the pulse interval 1.5 sec. The available computer memory (4000 input channels) and the need to provide multichannel excitation over the region of interest (seeep width 6800 Hz) limited the data acquisition time to 0.2 sec.

The free induction signal derived after each pulse was signitized and accumulated in a Varian 620/i computer (8K). Approximately 5000–7000 accumulations were made to obtain each spectrum. Field frequency regulation was maintained by a homonuclear internal lock system. The lock used was the proton-decoupled carbon-13 resonance of a 60% carbon-13 labeled methyl iodide sample contained in a precision coaxially spaced capillary (o.d. ca. 0.2 and 0.4 mm) inserted in the sample NMR tube (5 mm o.d.).

Fourier transformation of the accumulated free induction signal gave the frequency spectrum,[23,24] from which was measured the chemical shift of each signal, relative to the reference methyl iodide signal. All the chemical shifts reported here have been corrected to a Me_4Si reference by the relationship

$$\text{ppm } (Me_4Si) = \frac{H_2(\text{obsd}) - 977 - T\,(°C) \times 0.70}{25.2}$$

The ^{13}C NMR spectra for the remaining protonated diketones and precursors were obtained on a Varian Associates Model XL-100 spectrometer equipped with a broad decoupler and variable temperature probe. The instrument operates at 25.2 MHz for ^{13}C, and is interfaced with a Varian 620L computer. The combined system was operated in the pulse Fourier transform mode, employing a Varian Fourier transform accessory. Typically 3000–5000 pulses, each of width 20–30 μsec, needed to be accumulated in order to give a satisfactory signal to noise ratio for all signals of interest. Field frequency stabilization was maintained by locking on the ^{19}F external sample of fluorobenzene. Chemical shifts were measured from the ^{13}C signal of 5% ^{13}C enriched tetramethylsilane in a 1.75-mm capillary held concentrically inside the standard 12-mm sample tube.

Acknowledgment. Support of our work by the National Institutes of Health is gratefully acknowledged.

Registry No.—FSO_3H–SbF_5, 33843-68-4; SO_2ClF, 13632-84-8; SO_2, 7446-09-5.

References and Notes

(1) Part CLXXVII: L. A. Paquette, M. Oku, W. E. Farnham, G. A. Olah, and G. Liang, *J. Org. Chem.*, **40**, 700 (1975).
(2) Postdoctoral Research Fellow, 1971–1973.
(3) Predoctoral Research Fellow.
(4) (a) T. W. Lowry, *Chem. Rev.*, **4**, 231 (1927); (b) R. H. Thomson, *Q. Rev., Chem. Soc.*, **10**, 27 (1956); (c) P. R. Jones, *Chem. Rev.*, **63**, 461 (1963); (d) P. Rumpfand and R. LaRiviere, *C. R. Acad. Sci.*, **244**, 902 (1957); (e) S. T. Yoffe, E. M. Popov, K. V. Vatsuro, E. K. Talikova, and M. I. Kabachnik, *Tetrahedron*, **18**, 923 (1962).
(5) (a) A. Gero, *J. Org. Chem.*, **19**, 1960 (1954); (b) *ibid.*, **26**, 3156 (1961); (c) T. Riley and F. A. Long, *J. Am. Chem. Soc.*, **84**, 522 (1962).
(6) M. Tichy, *Adv. Org. Chem.*, **5**, 115–298 (1965).
(7) L. C. Jones and L. W. Taylor, *Anal. Chem.*, **27**, 228 (1955).
(8) G. O. Dudek and R. H. Holm, *J. Am. Chem. Soc.*, **83**, 2099 (1960); (b) G. O. Dudek and R. H. Holm, *ibid.*, **84**, 2691 (1962); (c) G. O. Dudek, *ibid.*, 85, 694 (1962); (d) E. W. Garbisch, Jr., *ibid.*, **85**, 1696 (1963); (e) J. L. Burdett and M. T. Rogers, *ibid.*, **86**, 2105 (1964); (f) B. N. Bhar, *Ark. Kemi*, **10**, 223 (1956); (g) H. S. Jarret, M. S. Sadler, and J/ N. Schoolery, *J. Chem. Phys.*, **21**, 2092 (1953); (h) L. W. Reeves, *Can. J. Chem.*, **35**, 1351 (1957); (i) L. W. Reeves and W. G. Schneider, *ibid.*, **36**, 793 (1958); (j) W. G. Schneider and L. W. Reeves, *Ann. N.Y. Acad. Sci.*, **70**, 858 (1958).
(9) M. Gorodetsky, Z. Luz, and Y. Mazur, *J. Am. Chem. Soc.*, **89**, 1183 (1967).
(10) J. B. Stothers and P. C. Lauterbur, *Can. J. Chem.*, **42**, 1563 (1964). See also J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972, p 288.
(11) D. M. Brouwer, *Recl. Trav. Chim. Pays-Bas*, **86**, 879 (1967); D. M. Brouwer, *Chem. Commun.*, 515 (1967).
(12) G. A. Olah and M. Calin, *J. Am. Chem. Soc.*, **90**, 4672 (1968).
(13) T. C. Farrar and E. D. Becker, "Pulse and Fourier Transform NMR", Academic Press, New York, N.Y., 1971, pp 34–45.
(14) R. R. Ernst and W. A. Anderson, *Rev. Sci. Instrum.*, **37**, 93 (1966).
(15) D. M. Grant and E. G. Paul, *J. Am. Chem. Soc.*, **86**, 2984 (1964).
(16) D. K. Dalling and D. M. Grant, *J. Am. Chem. Soc.*, **89**, 6612 (1967).
(17) G. E. Maciel and J. J. Natterstad, *J. Chem. Phys.*, **42**, 2752 (1965).
(18) G. E. Maciel and D. D. Traficante, *J. Am. Chem. Soc.*, **88**, 220 (1966).
(19) G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists", Wiley-Interscience, New York, N.Y., 1972, pp 112–113.
(20) F. J. Weigert and J. D. Roberts, *J. Am. Chem. Soc.*, **92**, 1338, 1347 (1970).
(21) J. B. Grutzner, M. Jautelat, J. B. Dence, J. A. Smith, and J. D. Roberts, *J. Am. Chem. Soc.*, **92**, 7107 (1970).
(22) G. A. Olah, A. M. White, and D. H. O'Brien, *Chem. Rev.*, **70**, 561 (1970).
(23) R. Ernst, *Adv. Magn. Reson.*, **2**, 74 (1966).
(24) A. Abragam, "Principles of Nuclear Magnetism", Oxford University Press, London, 1961, p 114.

Stable Carbocations. CLXXXI.[1] Dihydrodibenzotropylium and Dibenzotropylium Ions. Neighboring Methyl, Cyclopropyl, and Phenyl Substituent Effects in Geometrically Constrained Systems

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A series of dihydrodibenzotropylium and dibenzotropylium ions have been prepared under stable ion conditions and characterized by NMR spectroscopy. Neighboring methyl, cyclopropyl, and phenyl substituent effects are discussed in terms of ^{13}C NMR shift changes. The relative ability of neighboring methyl, cyclopropyl, and phenyl substituents in stabilizing carbenium ions via either inductive or conjugative charge-delocalizing effects is further discussed.

