over 95% of the material. Attempts to isolate the product bromide were frustrated by rapid dehydrohalogenation.

Procedure for Kinetic Runs for the Reaction of Bromotrichloromethane with the 4-Methyl-1-phenyl-4-(substituted phenyl)pentanes. Attempted analyses by gas–liquid chromatography were unsuccessful. The brominated hydrocarbons formed as products decomposed under analytical conditions and the decomposition products eluted with the starting material. The error thus introduced made such analyses useless.

Analysis of the mixtures, both before and after reaction, was carried out *via* nmr spectroscopy. Some part of the spectra that did not change during the reaction, usually the methyl singlet at approximately δ 1.15, was used as an internal standard. The disappearance of the benzylic proton triplet of the 4-methyl-1-phenyl-4-(substituted phenyl)pentane and the benzylic proton singlet of diphenylmethane was used to determine the relative rates.

Solutions of a 4-methyl-1-phenyl-4-(4-substituted phenyl)pentane, diphenylmethane, and bromotrichloromethane were prepared in the approximate molar ratios of 1:2:30. Approximately 0.75 ml of the solution was put in each of several Pyrex ampoules. The ampoules were cooled to Dry Ice–acetone temperature, evacuated, filled with nitrogen gas, and then warmed to room temperature. This process was repeated three times. After cooling and evacuation, the tubes were sealed. One ampoule was reserved for analysis of starting materials; the remainder were placed horizontally just below the surface of a mineral oil constant temperature bath maintained at 70.0 ± 0.5°. The samples were irradiated with ultraviolet light provided by a Ken-Rad 275-W sunlamp placed 20 cm above the surface of the oil. Reaction times varied from 3 to 5 hr, by which time 30 to 60% of the total hydrocarbons had reacted. The ampoules were then cooled and opened. All determinations were run in replicate.

Procedure for Kinetic Runs for the Reaction of Bromotrichloromethane with the 4-Phenyl-1-substituted Butanes. Solutions of 4-phenyl-1-substituted butanes, diphenylmethane, and bromotrichloromethane were prepared in the approximate molar ratio of 1:1:10. Analysis of the mixture both before and after reaction was carried out *via* nmr spectroscopy. Some part of the spectrum that did not change in integration during the reaction, usually all or part of the nonbenzylic aliphatic part of the spectrum, was used as an internal standard. The disappearances of the benzylic triplet of the 4-phenyl-1-substituted butane and the benzylic singlet of the diphenylmethane were used to determine the relative rates of reaction. In all other ways the procedure was the same as outlined above.

Determination of Relative Rates of Hydrogen Abstraction. The ratios of the relative rate constants were obtained using the usual competitive procedures.[34]

(34) G. J. Gleicher, *J. Org. Chem.*, **33**, 332 (1968).

Stable Carbocations. CLXIV.[1] The Relative Ability of Charge Delocalization by Phenyl, Cyclopropyl, and Methyl Groups in Carbenium Ions

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Abstract: The relative order of charge delocalization by neighboring phenyl, cyclopropyl, and methyl groups in related series of stable, long-lived carbocations was studied by ^{13}C nmr spectroscopy. The decreasing order of charge delocalization was generally found to be Ph > c-Pr > CH_3. The results are interpreted in terms of differentiating *delocalization* in the intermediate ions (as measured by cmr spectroscopy) from *participation* of the same groups, showing the decreasing order c-Pr > Ph > CH_3, in solvolytic reactions. The latter is obviously affected by the energy differences in the case of the more strained ground state of the precursor esters as compared to the less strained carbenium ion like transition states. Some electrophilic addition reactions to phenylcyclopropyl-substituted ethenes proceeding *via* carbenium ion like transition states show comparable results to the solvolysis studies. A number of carbocations have also been studied in which phenyl, methyl, and cyclopropyl groups are potentially capable of competing with each other to stabilize an adjacent carbenium ion center.

The ability of a cyclopropyl group to stabilize an adjacent carbocation center is well documented.[3] It has been stated[4] from measurements of tricyclopropylcarbenium ion–tricyclopropylmethyl alcohol and triphenylcarbenium ion–triphenylmethyl alcohol equilibria that the cyclopropyl group is capable of stabilizing an adjacent carbocation center to a greater degree than a phenyl group. From a consideration of the relative rates of solvolysis of *p*-phenyl- and -cyclopropyl-*tert*-cumyl chlorides, and the esters RMe_2COPNB (R = Ph, c-C_3H_5), Brown and Peters[5] also concluded that the cyclopropyl group is more electron releasing than the phenyl group.

