical shifts were measured from external (capillary) TMS.

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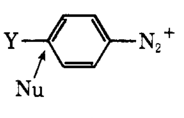
Onium Ions. XIII.[1] Carbon-13 Nuclear Magnetic Resonance Spectroscopic Study of Benzenediazonium Ions Indicating Ambident Character

George A. Olah* and James L. Grant

Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. *Received November 6, 1974*

Abstract: Carbon-13 nuclear magnetic resonance spectroscopic study of a series of benzenediazonium fluoroborate or hexafluorophosphate salts in sulfur dioxide solution at −30° was carried out. Data reflecting charge delocalization show the ambident nature of benzenediazonium ions. The Spiesecke–Schneider relationship is maintained when considering σ_p for $-N_2^+$ and the para cmr shift of the benzenediazonium ion.

One aspect of benzenediazonium ions which has received relatively little attention in the literature is nucleophilic aromatic substitution of the aromatic ring at ring positions other than that originally containing the $-N_2^+$ substituent. Several review articles[2] on diazonium ion chemistry have provided examples of substitution (**1** and **2**) of nucleofugal leaving groups (Y) such as nitro, hydroxide, or halides in the ortho or para positions to the diazonium group. We have recently reported[1] nucleophilic dediazoniation reactions of arenediazonium ions where substitution took place at positions other than the ipso position originally carrying the $-N_2^+$ group. These reactions indicate the ambident nature of benzenediazonium ions.



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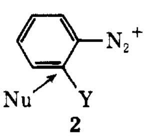

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Nu = NO_2, OH, halogens

It was considered of interest to study directly the ambident nature of benzenediazonium ions by cmr spectroscopy, a method well suited for such structural studies. In addition, a near-linear relationship between carbon-13 chemical shifts and Hammett σ_p parameters for a series of substituted benzenes has been reported.[3] We have, therefore, considered it of interest to extend this relationship to include $-N_2^+$, a substituent representing an outer limit of electron-withdrawing power, in the series of monosubstituted benzenes.

Results and Discussion

Previous experimental studies indicate that the diazonium group, as an aromatic ring substituent, is approximately twice as electronegative as the nitro group.[4] This behavior is in accordance with proton nmr studies.[5] A more sensitive method to study the structure and charge distribution of benzenediazonium ions is carbon-13 nmr since carbon-13 chemical shifts of phenyl ring carbons in substituted benzenes can be used to monitor changes in charge distribution at those carbons. The assignment of resonances was made by the now familiar procedures of Grant and coworkers.[6,7] In addition to showing the trend of charge delocalization, aryl carbon shieldings of substituted benzenediazonium ions show approximate additivity.[8] To assure correct assignments, "off-resonance" proton-decoupling experiments were also carried out. Table I summarizes carbon-13 chemical-shift parameters of substituted benzenediazonium salts studied as the stable tetrafluoroborate or hexafluorophosphate salts in SO_2 solution, generally at −30°.

As can be seen from Table I, there is a marked upfield shift of the C-1 (ipso) carbons bearing the $-N_2^+$ substituent