Methyl, cyclopropyl, and phenyl groups stabilize carbenium ions by inductive and/or resonance (conjugative) effects.[2–5] The degree of conjugation between π or σ bonds in phenyl or cyclopropyl rings with a neighboring empty p orbital on a carbenium center is significant in the degree of delocalization it can exercise and depends upon the orientation of these substituents. Since a phenyl group is larger than a cyclopropyl group, in a given sterically crowded system the former might be affected more in its ability for conjugative stabilization (i.e., effective overlap between p and π orbitals) than the latter. Therefore, if steric inhibition of conjugation becomes significant or overwhelming, phenyl-substituted carbenium ions might become less stable than either the parent (unsubstituted) or alkyl-substituted analogs. A typical example is seen in the case of dibenzotropylium ions.[6] The parent (unsubstituted) ion ($pK_{R^+} = -3.7$) is found to be considerably more stable than the phenyl-substituted ion ($pK_{R^+} = -5.7$) based on comparison of the corresponding pK_{R^+} values.[6a] The decrease in stability of the lattter ion is explained by the fact

Table I
^{1}H NMR Parameters of Dihydrodibenzotropylium (1-R) and Dibenzotropylium (2-R) Ions[a]

Ion	$H_{1,9}$	$H_{2,8}$	$H_{3,7}$	$H_{4,6}$	H_5	$H_{10,11}$	Others
1-H	8.22[b]	8.64	8.22	8.64	9.82	3.78	
1-CH_3	7.92[b]	8.40	7.92	8.88		3.88	3.44 (CH_3)
1-CH_2CH_3	8.02[c]	8.42	8.02	8.92		3.52	4.30 (CH_2), 1.92 (CH_3)
1-C_3H_5		← 7.50–8.10 →				3.40	4.40 (CH), 3.16 (CH_2)
1-C_6H_5	7.70	← 7.5–8.0 →		8.50		3.60	7.8–8.4 (aromatic)
1-OH		← 7.50–8.50 →		8.76		3.56	11.6 (OH)
2-H		← 8.9–9.4 →		9.54[d]	10.98	9.65	
2-CH_3		← 8.2–8.8 →		9.40[e]		9.20	4.25 (CH_3)
2-CH_2CH_3		← 8.4–9.0 →		9.62[f]		9.19	4.56 (CH_2), 2.22 (CH_2)
2-C_3H_5		← 9.4–8.8 →		9.92[f]		9.12	3.95 (CH), 2.00 (CH_3), 0.82 (CH)
2-C_6H_5		← 7.8–8.5 →				9.60	8.5–9.3 (aromatic)
2-OH		← 8.2–8.6 →		9.15[e]		8.40	11.20 (OH)
2-Cl		← 8.4–9.0 →		9.90[d]		9.20	

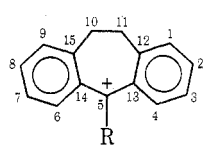
[a] ^{1}H chemical shifts (δ) are in parts per million (ppm) from external tetramethylsilane (capillary Me_4Si). [b] $J_{1,2}$ = 7.60, $J_{2,3}$ = 8.00, $J_{3,4}$ = 8.00 Hz. [c] $J_{1,2}$ = 7.60, $J_{2,3}$ = 8.00, $J_{3,4}$ = 8.80 Hz. [d] $J_{3,4}$ = 7.80 Hz. [e] $J_{3,4}$ = 8.00 Hz. [f] $J_{3,4}$ = 8.20 Hz.

that the phenyl group in this ion is kept from achieving coplanarity with the conjugated system and therefore cannot have much influence on the resonance stabilization of the ion, while the electron-withdrawing ability (inductive effect) of the phenyl ring still plays a major role and thus destabilizes the ion. Deno, Jaruzelski, and Schriesheim[7] also measured the stability of the parent and phenyl-substituted dibenzotropylium ions in aqueous sulfuric acid and found that the fusion of two benzene rings to the tropylium ion strongly destabilized the ion; likewise did a third phenyl group, as indicated by Berti.[6]

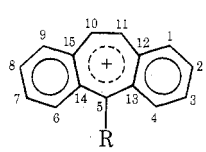
In addition to the unusual stability of dibenzotropylium ions, dihydrodibenzotropylium ions were also reported in the literature to show similar behavior.[6] Several stable dibenzo- and dihydrodibenzotropylium type ions have been reported by Looker,[6b] who also found that the dihydro systems were markedly stabilized by substituents. Many of these compounds were noticed to possess pharmacological activity characteristic of psychotropic agents.[8] The substituent effect of cyclopropyl groups[9] in these systems was not previously investigated. We have now chosen the geometrically constrained dibenzo- and dihydrodibenzotropylium ions as models for a further better understanding of substituent effects on carbenium ions bearing phenyl, cyclopropyl, and alkyl (methyl and ethyl) groups, and report their preparation and NMR spectroscopic study.

Results

Preparation of Dibenzotropylium (2-R) and Dihydrodibenzotropylium (1-R) Ions). The parent (R = H)

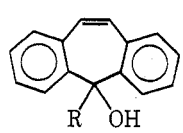


1-R

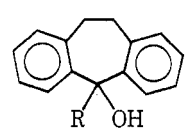


2-R

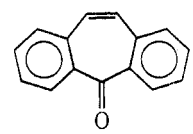
and tertiary alkyl (and phenyl) (R = CH_3, CH_2CH_3, C_3H_5, and C_6H_5) dibenzotropylium and dihydrodibenzotropylium ions, as well as the related protonated ketones (R = OH), were prepared from the corresponding secondary and tertiary alcohols, R = H, CH_3, CH_2CH_3, C_3H_5 and (or Cl), OH, and ketones, respectively, in FSO_3H–SO_2ClF solution at −78°. The chlorine-substituted dibenzotropylium ion (2-Cl) was prepared from its geminal dichloride precursor **7**.



3-R



4-R



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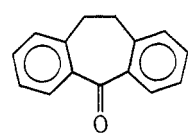

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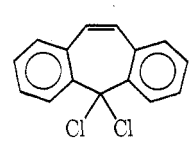
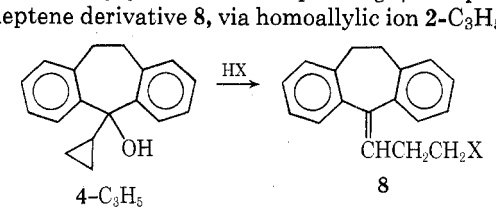


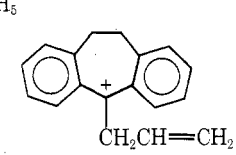
7

All the ions were stable under the reaction conditions studied and their solutions generally showed deep-red color.

When the solution of ion 2-C_3H_5 was warmed (above −45°), a mixture of two ions were formed. One of them has been identified (by ^{1}H NMR) as **9**; the other was not yet identified and is still under further investigation. Likewise a cyclopropyl-substituted derivative of dihydrodibenzocycloheptenol (4-C_3H_5) which has been noted owing to its relation to psychotherapeutic drugs,[8] upon treatment with hydrogen halides[8a] underwent homoallylic rearrangement to quantitatively yield the corresponding γ-halopropenylcycloheptene derivative **8**, via homoallylic ion 2-C_3H_5.[10]



4-C_3H_5 8



9

Proton and Carbon-13 Nuclear Magnetic Resonance Spectra. Tables I and II summarize the ^{1}H (60 MHz) and ^{13}C (25.16 MHz) NMR parameters for the studied dibenzotropylium and dihydrodibenzotropylium ions. [Both proton and carbon shifts are reported in parts per million from capillary tetramethylsilane (Me_4Si)]. Figures 1 and 2 show ^{1}H NMR spectra of both secondary and tertiary ions for 1-R and 2-R (R = H, CH_3, c-C_3H_5, C_6H_5), respectively. The ^{13}C NMR spectrum of the particularly interesting cy-

Table II
^{13}C NMR Parameters of Dihydrodibenzotropylium (1-R) and Dibenzotropylium (2-R) Ions[a]

Ion	$C_{1,9}$[b]	$C_{2,8}$(para)	$C_{3,7}$[b]	$C_{4,6}$(ortho)	Δ_1[c]	C_5	Δ_2[c]	$C_{10,11}$	$C_{12,15}$	$C_{13,14}$	Δ_3[c]	Others
1-H	132.5	150.6	130.5	150.6	0.0	195.1	0.0	31.7	156.6	137.3	19.3	
1-CH_3	132.5	148.1	129.8	141.2	6.9	218.4	23.3	35.8	157.5	140.0	17.5	33.4 (CH_3)
1-CH_2CH_3	132.5	151.2	130.5	140.8	10.4	221.2	26.1	35.8	157.2	140.2	17.0	33.7 (CH_2), 22.9 (CH_3)
1-C_3H_5	133.5	150.0	131.6	141.6	8.4	217.1	22.0	36.6	158.4	141.2	17.2	42.1 (CH), 37.0 (CH_2)
1-C_6H_5	131.7	148.4	128.8	148.4	0.0	205.2	10.1	35.4	158.0	140.1	17.9	144.2 (C_i), 129.4 (C_o), 137.8 (C_m), 136.8 (C_p)
1-OH	130.9	135.2	130.2	134.7	0.5	202.0	6.9	35.5	144.5	132.9	11.6	
2-H	136.2	144.9	135.0	143.6	1.3	170.7	0.0	138.3	147.1	142.5	4.6	
2-CH_3	133.3	143.0	133.3	140.9	2.1	190.3	19.6	134.4	144.6	139.5	5.1	30.8 (CH_3)
2-CH_2CH_3	135.1	144.8	134.6	141.7	3.1	193.3	22.6	137.0	146.6	139.6	7.0	37.2 (CH_2), 21.2 (CH_3)
2-C_3H_5	134.7	145.3	132.8	141.0	4.3	191.8	21.1	135.6	143.5	140.6	2.9	25.0 (CH), 13.1 (CH_2)
2-C_6H_5	134.2	145.8	130.5	140.9	4.9	183.7	13.0	137.4	148.2	140.1	8.1	145.8 (C_i), 129.8 (C_o), 142.4 (C_m), 131.4 (C_p)
2-OH	134.9	140.4	132.9	137.6	2.8	190.2	19.5	131.0	142.6	129.3	3.3	
2-Cl	137.4	146.0	136.8	143.3	2.7	195.3	24.6	137.8	146.3	139.3	7.0	