In contrast to the above, on the basis of the ^{13}C chemial shifts of the carbenium ion centers in the phenyldimethylcarbenium ion,[6a,b] the cyclopropyldimethylcarbenium ion,[6c,d] and the trimethylcarbenium ion,[6e] in our preceding studies we concluded[6f] that the relative

(1) (a) Part CLXIII: G. A. Olah, P. Schilling, J. M. Bollinger, and J. Nishimura, *J. Amer. Chem. Soc.*, **96**, 2221 (1974); (b) Preliminary communication: G. A. Olah and P. W. Westerman, *ibid.*, **95**, 7530 (1973).

(2) Postdoctoral Research Associates 1971–1973.

(3) For recent reviews, see (a) K. B. Wiberg, B. A. Hess, Jr., and A. J. Ashe III in "Carbonium Ions," Vol. III, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N. Y., 1972, pp 1295–1345; (b) H. G. Richey, Jr., ref 3a, pp 1201–1294.

(4) N. C. Deno, H. G. Richey, Jr., J. S. Liu, D. N. Lincoln, and J. O. Turner, *J. Amer. Chem. Soc.*, **87**, 4533 (1965).

(5) H. C. Brown and E. N. Peters, *J. Amer. Chem. Soc.*, **95**, 2400 (1973).

(6) (a) G. A. Olah, C. L. Jeuell, and A. M. White, *J. Amer. Chem. Soc.*, **91**, 3961 (1969); (b) G. A. Olah, R. D. Porter, C. L. Jeuell, and A. M. White, *ibid.*, **94**, 2044 (1972); (c) G. A. Olah, D. P. Kelly, C. L. Jeuell, and A. D. Porter, *ibid.*, **92**, 2544 (1970); (d) G. A. Olah, C. L. Jeuell, D. P. Kelly, and R. D. Porter, *ibid.*, **94**, 146 (1972); (e) G. A. Olah and A. M. White, *ibid.*, **91**, 5801 (1969); (f) G. A. Olah, R. D. Porter, and D. P. Kelly, *ibid.*, **93**, 464 (1971). (g) In subsequent studies with Dr. D. A. Forsyth this spectrum was, however, obtained and will be reported.

Table I. ^{13}C Shifts of Phenyl-, Cyclopropyl-, and Methylcarbenium Ions[a]

Ion	C^+	Cyclopropyl		CH_3	Phenyl			
		α-CH	β-CH_2		C_i	C_o	C_m	C_p
$(CH_3)_2CH^+$ [b]	−125.0			132.8				
$(c\text{-Pr})_2C^+H$	−59.9	148.1	155.1					
Ph_2CH^+	−6.9				55.4	44.6	60.0	42.8
						50.3		
c-$PrCH^+Ph$	−32.6	148.6	148.6		56.1	48.5	61.5	44.7
						57.3		
c-$PrCH^+CH_3$ [c]	−59.1	126.5	136.3	160				
PhC^+HCH_3 [d]	−40							
$(CH_3)_3C^+$ [b]	−135.4			145.3				
$(c\text{-Pr})_3C^+$	−77.8	161.2	162.9					
Ph_3C^+ [e]	−18.1				52.9	49.5	62.5	49.7
$(c\text{-Pr})_2C^+CH_3$	−81.6	148.6	155.4	155.4				
$Ph_2C^+CH_3$	−35.5			162.5	52.2	52.5	62.2	45.6
$Ph(c\text{-Pr})C^+CH_3$	−52.5	147.9	148.7	170.3	53.9	58.9	62.5	48.2
$Ph_2(c\text{-Pr})C^+$	−41.3	152.8	157.8		51.8	54.7	62.3	43.5
					56.4	59.0	63.8	48.5
$Ph(c\text{-Pr})_2C^+$	−67.3	151.0	156.7		58.4	64.1	65.7	57.2
$PhC^+(CH_3)_2$	−60.6			158.8	53.7	51.3	60.4	37.8
c-$PrC^+(CH_3)_2$ [c]	−86.8	133.8	140.4	153.9				
				162.7				
c-PrC^+H_2 [f]	(−31)	(118)	(132)					
PhC^+H_2	(−10)[g]							

[a] Recorded in SO_2ClF–SbF_5 or SO_2ClF–FSO_3H–SbF_5 at −60 to −90°. Chemical shifts are in parts per million from $^{13}CS_2$. Positive sign indicates shielding from the reference. [b] Reference 6e. [c] Reference 6c. [d] Reference 6f. [e] G. J. Ray, R. J. Kurland, and A. K. Colter, *Tetrahedron*, **27**, 735 (1971). [f] Reference 6d. [g] Reference 6b.

effectiveness of the phenyl, methyl, and cyclopropyl groups to delocalize charge shows the order

$$Ph- > c\text{-}Pr- > CH_3-$$

Because the solvolytic (and equilibrium) measurements and nmr spectral results lead to different conclusions, we decided to examine this apparent discrepancy in greater detail.

We would like first to point out that solvolytic rates and equilibrium constants are only giving indication of energy differences between ion and precursor, whereas ^{13}C chemical shifts are a direct function of the carbocations and thus can be expected to reflect their properties. The two approaches therefore measure on a different basis. It is entirely feasible that the cyclopropyl group is a better participating group in solvolysis than phenyl but the phenyl group in the intermediate ions delocalizes charge away from the carbocation center better than the cyclopropyl group.

In our studies, three experimental approaches have been followed. (A) The complete proton decoupled carbon-13 nmr spectra of a comprehensive series of methyl, phenyl, and cyclopropyl substituted carbenium ions have been obtained at low temperature and in solvents of low nucleophilicity. Although the pmr spectroscopic data of comparable cyclopropyl and phenyl substituted ions also could be used to deduce the relative delocalizing abilities of phenyl and cyclopropyl groups, we believe that the ^{13}C data are more reliable for the following reasons. The center of greatest electron deficiency in the carbocation, rather than just the positions α or β to it as in ^1H nmr spectroscopy, may be observed directly by ^{13}C nmr spectroscopy; solvent and anisotropy effects are comparably smaller than change polarization effects on the ^{13}C shift, whereas this is not necessarily true for the ^1H shift. In addition, the cmr spectra of related protonated cyclopropyl ketones and their parent compounds have been measured. (B) Carbocations have been prepared, in which phenyl, methyl, and cyclopropyl groups are potentially capable of competing with each other to stabilize an adjacent carbenium ion center. Similar competitive type experiments have been reported recently by Sorensen.[7] (C) Some electrophilic addition reactions to phenylcyclopropyl-substituted ethenes, proceeding *via* carbenium ion like transition states, were studied to determine the relative directive effects of phenyl and cyclopropyl groups.

Experimental approaches B and C should give measures of the delocalization ability, which are the same as those involved in solvolysis reactions. That is the same structural changes should be experienced by the cyclopropyl, phenyl, and methyl groups in the equilibria and addition reactions as are involved in the solvolysis processes.

Results and Discussion

(A) Carbon-13 Nmr Spectroscopic Studies. The complete proton decoupled carbon-13 nmr spectra of a series of methyl-, phenyl-, and cyclopropylcarbenium ions, as well as their precursors, were obtained by the Fourier transform method. The assignment of signals was made by the usual methods,[8] which included "off-resonance" decoupling experiments, considerations of relative signal intensities and molecular symmetry, and the observation that polar groups exert a large inductive effect on the shifts of directly attached carbons. Data are summarized in Table I, with those of related precursors shown in Table II. Chemical shifts for related protonated methyl, phenyl, and cyclopropyl ketones and their parent compounds are shown in

(7) (a) T. S. Sorensen, I. J. Miller, and K. Ranganayakulu, *Aust. J. Chem.*, **26**, 311 (1973); (b) T. S. Sorensen, *J. Amer. Chem. Soc.*, **89**, 3794 (1967).

(8) (a) D. M. Grant and E. G. Paul, *J. Amer. Chem. Soc.*, **86**, 2984 (1964); (b) D. K. Dalling and D. M. Grant, *ibid.*, **89**, 6612 (1967).

Table II. Carbon-13 Chemical Shifts in Methyl, Phenyl, and Cyclopropyl Carbinols[a]

Compd	Cyclopropyl				Phenyl			
	COH	CH	CH_2	CH_3	C_1	C_2[f]	C_3[f]	C_4
c-PrCOH	123.4	172.9	191.9					
c-Pr_2CHOH	111.8	175.5	189.8					
c-$PrCH_2OH$	126.5	179.2	189.7					
			189.3					
c-$PrC(OH)CH_3$	121.4	173.6	190.3	169.9				
c-$PrC(CH_3)_2OH$	124.0	170.0	191.4	163.8				
c-$PrC(OH)CH_3$	123.4	171.8	191.6	166.5				
Ph_3COH[b]	113.4				43.6	65.1	65.1	65.1
Ph_2CHOH[c]	116.6				45.9	63.3	64.9	64.6
$PhCH_2OH$[d]	127.8				51.8	63.7	64.8	65.0
$PhC(OH)CH_3$	122.3			166.8	45.8	63.7	66.4	65.0
$PhC(CH_3)_2OH$	119.7			160.1	42.4	63.8	67.1	65.5
$PhC(OH)CH_3$[c]	116.2			161.3	44.8	64.6	66.7	65.9
PhCOH(c-Pr)[c]	115.8	169.8	189.8		42.6	63.7	64.5	65.0
PhC(OH)c-Pr_2	118.0	170.9	189.8		44.3	64.1	65.7	65.2
			191.3					
PhC(OH)(c-Pr)	115.1	173.1	188.4		48.5	64.8	66.6	65.9
			189.3					
		(174.1)[e]	(190.1)[e]					
$Ph(CH_3)(OH)$(c-Pr)	118.8	168.9	189.8	163.2	43.3	63.9	66.4	65.3
			190.5					