[a] ^{13}C chemical shifts (δ ^{13}C) are in parts per million from external Me_4Si (capillary). [b] Interchangeable values. [c] $\Delta_1 = \delta_{13} - \delta_{^{13}C_4}$, $\Delta_2 = \delta_{^{13}C_5}$ (tertiary ion) $- \delta_{^{13}C_5}$ (secondary ion), $\Delta_3 = \delta_{^{13}C_{12}} - \delta_{^{13}C_{13}}$.

clopropyl-substituted dibenzotropylium ion is shown in Figure 3. (^{13}C NMR spectra were obtained by using the Fourier transform method. See Experimental Section for details.) Assignment of carbon shifts was made with the aid of off-resonance spectra.

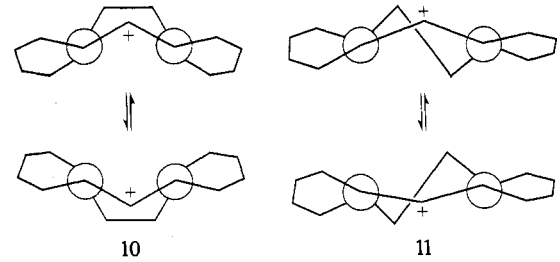
The ortho protons (H_4 and H_6's) in both ions 1-R and 2-R are deshielded from the rest of the ring protons, which are less resolved in the latter. The proton attached directly at the carbenium center (C_5) in 2-H is more deshielded than that in 1-H. The methylene and methyne bridge protons (H_{10} and H_{11}) in 1 and 2, respectively, are sharp singlets, indicating that the ions are symmetrical.

Assignments for the ^{13}C NMR shifts are more complicated than those for the ^1H NMR shifts. The lowest field shifts are naturally assigned to the carbenium carbons. In off-resonance spectra, the secondary carbenium carbons for both 1-H and 2-H are doublets. The two sets of carbons at the ring junctions (C_{12} and C_{15}, C_{13} and C_{14}) are easily identified, since they are singlets in their off-resonance spectra. C_{12}'s (and C_{15}) which are at ortho positions to the electron-deficient center are assigned to the lower field singlet, while the higher field singlets are assigned to C_{13}'s (and C_{14}'s). The differences in carbon shifts between C_{12} and C_{13} in dihydrodibenzotropylium ions (1-R), $\Delta_3 = \delta_{^{13}C_{12}} - \delta_{^{13}C_{13}}$, are generally larger than those in the dibenzo analogs (2-R). Carbons (C_1 and C_3) at positions meta to the carbenium center are assumed to have more shielded shifts than those at ortho and para positions. Assignments for C_1 (and C_9) and C_3 (and C_7) are, however, tentative and could be reversed. The carbon shifts for the ortho positions (C_4 and C_6), which are assigned upfield from that of the para carbons (C_2 and C_8), vary more substantially upon substitution than those of the rest of the molecule except the carbenium carbons (C_5's).

Discussion

Dihydrodibenzotropylium Ions. The ^1H NMR pattern of the aromatic ring protons in substituted dihydrodibenzotropylium ions 1-R varies with the substituents. Ring protons for both secondary and tertiary ions 1-R generally show deshielded coupling patterns as found in diphenylcarbenium ions, with one exception, i.e., the cyclopropyl-substituted ion 1-C_3H_5 (Figure 1). The cyclopropyl ring protons in this ion are considerably deshielded in comparison with those of the precursor (4-C_3H_5), indicating that substantial positive charge has been conjugatively drawn into the cyclopropane ring or alternatively inductive electron withdrawal by a neighboring, but nonconjugative, cation center (for the latter case the cyclopropylammonium ion c-C_3H_5-NH_3^+ was studied as a suitable model). In addition, the methylene-bridge protons in 1-C_3H_5 are less deshielded, but these carbons are more deshielded than those in other analogous ions. In contrast benzo ring protons in the phenyl-substituted ion 1-C_6H_5 show normal splitting patterns (Figure 1), similarly as in methyl- or ethyl-substituted ions. Thus apparently the phenyl group could not reach coplanar alignment with the empty p orbital for effective p–π overlap. The cyclopropane ring, on the other hand, can achieve a certain degree of conjugation between the empty p orbital and C–C bonds of cyclopropane ring, even if steric restriction would prevent the most favorable bisected arrangement.

Consideration of models show that the dihydrodibenzotropylium skeleton itself cannot be planar.[11] It should adopt either a boat form 10 or skew conformation 11. Either form should, however, undergo rapid conformational transformation with minimum nuclear movement, therefore making the molecule symmetrical as indicated by NMR studies.



10 11

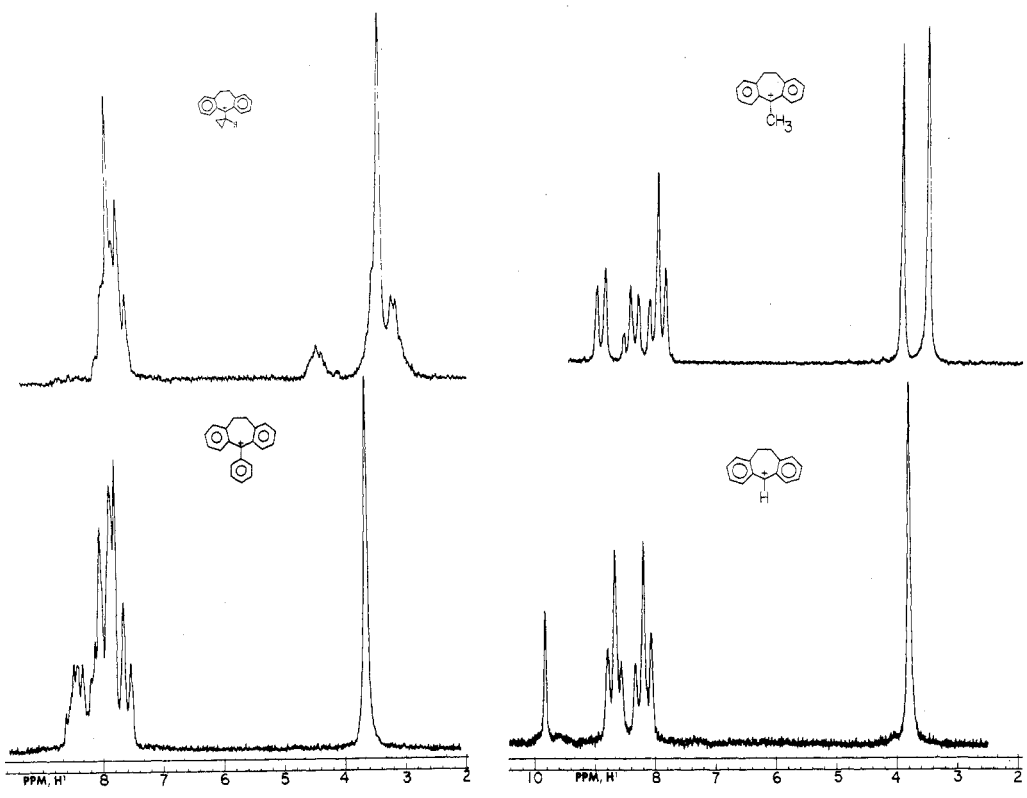


Figure 1. 60-MHz ^1H NMR spectra of the 9,10-dihydro-5-dibenzotropylium ions (a) 1-H, (b) 1-CH_3, (c) 1-C_3H_5, and (d) 1-C_6H_5, in FSO_3H–SO_2ClF solution at −78°.