[a] As neat liquids at probe temperature (37°) unless otherwise indicated. In parts per million from $^{13}CS_2$. Positive sign indicates shielding from the reference. [b] G. J. Ray, R. J. Kurland, and A. K. Colter, *Tetrahedron*, **27**, 735 (1971). [c] Saturated solution in DMSO-d_6. [d] G. E. Maciel and J. J. Natterstad, *J. Chem. Phys.*, **42**, 2427 (1965). Data converted using $\delta_C{}^{C_6H_6}$ 64.1. [e] P. G. Weiner and E. R. Malinowski, *J. Phys. Chem.*, **71**, 2791 (1967). Data converted using $\delta_C{}^{CH_3I}$ 213.3. [f] Assignments may be reversed.

Table III. Comparison of Carbenium Center Carbon-13 Chemical Shifts in Methyl-, Phenyl-, and Cyclopropyl-Substituted Carbenium Ions[a]

Ion	C^+ chemical shift	Ion	C^+ chemical shift
$CH^+(CH_3)_2$	−125.0	$CH_3CH^+-CH_3$	−125.0
$(c\text{-}Pr)_2$	−59.9	c-Pr	−59.1
Ph_2	−6.9	Ph	−40
$C^+(CH_3)_3$	−135.4	$(CH_3)_2C^+-CH_3$	−135.4
$(c\text{-}Pr)_3$	−77.8	c-Pr	−86.8
Ph_3	−18.1	Ph	−60.6
c-$PrCH^+-CH_3$	−59.1	$PhCH^+-CH_3$	−40
c-Pr	−59	c-Pr	−32.6
Ph	−32.6	Ph	−6.9
$(c\text{-}Pr)_2C^+-CH_3$	−81.6	$Ph_2C^+-CH_3$	−35.5
c-Pr	−77.8	c-Pr	−41.3
Ph	−67.3	Ph	−18.1

[a] See footnote *a*, Table I.

Table III and for some simple monosubstituted benzenes in Table IV.

(a) Carbenium Ions. In order to utilize cmr spectral parameters to study the relative electron donating abilities of cyclopropyl and phenyl rings, we recorded the complete proton decoupled cmr spectra of a comprehensive series of methyl-, phenyl-, and cyclopropyl-substituted carbenium ions and, for comparison, their alcohol precursors. Chemical shift data for the precursors are shown in Table II.

The data show that successive replacement of the methyl protons in methanol by cyclopropyl groups results in downfield shifts of 17.9 and 14.7 ppm, followed by an upfield shift of 11.6 ppm ($\delta_{^{13}C}(CH_3OH)$ 143.5). A trend similar to this is found for the methylene carbon shift of benzyl alcohol, where replacement of the protons by cyclopropyl groups causes downfield and upfield shifts in succession of 12.7 and 2.9 ppm. It is apparent that at least two opposing effects are contributing to the α-substituent effect of a cyclopropyl group. For the comparable series of methyl- and phenyl-substitituted carbinols, downfield shifts only occur with increasing substitution.

The methyl carbon shifts of ethanol, cyclopropylmethylcarbinol, and dicyclopropylmethylcarbinol (Table II) show that the β-substituent effect on an sp^3 hybridized carbon atom of a cyclopropyl group is deshielding.

Some examples of molecular asymmetry effects on the ^{13}C shieldings of cyclopropylcarbinols are evident in Table II. Similar effects in freely rotating systems have been reported[9] for analogous compounds of the type $(CH_3)_2CHC(OH)HR'$, where the methyl group carbon signals are nonequivalent. If the isopropyl group is replaced in the above compounds by a cyclopropyl group, then shift differences between the ring methylene carbons of 1.3 and 0.9 ppm are observed for $R' = CH_3$ and C_6H_5, respectively. For methylphenylcyclopropylcarbinol the corresponding shift difference is 0.7 ppm. The nonequivalence of the methylene carbon signals in the cmr spectrum of dicyclopropylphenylcarbinol is not asymmetrically induced and may result from some type of restricted rotation in the highly crowded molecule.

Carbon-13 nmr spectral parameters for 15 methyl-, phenyl-, and cyclopropyl-substituted carbenium ions are shown in Table I. Assignments were made by the usual methods. The structure of many of these ions has already been discussed on the basis of their pmr spectra.[4,6,10-12] The cmr spectra reveal additional details about some ions.

The pmr spectrum at room temperature of the benzhydryl cation has been analyzed by Farnum.[13] The

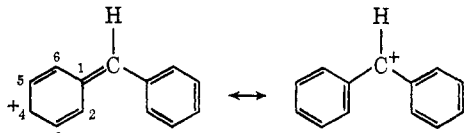
(9) J. I. Kroschwitz, M. Winokur, H. J. Reich, and J. D. Roberts, *J. Amer. Chem. Soc.*, **91**, 5927 (1969).
(10) C. U. Pittman, Jr., and G. A. Olah, *J. Amer. Chem. Soc.*, **87**, 5123 (1965).
(11) C. U. Pittman, Jr., and G. A. Olah, *J. Amer. Chem. Soc.*, **87**, 2998 (1965).
(12) T. J. Sekuur and P. Kranenburg, *Tetrahedron Lett.*, 4769 (1966).
(13) D. G. Farnum, *J. Amer. Chem. Soc.*, **86**, 934 (1964).

Table IV. Carbon-13 Chemical Shifts[a] in Protonated Methyl, Phenyl, and Cyclopropyl Ketones[b] and Their Parent Compounds[c]

Compd	Carbonyl	CH_3	Cyclopropyl CH	Cyclopropyl CH_2	Phenyl C_i	Phenyl C_o	Phenyl C_m	Phenyl C_p
CH_3COCH_3	−12.3[d]	164.7[e]						
CH_3CO(c-Pr)	−14.8	162.8	171.5	182.4				
	(−14.0)[f]	(163.8)[f]	(172.0)[f]	(183.5)[f]				
$CH_3COC_6H_5$	−3.2[d]	167.9[g]			56.2[h]	64.4[h]	64.4[h]	61.2[h]
$C_6H_5COC_6H_5$	−2.4[d]				55.3	63.0[i]	64.6[i]	60.5
C_6H_5CO(c-Pr)	−7.2 (−4.7)[i]		175.7	181.2	54.3	63.9[i]	64.5[i]	59.8
			(176.5)[i]	(182.2)[i]				
(c-Pr)CO(c-Pr)	−17.3 (−17.4)[k]		171.6	182.1				
Protonated ketones								
$(CH_3)_2COH^+$	−55.7[l]	162.0[l]						
		163.3						
CH_3COH^+(c-Pr)	−48.8	(172.4, 165.6, 164.1						
	45.9	163.5, 162.8, 160.4)[m]						
$CH_3COH^+C_6H_5$	−25.8	166.8			63.2	61.2	61.2	46.7
					(64.1)	(58.3)	(62.7)	(48.8)[n]
$(C_6H_5)_2COH^+$	−15.4				62.3	53.6	61.3	48.3
					63.2	57.1		50.4
$C_6H_5COH^+$(c-Pr)	−28.6		168.2	161.3	62.4	61.5	61.5	50.2
$(c\text{-Pr})_2COH^+$	−43.6		174.0	166.8				
			164.7	167.4				

[a] In parts per million from $^{13}CS_2$. Positive sign indicates shielding from the reference. [b] In HSO_3F–SbF_5 (1:1)–SO_2Cl at −70°. [c] As a neat liquid at probe temperature or as reported in the appropriate reference. [d] J. B. Stothers and P. C. Lauterbur, *Can. J. Chem.*, **42**, 1563 (1964). [e] L. M. Jackman and D. P. Kelly, *J. Chem. Soc. B*, 102 (1970). [f] G. E. Maciel and G. B. Savitsky, *J. Phys. Chem.*, **69**, 3925 (1965). Data converted using $\delta_C^{C_6C_6}$ 65.2. [g] K. S. Dhami and J. B. Stothers, *Can. J. Chem.*, **43**, 498 (1965). [h] K. S. Dhami and J. B. Stothers, *ibid.*, **43**, 479 (1965). [i] Assignments may be reversed. [j] Reference 1; data converted using $\delta_C^{CH_3I}$ 213.3. [k] E. Lippmaa, A. Olivson, and J. Past, *Eesti NSV Tead. Akad. Tiom., Fuus. Mat.*, **14**, 473 (1965). Data converted using δ_C^{TMS} 193.7. [l] Reference 6a. [m] Assignments uncertain. [n] Reference 24; data converted using $\delta_C^{C_6H_6}$ 65.2.

proton decoupled cmr spectrum of this carbocation in FSO_3H–SO_2ClF and HSO_3F–SbF_5–SO_2ClF at −60° shows the ortho carbon resonances to be nonequivalent (Figure 1), indicating that there is restricted rotation about the C_{ipso}–C_{CH} single bonds, *i.e.*, a large contribution from resonance forms analogous to **1a**.