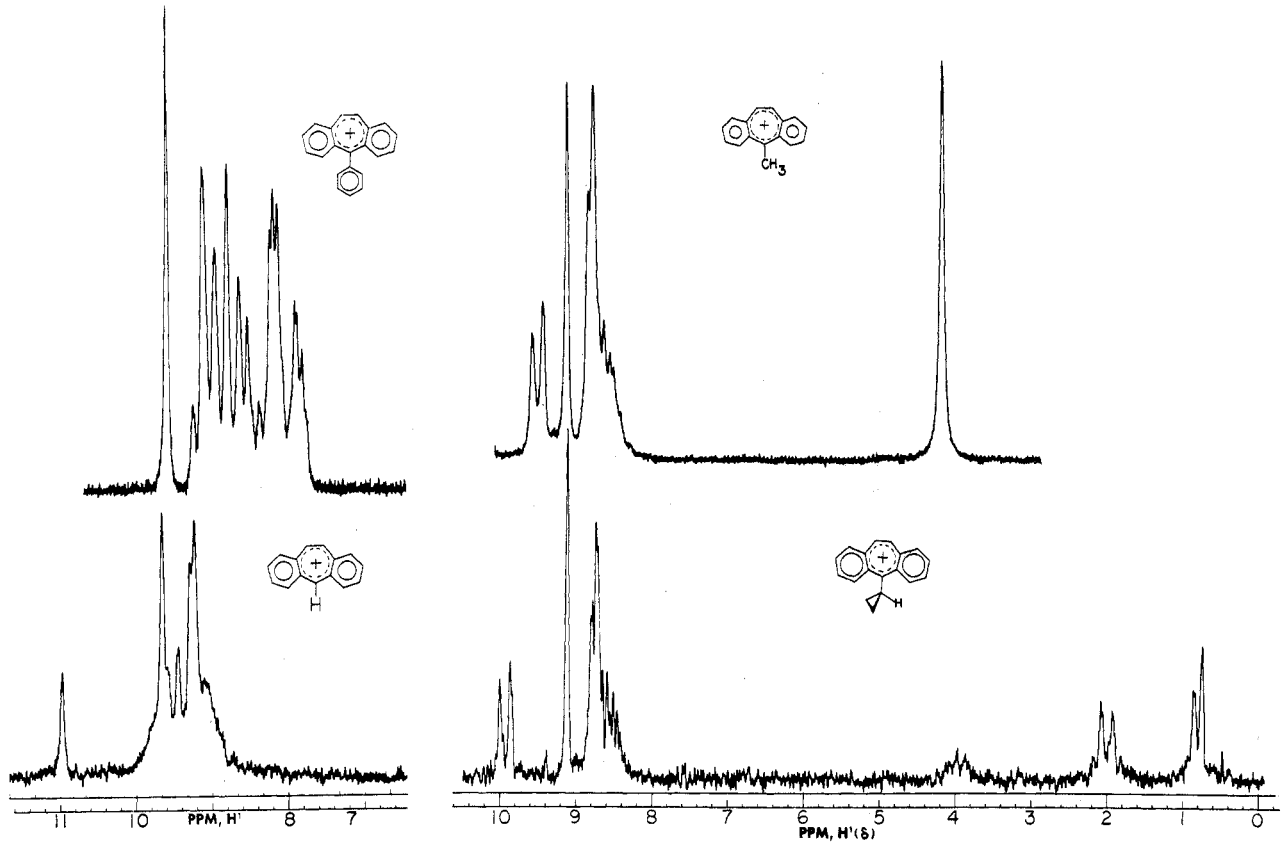


Figure 2. 60-MHz ^1H NMR spectra of the 5-dibenzotropylium ions, (a) 2-H, (b) 2-C_3H_5, (c) 2-C_6H_5, (d) 2-CH_3, in FSO_3H–SO_2ClF solution at −78°.

The ^{13}C NMR studies, through deshielding effects, indicate that substantial positive charge has been delocalized into the dihydrodibenzotropylium ring system. In the case of the cyclopropyl-substituted ion 1-C_3H_5 both methine and methylene carbons of the cyclopropane ring are substantially deshielded, indicating that the positive charge has also been shared by the cyclopropyl ring. Thus the cyclopropyl ring in the sterically constrained systems delo-

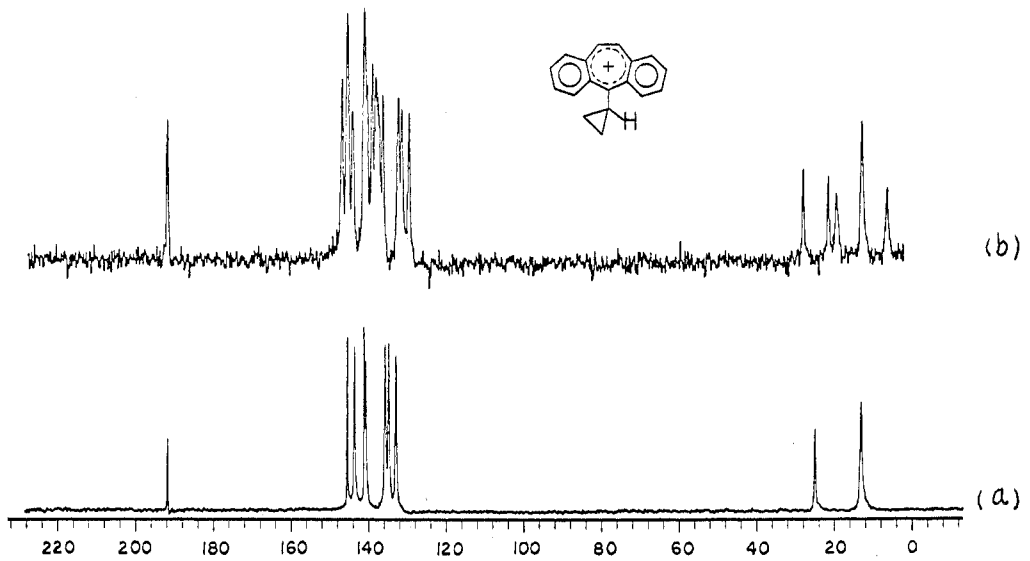
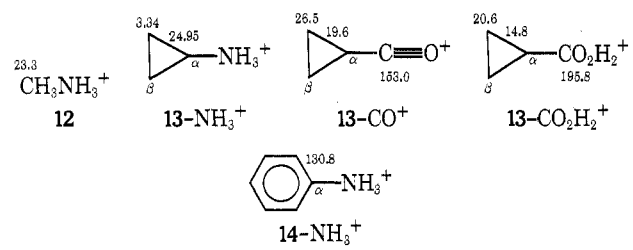


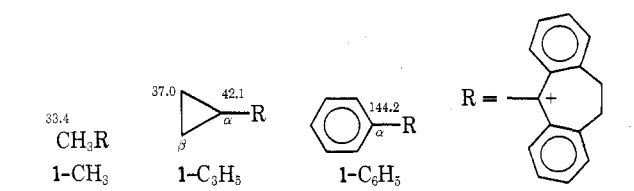
Figure 3. Carbon-13 NMR spectra (25.16 MHz) of the 5-cyclopropyl-5-dibenzotropylium ion (2-C_3H_5) in FSO_3H–SO_2ClF solution at −78°: (a) proton noise decoupled; (b) proton coupled.

calizes charge better than the phenyl group, probably also since the latter cannot achieve planarity for suitable overlap with the empty 2p orbital.