1a **1b**

Using very long pulse intervals in the Fourier transform nmr experiment, the relative signal intensities indicated that the meta carbon absorptions were accidentally equivalent and, as expected, the least removed from the chemical shift of benzene.[14c] The furthest downfield signal was assigned to the two para carbons and the remaining two signals at $\delta_{^{13}C}$ 44.6 and 50.3 to the ortho carbons. The more shielded signal may arise from C_2 (**1a**) which is upfield of C_6 because of H–H steric interactions between the two phenyl rings.[15]

The equivalence of the ortho carbon (and of the meta carbon) absorptions in the triphenylcarbenium ion may be attributed to rapid rotation about the C_{ispo}–C^+ bond because of reduced electron demand or if rotation is slow to accidental equivalence of these positions.

The parent benzyl cation has not yet been observed under stable ion conditions, although ring-substituted derivatives were successfully studied under these conditions. The methylene carbon shift in the parent

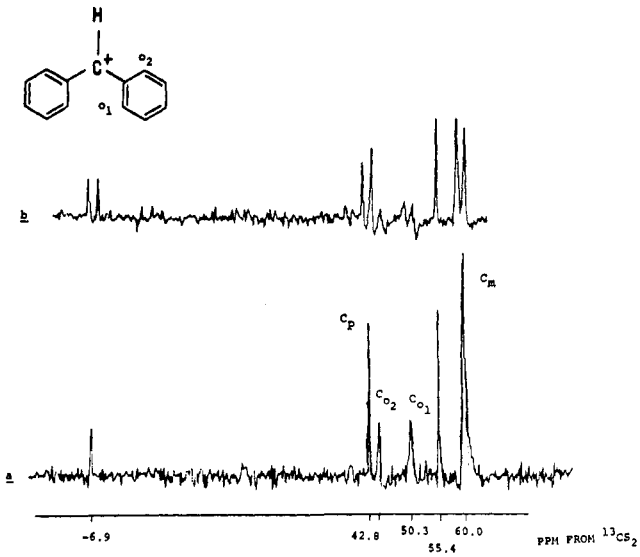


Figure 1. (a) Proton decoupled ^{13}C nmr spectrum at 25.16 MHz of the benzhydryl cation in HSO_3F–SbF_5–SO_2ClF at −60°. (b) Off-resonance decoupled.

benzyl cation was estimated from the shift of the corresponding carbon in the para-methoxy derivative,[6b] after allowance was made for the observed para-methoxy-substituent effect in several related benzyl cations.[6b] The α-styryl cation[6f] could not be prepared in sufficiently high concentration to obtain a satisfactory ring cmr spectrum.[6g]

The 60- and 100-MHz pmr spectra of the tricyclopropylcarbenium ion in a variety of solvents and at several temperatures consist of a singlet at about δ 2.[4,16] In the 300-MHz spectrum of this ion in SO_2ClF

(14) J. B. Stothers, "Carbon-13 NMR Spectroscopy," Academic Press, New York, N. Y., 1972: (a) Table 3.26; (b) p 280; (c) p 197; (d) p 140; (e) Table 3.29.

(15) (a) D. M. Grant and B. V. Cheney, *J. Amer. Chem. Soc.*, **89**, 5315 (1967); (b) W. R. Woolfenden and D. M. Grant, *ibid.*, **88**, 1496 (1966).

(16) N. Deno, H. G. Richey, Jr., J. S. Liu, J. D. Hodge, J. J. Houser, and M. J. Wisotsky, *J. Amer. Chem. Soc.*, **84**, 2016 (1962).

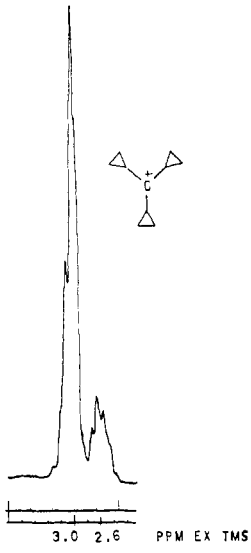
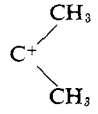


Figure 2. ^1H nmr spectrum (300 MHz) of the tricyclopropylcarbenium ion in HSO_3F–SbF_5–SO_2ClF at $-60°$.

at $-60°$ the methine and methylene proton signals appear to be nonequivalent and are found at δ 2.6 and 3.0, respectively (Figure 2). Unlike other cyclopropylcarbenium ions the β-proton signals are upfield of the α-proton signals.

In the dimethylcyclopropylcarbenium ion, the nonequivalence of the methyl groups in both the ^1H and ^{13}C nmr spectra has been interpreted as evidence for the cyclopropyl rings lying in a plane perpendicular to the plane of the



system. The shielded methyl signal was assigned to the methyl group lying in the face of the cyclopropyl ring and experiencing its diamagnetic anisotropic shielding effect. Part of the shielding of this methyl carbon resonance may result from steric perturbations of the C–H methyl bonds by the β protons of the cyclopropyl ring,[15] interactions which a model of the ion shows may be quite substantial.

The characteristic bisected conformation of a cyclopropyl ring, α to a carbenium center, observed above, also results in nonequivalence of the two phenyl ring carbon shifts in the diphenylcyclopropylcarbenium ion and of the ortho carbons in the phenylcyclopropylcarbenium ion.

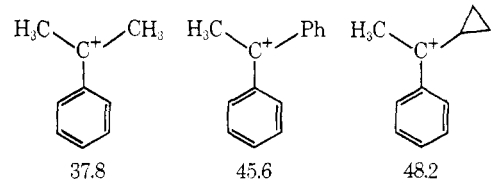
To estimate the extent of charge delocalization by various substituents from the carbenium center in the above ions (Table I), we have compared the chemical shifts of corresponding carbon atoms in these ions.

Carbocation Centers. Although ^{13}C chemical shifts obviously cannot be equated with charge densities, they do *reflect* the charge densities at carbons of similar hybridization and substitution.[17] The shielding constant for a particular atom is generally assumed[18] to be composed of a paramagnetic term (σ_p) reflecting charge polarization, variation in bond order, and average excitation energy, a diamagnetic term (σ_d), and a term reflecting neighboring group effects ($\sigma' = \sigma - (\sigma_p + \sigma_d)$).[19] For the carbon nucleus, the latter two terms are considered to be much less significant than the paramagnetic term which, it has been argued, is dominated by charge polarization effects. It has become apparent in recent work that contributions arising from variations in the ΔE factor may be more important than had been previously realized, for some types of carbons.[20] Also it has been suggested[21] that contributions to the σ_d term arising from nearest neighbor atoms may account for the curious anomalies in the trends exhibited by hydrocarbons and a variety of substituted methanes.

However, despite these uncertainties in the present state of ^{13}C chemical shift theory, there is considerable experimental evidence[17] that the chemical shifts for carbon atoms of similar hybridization and substitution in hydrocarbon molecules of comparable size[22] do reflect π-electron densities.

An upper limit to the differences in the carbenium center chemical shift between comparable methyl-, cyclopropyl-, and phenyl-substituted carbenium ions, which could possibly arise from different substituent contributions to the local σ_d term (C^+), may be estimated by comparing similarly substituted alcohol precursors (*e.g.*, the carbinol carbon shifts in diphenylcyclopropylcarbinol and triphenylcarbinol are $\delta_{^{13}C}$ 123.4 and 115.8, respectively). It appears that the chemical shift difference between the carbenium centers of closely related ions (*i.e.*, comparing related secondary or tertiary systems) summarized in Table III are too large to be accounted for, solely, by these differences or by differences in the σ' term (solvent effects, etc.). The ^{13}C chemical shifts of the carbenium centers in the following closely related series of carbocations thus clearly indicate the trend of charge delocalization by neighboring methyl, phenyl, and cyclopropyl groups is Ph > c-Pr > CH_3.

Particular success has been achieved in correlating para carbon shifts with calculated charge densities in simple monosubstituted benzenes (see also subsequent discussion).[23-25] A cursory examination of the para carbon shifts in the following ions seems to suggest that the ability of the cyclopropyl ring to delocalize charge is greater than that of the phenyl ring.[25b] We feel, however, that such a comparison would neglect the signifi-



(17) (a) P. C. Lauterbur, *J. Amer. Chem. Soc.*, **83**, 1838 (1961); (b) H. Spiesecke and W. G. Schneider, *Tetrahedron Lett.*, 468 (1961); (c) E. A. LaLancette and R. E. Benson, *J. Amer. Chem. Soc.*, **87**, 1941 (1965); (d) G. A. Olah, J. M. Bollinger, and A. M. White, *ibid.*, **91**, 3667 (1969); (e) G. A. Olah and G. D. Mateescu, *ibid.*, **92**, 1430 (1970).

(18) M. Karplus and J. A. Pople, *J. Chem. Phys.*, **38**, 2803 (1963).

(19) For theoretical treatments of carbon-13 chemical shifts, see G. E. Maciel, J. L. Dallas, R. L. Elliott, and H. C. Dorn, *J. Amer. Chem. Soc.*, **95**, 5857 (1973), and ref 1–19 therein.

(20) A. J. Jones, D. M. Grant, J. G. Russell, and G. Fraenkel, *J. Phys. Chem.*, **73**, 1624 (1969).