A neighboring positive center also could cause either shielding or deshielding effect on an attached cyclopropyl group. The effect on C_β seems to be particularly dependent on the nature of the substituent bearing positive charge. This is shown by comparing the ^{13}C NMR shifts for cyclopropanes bearing different positively charged ligands. C_β in the cyclopropylammonium ion ($\delta_{^{13}C}$ 3.34) is hardly deshielded, while C_α is deshielded.[12] On the other hand, C_β in



cyclopropylacylium ion becomes even more deshielded than C_α. The same trend is also found in protonated cyclopropanecarboxylic acid.[12] Apparently when the C–C bonds in cyclopropane are conjugatively able to share positive charge with a neighboring positively charged center, ring carbons are usually deshielded. This is the case in systems such as cyclopropylcarbinyl-type cations.[9,13] In contrast, C_α will experience mostly inductive deshielding effect from neighboring groups bearing positive charge, while C_β is hardly affected when resonance conjugation becomes unlikely. Table II shows that both C_α and C_β of the cyclopropyl ring in 1-C_3H_5 are deshielded. Clearly the dihydrodi-

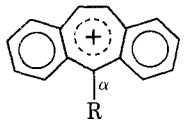


benzotropylium moiety in 1-R causes deshielding of C_α in 1-C_3H_5 via mostly inductive effect, but also deshielding on C_β via a certain degree of conjugative effect. If only the inductive deshielding effect would operate, C_β in 1-C_3H_5 should not be deshielded to any great extent.

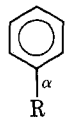
In the parent, secondary dihydrodibenzotropylium ion 1-H, ortho and para carbons (C_2, C_4, and C_{12}) show resonances deshielded from that of meta carbons (C_1, C_3). This is also in accordance with the ^1H NMR observations (Table I). Substituents at C_{12} (and C_{15}) cause a small deshielding effect. Proton and carbon-13 data, therefore, indicate that positive charge in the secondary ion is very evenly distributed among the ortho and para positions. When an *alkyl* substituent is introduced unto the carbenium center (C_5), the latter becomes deshielded. Carbon resonances of the rest of the molecule are, however, not much affected. When a phenyl group is introduced unto the carbenium ion center, carbon resonances in the dihydrodibenzotropylium moiety do not show significant changes, except C_5, which experiences a moderate deshielding (10 ppm) effect. Both ortho and para carbons in 1-C_6H_5 are experiencing the same degree of deshielding effect as found in 1-H. The deshielding effects upon substitution, directly reflected by the C_5 resonances, are small for phenyl substitution ($\Delta_2 \simeq$ 10 ppm) and larger for alkyl substitutions ($\Delta_2 > 22$ ppm). The shielding effect at C_4 induced by alkyl substituents, as shown in Table II, is about 7–10 ppm (Δ_1) and practically zero in the case of phenyl substitution (which cannot conjugatively interact).

For the presently studied series of dihydrodibenzotropylium ions 1-R, ^{13}C NMR data reveal (Table III) that alkyl (or even aryl) substituents exert only minimal effect at the meta positions (C_1 and C_3). Such substitution, however, causes a shielding effect at the ortho (C_4) positions ranging from 6.9 ppm for methyl and 8.4 ppm for cyclopropyl to 10.4 ppm for ethyl, similar to γ substituent effects observed in aliphatic hydrocarbons.[14] These effects in the presently investigated dihydrodibenzotropylium ions apparently show the decreasing order ethyl > cyclopropyl > phenyl. The substituent effects observed for shielding the ortho positions in 1-R indicates the following order: ethyl > cyclopropyl > methyl > phenyl. The same trend is also found in the deshielding effect of the carbenium centers (Δ_2 values in Table II) with slight modification, i.e., methyl $\simeq$ cyclopropyl. The change in shifts of the ortho carbons or carbenium carbon upon substitution, especially by cyclopropyl group, cannot wholly be explained by substituent effects, since the cyclopropyl ring in 1-C_3H_5 also shares positive charge via σ–p conjugation. In addition, the deshielding effect at the carbenium center (α carbon) upon

Table III
Carbon-13 NMR Shifts in Methyl-, Ethyl-, Cyclopropyl-, and Phenyl-Substituted Dibenzotropylium Ions and Related Substituted Benzenes



2-R



14-R

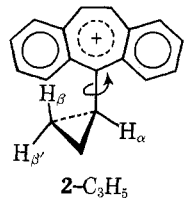
R	C_α^+	CH	CH_2	CH_3	C_α	CH	CH_2	CH_3
H	170.7				129.7			
CH_3	190.3			30.8	138.0			22.4
CH_2CH_3	193.7		37.2	21.2	145.1		29.3	16.8
C_3H_5	191.8	25.0	13.1		144.3	16.4	9.8	
C_6H_5	183.7				142.2			

phenyl substitution in 1-C_6H_5 (Δ_2 = 10.1 ppm) is very similar to that observed (12.5 ppm) between diphenyl- and triphenylcarbenium ions.[9]

Dibenzotropylium Ions. Several dibenzotropylium ions have been studied previously,[6] but no systematic NMR studies were carried out. We have now obtained detailed ^1H and ^{13}C NMR parameters for a series of dibenzotropylium ions. The parent, secondary dibenzotropylium ion (2-H) shows a more deshielded methine proton (δ 10.98) than that in its dihydro analog, 2-H (δ 9.82). The carbon shift for the carbenium center (C_5) in the former is, however, about 25 ppm less deshielded than that in the latter. This might be the result of a stronger ring current effect involved in the former seven-membered aromatic ring (tropylium)[15] system. This is also in accord with the fact that both methyl and ethyl groups are more deshielded in dibenzotropylium ions than those in their dihydro analogs.

When the C_5 position in 1-H is consecutively substituted by phenyl, methyl, ethyl, cyclopropyl, chloro, or hydroxy groups, the two equivalent olefinic protons (H_{10} and H_{11}) become less deshielded. Carbon shifts for the carbenium center (C_5) show shielding in the order of H > C_6H_5 > CH_3 (~OH) > C_3H_5 > CH_2CH_3 > Cl. The substituent effects in dibenzotropylium and dihydrodibenzotropylium ions are also generally in accord with this sequence. C_5 is more shielded in the secondary than in tertiary ions, and alkyl substituents cause a greater deshielding than aryl groups. The cyclopropyl group generally causes a similar deshielding effect as the methyl and ethyl groups.

Particularly interesting is the NMR spectrum of the cyclopropyl-substituted dibenzotropylium ion 2-C_3H_5. In its ^1H NMR spectrum (Figure 2b) the cyclopropyl ring protons do not show a typical deshielding pattern due to substantial charge delocalization into the three-membered ring. Normally, when positive charge is delocalized into the cyclopropane ring in cyclopropyl-substituted carbenium ions, both α and β protons are deshielded,[9,14] as seen in the case of 1-C_3H_5. The ^1H NMR chemical shift difference between H_α and H_β in 1-C_3H_5 is only 1.24 ppm. The difference in 2-C_3H_5 is much bigger (1.95 and 3.13 ppm, respectively, for the two different kinds of β protons). In addition, the dibenzotropylium framework in ion 2-C_3H_5 shows a similar charge-delocalization pattern as in its other analogs. This indicates that the cyclopropane ring bears a minimum amount of positive charge (i.e., minimum degree of charge delocalization). Apparently, the cyclopropane ring in 2-C_3H_5 does not significantly affect the aromatic nature of tropylium ion systems, i.e., the dibenzotropylium framework. Since two sets of cyclopropane protons are observed at the β position, having a chemical shift difference of 1.18 ppm, the cyclopropane ring is considered in ion 2-C_3H_5 to be perpendicular relative to the rest of the molecule. Models show that two of the hydrogens, H_β's, are closely located in the deshielding region of the benzene ring, while the two others, $H_{\beta'}$, are further away. A deshielding effect caused by ring current must therefore account for the slight difference in chemical shifts between these two types of hydrogens. Furthermore, restricted rotation around the C_5–C_α bond always should put the two H_β atoms into the deshielding region and the two $H_{\beta'}$ hydrogens away from it.



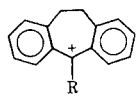
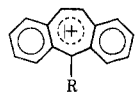
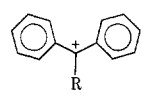
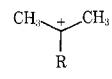
2-C_3H_5

The fact that the cyclopropane ring in 2-C_3H_5 does not delocalize positive charge to any substantial degree is also seen from the corresponding ^{13}C NMR parameters. Both the C_α and C_β carbons of the cyclopropane ring in 2-C_3H_5 are substantially less deshielded than those in 1-C_3H_5. We have previously reported several cyclopropyl-substituted carbocations[9,13] in which substantial charge delocalization takes place as indicated by the substantial deshielding of C_α and C_β in the cyclopropane rings. In certain cases, C_β even becomes more deshielded than C_α.[13] Considering these ^{13}C NMR parameters, ion 2-C_3H_5 can be considered as a further example of a cyclopropylcarbinyl cation in which the cyclopropane ring does not substantially delocalize charge. At the same time it must also be realized that the aromatic dibenzotropylium ion should be considerably less susceptible to substituent effects than its more localized dehydro analog.

In comparing the carbon shifts of the carbenium centers in dibenzotropylium ions and their dihydro analogs (Table II), one notices that the carbenium ion centers in the former are less deshielded than those in the latter. For example, the secondary, parent dibenzotropylium ion (2-H) shows a carbenium shift shielded by about 25 ppm from that in its dihydro analog, 1-H. The presence of the additional two π electrons in 2-R must allow retaining of a substantial degree of aromatic tropylium ion character so that positive charge becomes more delocalized into the seven-membered ring, making C_5's less deshielded. The aromatic nature of dibenzotropylium ions must resist any substantial delocalization which would substantially weaken the six π electron system. The cyclopropane ring can therefore not effectively compete with the tropylium ion systems in sharing (delocalizing) the positive charge.

One further notices that carbon chemical shift differences between the two quaternary carbons (C_{12} and C_{13}) in dibenzotropylium ions are much smaller than those in the dihydro analogs. This also can be accounted for as a consequence of the fact that the positive charge has been further spread out over the seven-membered tropylium ring in 2, in order to maintain six-π aromaticity. It is therefore of interest to compare dibenzotropylium ions with other aromatic six π electron systems. We have chosen the corresponding substituted benzenes as models for comparison. Table III summarizes the relevant ^{13}C NMR data for these two systems: the dibenzotropylium ions and related substituted benzenes 14. Carbon deshielding effects caused by substitution in 2-R exhibit the order ethyl > cyclopropyl > methyl > phenyl. A slightly different order is observed in 14: ethyl ≥ cyclopropyl ≥ phenyl > methyl. All carbon resonances in 2-R are substantially deshielded from the corre-

Table IV
Comparison of Carbenium Center Carbon-13 Shifts

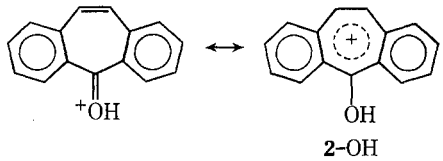
	 1-R		 2-R		 15-R		 16-R	
R	δC^+	Δ^a	δC^+	Δ	δC^+	Δ	δC^+	Δ
H	195.1	0.0	170.7	0.0	200.7	0.0	318.8	0.0
CH_3	218.4	(23.3)	190.3	(19.6)	229.3	(28.6)	329.4	(10.6)
C_3H_5	217.1	(22.0)	191.8	(21.1)	235.1	(34.4)	280.6	(−38.2)
C_6H_5	205.2	(10.1)	183.7	(13.0)	211.9	(11.2)	264.6	(−54.2)
OH	202.0	(6.9)	190.2	(19.5)	209.2	(8.5)	249.5	(−69.3)

$^a \Delta = \delta_{C_R^+} - \delta_{C_H^+}$.

sponding shifts in **14-R**. The dibenzotropylium ions, when substituted, can be considered as substituted six-π aromatic systems without substantial charge delocalization into the substituents. For example, the carbon shift difference between CH_2 and CH_3 in **2**-CH_2CH_3 is about 16 ppm, and that in ethylbenzene is 12.5 ppm. Apparently, the six-π aromatic systems in both dibenzotropylium ions and substituted benzenes produce a similar inductive deshielding effect toward substituents.

We have already suggested that the cyclopropyl group in **2**-C_3H_5 does not show significant charge delocalization, as in other cyclopropylcarbenium ions.[13] It thus might behave merely as a substituent experiencing inductive electronic effect from the adjacent electron-deficient center. This is indeed indicated when comparing cyclopropyl-substituted dibenzotropylium ion **2**-C_3H_5 and benzene **14**-C_3H_5.

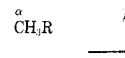
Comparison of Dibenzotropylium, Dihydrodibenzotropylium, and Diphenylcarbenium Ions. Although we cannot directly compare two series of ions having different steric environment, a comparison of substituent effects within a given series of closely related ions is reasonable. Table IV summarizes the ^{13}C NMR shifts for the carbenium centers in a series of related ions bearing hydrogen, methyl, cyclopropyl, and phenyl groups as substituents. For the three series of ions shown, one recognizes that a similar trend of substituent effects exists, i.e., carbenium centers in secondary ions are less deshielded than those of the phenyl-substituted tertiary ions, which in turn are less deshielded than those in alkyl- (or hydroxy-) substituted ions. When one makes comparison between secondary and tertiary ions within a given series, methyl substitution generally causes deshielding of the carbenium center (Δ's in Table IV) to a more or less similar degree as cyclopropyl, while phenyl substitution causes a smaller deshielding effect. The effect produced by hydroxy group is even smaller (Δ 7–9 ppm), with one exception, i.e., the 5-hydroxydibenzotropylium ion **2**-OH (Δ 19.5 ppm). The larger deshielding effect of the carbenium ion center in the latter might be due to the greater stability of the tropylium (or dibenzotropylium) moiety.[15] Structure such as **2**-OH should be more suitable to represent the ion.



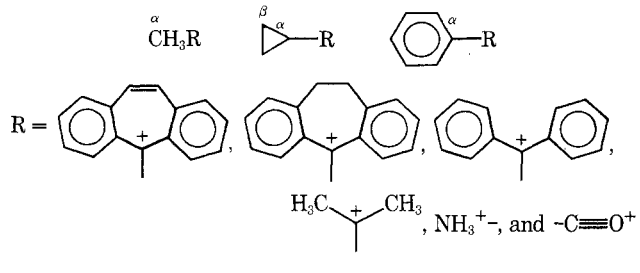
2-OH

In our preceding paper[1] we have shown similar deshielding effects in a series of methyl-, cyclopropyl-, and phenyl-substituted allylic ions. Carbon resonances of carbenium centers are not only affected by the inductive deshielding effects, but also by the resonance shielding effects of the substituents. A methyl substituent in presently studied systems causes similar shielding of carbenium centers; a phenyl substituent causes a smaller effect. In **1-R** and **2-R** the methyl substituents cause deshielding of the carbenium centers of about 20 ppm. A similar deshielding is observed for cyclopropyl substituents. Both methyl and cyclopropyl substituents, however, cause larger deshielding of carbenium centers (≥30 ppm) in diphenylcarbenium ions **15-R** (Table IV). Phenyl substituents cause about 12 ppm deshielding effects in all three series of ions.

Table V
Comparison of C_α(and C_β) Carbon-13 Shifts in Substituted Methanes, Cyclopropanes, and Benzenes

	$^{\alpha}CH_3R$				
R	C_α	C_α	C_β	C_α	C_p
1. Dihydrodibenzotropylium	33.4	42.1	37.0	144.2	136.8
2. Dibenzotropylium	30.8	25.0	13.1	145.8	131.4
3. Diphenylcarbenium	31.3	41.0	36.0	140.9	144.1
4. Dimethylcarbenium	48.5	56.8	53.5	140.1	156.0
5. Ammonium	23.3	24.95	3.34	130.8	130.8
6. Acylium	7.5	19.6	20.6	87.7	149.9
7. 3-Methylallyl	29.8	45.8	42.2	135.1	149.9

The present NMR spectroscopic data no doubt indicate that positive charge has mainly been delocalized into the dibenzo rings in **1-R** and **2-R**. For comparison and to obtain further information, attention should be also given to C_α (and C_β) carbon resonances in the following series of substituted methanes, cyclopropanes, and benzenes. Table



V summarizes carbon-13 shifts for comparable carbon atoms in these compounds.

Neighboring charged groups can produce either shielding or deshielding effects on C_α (and/or C_β). Substituents

carrying positive charge generally cause deshielding of carbon atoms to which they are directly attached. Both C_α and C_β in substituted cyclopropanes, however, are also deshielded, except in the cyclopropylammonium ion, in which C_β is hardly affected. The $-C\equiv O^+$ substituent causes an unusual shielding effect on C_α in all three series. The particularly interesting ketene-type resonance stabilization in acylium ions has recently been noted.[17]

$$R-\overset{+}{C}\equiv O \longleftrightarrow {}^{+}R=C=O$$

The deshielding on C_β in substituted cyclopropanes is generally observed in cases where the cyclopropyl C–C bonds can share positive charge with neighboring electron-deficient centers via a certain degree of conjugation.[13] Similar deshielding is not observed in the cyclopropylammonium ion, where only inductive effect operates.

Methyl, cyclopropyl, and phenyl groups are clearly three different types of neighboring groups for charge delocalization in carbocations. The effectiveness of the π-electron system of the phenyl group in delocalizing neighboring electron-deficient centers (i.e., carbenium ions) is well known.[3,4] σ electrons of saturated bonds (i.e., C–H in methyl and C–C in cyclopropyl groups) can, however, also delocalize neighboring positive charge to various degrees. The nucleophilicity of C–H bonds is known to be weaker than that of C–C bonds.[18] We have recently shown that neighboring cyclopropyl groups can delocalize charge to substantially differing degree depending on the internal strain involved in the cyclopropyl ring.[13] Cyclopropyl groups which do not possess other internal strain than that initially present in the three-membered ring delocalize charge to a lesser degree than do more strained systems. For example, the C_β shifts for cyclopropyl carbons in the methylcyclopropylcarbenium ion[13a] and the 3-methyl-3-nortricyclyl[13a] and the 2-methyl-8,9-dehydro-2-adamantyl[13b] cations are δ ^{13}C 53.5, 83.7, and 100.7, respectively, while carbon shifts for C_α are of comparable magnitude, i.e., δ ^{13}C 56.8, 67.5, and 71.8, respectively. Carbenium ions having neighboring cyclopropyl groups apparently show varied carbon resonances of the carbenium centers depending on how strained the C–C bonds are in the cyclopropyl group and the substituent effect caused by the cyclopropyl group.

Methyl, cyclopropyl, and phenyl substituents, in the presently studied systems, generally cause deshielding of the carbenium ion centers (C_5's) and a slight shielding at ortho positions (C_4 and C_6) of the dibenzo moiety. The methyl group causes a net deshielding of about 20 ppm of the carbenium centers in **1**-R and **2**-R. Similar replacement of hydrogen by methyl causes an about 30 and 10 ppm deshielding at carbenium centers in the diphenyl- and dimethylcarbenium ions, respectively. Replacement of hydrogen in secondary diphenylcarbenium type ions (**1**-R, **2**-R, and **15**-R) by cyclopropyl or phenyl groups causes an opposite effect (i.e., deshielding) than that observed at the carbenium ion centers of dimethylcarbenium ions (Table IV). It is apparent that cyclopropyl and phenyl substituents not only cause inductive deshielding but also conjugative shielding effects at neighboring carbenium ion centers depending upon the steric crowding of the system.[19]

It is difficult to divide the total effect of substituents at carbenium centers into the corresponding inductive and conjugative components, particularly when one attempts to directly compare cyclopropyl and phenyl groups. A reversed trend is observed in diphenylcarbenium type ions and dimethylcarbenium ions, indicating that steric inhibition of conjugation in the former system renders the cyclopropyl and phenyl groups unable to share positive charge as fully as in the latter case, where no severe steric crowding exists. These effects are more significant for phenyl than for cyclopropyl substituents. When conjugation between the phenyl group and the empty 2p orbital is possible, positive charge is nearly equally distributed among the ortho and para positions of the phenyl ring. However, ortho shifts are also easily affected by steric effects of substituents.[14] Para shifts, which are not similarly affected, have been utilized as a reliable indicator for the extent of charge delocalization into the phenyl ring in phenylcarbenium ions.[14,16] For example, the para shift in the dimethylphenylcarbenium ion is substantially deshielded (δ ^{13}C 156, Table V), while the corresponding carbenium ion center is shielded by about 54 ppm (Table IV) when the methine hydrogen in the dimethylcarbenium ion is replaced by a phenyl group. In cases where conjugation is not possible, the para shift of the phenyl ring is much less deshielded. Examples are found in the protonated aniline and the 5-phenyl-5-dibenzotropylium ion **2**-C_6H_5. The more shielded para shifts of the phenyl-substituted carbenium ions seems to indicate that less positive charge has been delocalized into the phenyl ring.

It is interesting to notice that para carbon shifts in phenyl-substituted dihydrodibenzo- and dibenzotropylium ions (**1**-C_6H_5 and **2**-C_6H_5, respectively), although are both shielded, differ by about 5 ppm. The para shift (δ ^{13}C 131.4) in the latter approaches that in the protonated aniline (δ ^{13}C 130.8). It seems to indicate that the phenyl group in **1**-C_6H_5 still experiences a limited degree of conjugation, while in **2**-C_6H_5 it does not. Although the replacement of hydrogen in **1**-H by a phenyl group does not change much the carbon shifts of the dihydrodibenzotropylium moiety, the deshielding of the carbenium center (10 ppm) caused by phenyl substitution might be a net result of the combined inductive deshielding and conjugative shielding effects. Comparison of the para shifts of the phenyl substituents in **1**-C_6H_5 and **15**-C_6H_5 (Table V) shows that the phenyl ring in the former experiences more steric repulsion than that in the latter. Carbon shifts for C_α and C_β of the cyclopropyl rings in **1**-C_3H_5 and **15**-C_3H_5, respectively, are of equal magnitude, indicating that the cyclopropyl ring, being smaller in size than the phenyl group, can share positive charge to a relatively similar degree (even if not necessarily in the most favorable bisected in-plane configuration) in these two ions while the phenyl groups cannot. Cyclopropyl rings in **1**-C_3H_5 and **15**-C_3H_5 experience, however, less conjugative deshielding from neighboring electron-deficient centers than does that in **16**-C_3H_5 (dimethylcyclopropylcarbenium ion) owing to a difference in charge demand. When the conjugation of cyclopropyl groups is further reduced (or limited) as in the cases of **2**-C_3H_5 and cyclopropylammonium ion (**13**-NH_3^+), both C_α and C_β of the cyclopropyl ring are becoming much less deshielded. As para shifts of adjacent phenyl rings in carbenium ion have been utilized as a measurement of charge delocalization into the phenyl ring in phenylcarbenium ions, C_β shifts of cyclopropyl rings can also be used as an indicator of charge delocalization into the cyclopropyl ring in cyclopropylcarbenium ions, although obviously our present understanding of charge effects on the overall chemical shifts in cyclopropyl rings is still inadequate.

Experimental Section

Materials. Secondary alcohols (**3**-H and **4**-H) and ketones (**5** and **6**) used in the present study were obtained from the Aldrich Chemical Co., and were used without further purification. The tertiary alcohols (**3**-R and **4**-R) were prepared by the reaction of the appropriate Grignard reagent with the related ketones **5** and **6**, respectively, in the usual manner.[6,8,16] The dichloride **7** was prepared according to the reported procedure.[20]

Preparation of Carbocations. Freshly distilled FSO_3H was dissolved in an appropriate amount of SO_2ClF as solvent at Dry Ice–acetone temperature (ca. −78°). To this was slowly added with vigorous stirring a cold solution of appropriate precursor dissolved in SO_2ClF, to give an approximately 15–20% solution of the ion. Except for the protonated ketones **1**-OH and **2**-OH, both secondary and tertiary dihydrodibenzotropylium and dibenzotropylium ions generally gave deep-red colored solutions.

Proton and Carbon-13 NMR Spectroscopy. Both proton and carbon-13 NMR spectra were obtained as previously reported.[21]

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Registry No.—**1**-H, 55090-25-0; **1**-CH_3, 55090-26-1; **1**-CH_2CH_3, 55090-27-2; **1**-C_3H_5, 55124-05-5; **1**-C_6H_5, 30880-08-1; **1**-OH, 55090-28-3; **2**-H, 55090-18-1; **2**-CH_3, 55090-19-2; **2**-CH_2CH_3, 55090-20-5; **2**-C_3H_5, 55090-21-6; **2**-C_6H_5, 55090-22-7; **2**-OH, 55090-23-8; **2**-Cl, 55090-24-9; **3**-H, 10354-00-4; **3** (R = CH_3), 10354-00-4; **3** (R = CH_2CH_3), 18259-45-5; **3** (R = C_3H_5), 55124-06-6; **3** (R = C_6H_5), 55090-29-4; **3** (R = OH), 55090-30-7; **4**-H, 1210-34-0; **4** (R = CH_3), 15323-25-8; **4** (R = CH_2CH_3), 55090-31-8; **4** (R = C_3H_5), 3241-97-2; **4** (R = C_6H_5), 55090-32-9; **4** (R = OH), 55090-33-0; **7**, 13099-45-1; FSO_3H, 7789-21-1.

References and Notes

(1) Part CLXXX: G. A. Olah and A. Spear, *J. Am. Chem. Soc.*, **97**, 1539 (1975).
(2) (a) For recent review, see G. A. Olah, *Angew. Chem., Int. Ed. Engl.*, **12**, 173 (1973); (b) G. A. Olah and A. M. White, *J. Am. Chem. Soc.*, **91**, 5801 (1969).
(3) See, for example, D. G. Farnum, *Chem. Rev.*, **74**, 315 (1974).
(4) See, for example, G. A. Olah and P.v.R. Schleyer, Ed., "Carbonium Ions", Vol. 1, Wiley-Interscience, New York, N.Y., 1968, Chapters 3 and 7.
(5) For reviews see (a) H. G. Richey, Jr., in ref 4, Vol. 2, Chapter 25; (b) K. B. Wiberg, B. A. Hess, Jr., and A. J. Ashe in ref 4, Vol. 3, Chapter 26.
(6) (a) G. Berti, *J. Org. Chem.*, **22**, 230 (1957); *Gazz. Chim. Ital.*, **87**, 293 (1957); *Ann. Chim. (Rome)*, **49**, 1237 (1959); (b) J. J. Looker, *ibid.*, **33**, 1304 (1968); (c) E. Heilbronner et al., *Helv. Chim. Acta*, **41**, 57 (1958); **33**, 1221 (1960); (d) P. Rumpf and R. Reynaud, *Bull. Soc. Chim. Fr.*, 558 (1964); (e) H. Fernholz, *Justus Liebigs Ann. Chem.*, **568**, 63 (1950).
(7) N. C. Deno, J. J. Jaruzelski, and A. Schriesheim, *J. Am. Chem. Soc.*, **77**, 3047 (1955).
(8) (a) R. D. Hoffsommer, D. Taube, and N. L. Wendler, *J. Org. Chem.*, **28**, 1751 (1963); **27**, 4134 (1962); (b) S. O. Winthrop, M. A. Davis, G. S. Myers, J. G. Gavin, R. Thomas, and R. Barber, *ibid.*, **27**, 230 (1962).
(9) (a) G. A. Olah, P. W. Westerman, and J. Nishimura, *J. Am. Chem. Soc.*, **96**, 3548 (1974); (b) G. A. Olah and P. W. Westerman, *ibid.*, **95**, 7530 (1973).
(10) J. J. Looker, *J. Org. Chem.*, **31**, 3599 (1966); **37**, 1059 (1972).
(11) Dipole moment studies of dibenzocycloheptenone and dihydrodibenzocycloheptenones show that the molecules are nonplanar. See (a) H. Weiler-Feilchenfeld and A. Solomonovici, *J. Chem. Soc. B*, 869 (1971); (b) W. Tochtermann and G. H. Schmidt, *Justus Liebigs Ann. Chem.*, **754**, 90 (1971); (c) K. Ibata, T. Hata, H. Shimanouchi, and Y. Sasada, *J. Chem. Soc., Chem. Commun.*, 339 (1972), and references cited therein.
(12) G. A. Olah and G. Liang, unpublished results.
(13) (a) G. A. Olah and G. Liang, *J. Am. Chem. Soc.*, **95**, 3792 (1973); **97**, 1920 (1975); (b) G. A. Olah, G. Liang, R. K. Murray, and K. A. Babiak, *ibid.*, **96**, 6794 (1974).
(14) J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972.
(15) For a review on tropylium ions, see K. M. Harmon, in "Carbonium Ions", Vol. 4, G. A. Olah and P.v.R. Schleyer, Ed., Wiley-Interscience, New York, N.Y., 1973, Chapter 29.
(16) (a) G. A. Olah, P. W. Westerman, and D. A. Forsyth, *J. Am. Chem. Soc.*, **96**, 6908 (1974) (b) G. L. Nelson, G. C. Levy, and J. D. Cargioli, *ibid.*, **94**, 3089 (1972).
(17) G. A. Olah, P. W. Westerman, and R. J. Spear, *J. Am. Chem. Soc.*, **96**, 5855 (1974).
(18) G. A. Olah, *J. Am. Chem. Soc.*, **94**, 808 (1972).
(19) (a) H. Volz, J.-H. Shin, and H.-J. Streicher, *Tetrahedron Lett.*, 1297 (1975); (b) J. F. Wolf, P. G. Harch, R. W. Taft, and W. J. Hehre, *J. Am. Chem. Soc.*, **97**, 2902 (1975).
(20) (a) A. C. Cope and S. W. Fenton, *J. Am. Chem. Soc.*, **73**, 1673 (1951); (b) W. Treibs and H. Klinkhammer, *Chem. Ber.*, **83**, 367 (1950).
(21) G. A. Olah and G. Liang, *J. Am. Chem. Soc.*, **96**, 189 (1974).

Delocalized Carbanions. V.[1] A Tetraanion from the Lithium Reduction of *cis,cis*-1,2,3,4-Tetraphenylbutadiene

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The reduction of *cis,cis*-1,2,3,4-tetraphenylbutadiene with lithium in tetrahydrofuran yields 1,2,3,4-tetralithio-1,2,3,4-tetraphenylbutane, which upon hydrolysis with D_2O gives *dl*- and *meso*-1,2,3,4-tetradeuterio-1,2,3,4-tetraphenylbutane in yields up to 86%. The progress of the reduction was followed through the radical anion and dianion stages to the tetraanion by EPR and uv–visible spectroscopy. No trianion radical intermediate was detected. The tetraanion is apparently stable for weeks in the presence of excess lithium, but gradually cyclizes to give 3-benzyl-1,2,-diphenylindene upon hydrolysis. This amazing stability is attributed to a cyclic reaction scheme which regenerates tetraanion from partially protonated species. In ether, reduction with Li for 4 hr, Na for 24 hr, or K for 50 hr yielded *cis*- and *trans*-1,2,3,4-tetraphenyl-2-butene in 4:1, 5:1, and 1.4:1 ratios, respectively. Reduction for 24 hr with Li or Na for 20 days yielded 1,4-dihydro-1,2,3-triphenylnaphthalene. Reduction for 4 days with Li yielded 9,14-dihydro-9-phenyldibenz[*a,c*]anthracene.

Brook, Tai, and Gilman[2] have reported the reduction of *cis,cis*-1,2,3,4-tetraphenylbutadiene (**1**) with lithium metal, followed be ethanolysis to yield *dl*- and *meso*-1,2,3,4-tetraphenylbutanes.[3] The intriguing possibility of a 1,2,3,4-tetralithio-1,2,3,4-tetraphenylbutane (**2**) intermediate in this reaction prompted the present investigation. Although West and coworkers[4] have prepared several polylithium derivatives of acetylenes containing four or more lithium atoms, the tetralithium compound (**2**) differs from these compounds in that each carbon–lithium bond is benzylic in nature, and may give rise to delocalized carbon–metal bonding. Since delocalization greatly affects the physical and chemical properties of organometallic compounds, the preparation of **2** and the investigation of its properties were of considerable interest.

Our case for the intermediacy of **2** in the reduction of **1** rests primarily upon obtaining *dl*- and *meso*-1,2,3,4-tetradeuterio-1,2,3,4-tetraphenylbutanes (**3a**-d_4 and **3b**-d_4) in up to 86% yield when **1** is reduced with lithium in tetrahydrofuran (THF) and hydrolyzed with D_2O. In addition to the detection of **2** and the investigation of the reaction sequence leading to it, preparatively useful reductions of **1** with lithium, sodium, and potassium are here reported.

Reduction of *cis,cis*-1,2,3,4-Tetraphenylbutadiene (1) with Li in THF. When a solution of **1** in THF was treated with a large excess of lithium under argon, reduc-