(21) J. Mason, *J. Chem. Soc. A*, 1038 (1971).

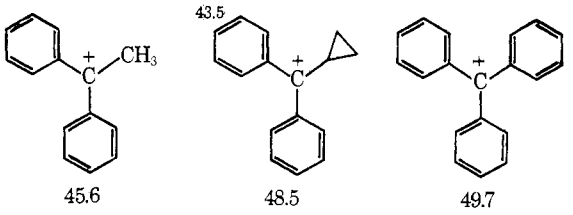
(22) (a) R. Ditchfield, D. P. Miller, and J. A. Pople, *Chem. Phys. Lett.*, **6**, 573 (1970); (b) *J. Chem. Phys.*, **54**, 4186 (1971).

(23) P. C. Lauterbur, *Tetrahedron Lett.*, 274 (1961).

(24) G. L. Nelson, G. C. Levy, and J. D. Cargioli, *J. Amer. Chem. Soc.*, **94**, 3089 (1972).

(25) (a) H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35**, 731 (1961). (b) Suggestion made by Professor H. C. Brown in his referee's remarks on the preliminary communication of our work (see ref 1b).

cant effect that a cyclopropyl ring has on the phenyl ring shifts. When considering, for example, the para carbon shifts in the subsequently shown series of ions, one would be forced to arrive at the opposite conclusion.



45.6 48.5 49.7

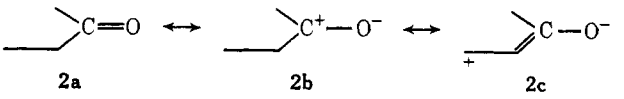
Significantly, the difference of 5 ppm in the para carbon shifts of the diphenylcyclopropylcarbenium ion, in which one phenyl ring lies in the face of the cyclopropyl ring, clearly shows substituent group effects (σ') to be important even at this distant para position.

For similar reasons, in the cyclopropylmethylphenylcarbenium ion, the substituent group effects could cause the para shift to be more shielded than that expected from a consideration of the paramagnetic term alone. For the same reason the para carbon shifts in toluene, biphenyl, and cyclopropylbenzene (discussed subsequently) may not reflect the relative electron densities at the para carbons in these compounds.

In the carbocation systems studied, we feel the same trend is apparent; phenyl delocalizes charge from neighboring carbenium centers more than cyclopropyl, which in turn is more effective than methyl. We feel that this order is, indeed, the expected one considering the nature of charge delocalization by these neighboring groups. The π-electron system of a phenyl group when not hindered by steric effects can conjugatively (*i.e., via* p–π interaction) delocalize charge more effectively than hyperconjugation with the bent σ C–C bonds of the cyclopropane system, which in turn is more effective than the C–H hyperconjugation by the methyl group.

(b) Protonated Ketones. It has been observed that the carbonyl carbon resonance in conjugated aldehydes and ketones is more shielded than that in simple carbonyl compounds.[14b] This trend is quite general for aryl and α,β-unsaturated carbonyl derivatives and is rationalized in terms of a decreased electron deficiency at the carbonyl carbon, because of electron release from the conjugated system. Such a trend is evident from a consideration of the chemical shift data in Table IV. The carbonyl carbon resonance of acetone shifts upfield on replacement of the methyl groups by one and two phenyl groups by 8.1 and 8.3 ppm, respectively. When the methyl groups are replaced by cyclopropyl groups, however, downfield shifts of 3.5 and 6.0 ppm are observed. The differences in the effects of the cyclopropyl and phenyl groups on the α-carbonyl carbon resonance are quite large and its seems unlikely that they can be explained entirely in terms of additional contributing factors apart from those described above.

For closely related compounds we have noted that methyl carbon shieldings may reflect the extent of positive charge on a directly bonded carbon atom. Consideration of the methyl shifts in acetone, methylcyclopropyl ketone, and acetophenone ($\delta_{^{13}C}$ 162.4, 162.8, and 167.9, respectively) suggest that, unless there is a significant anisotropic shielding of the carbonyl carbon by the phenyl group in acetophenone, there is a larger contribution of resonance form **2b** in methylcyclopropyl ketone than in acetophenone. This observation and the above suggest that the phenyl group is more effective in delocalizing charge than the cyclopropyl group.



2a **2b** **2c**

Although the para carbon resonance in monosubstituted benzenes has been found, in many cases, to reflect the electron withdrawing or donating properties of the substitutent,[26–28] the difference in the para carbon shieldings of benzophenone and phenylcyclopropyl ketone is too small to be significant.

It might be anticipated that the relative contribution of a resonance form, corresponding to **2b**, will be increased in the case of a protonated ketone, since the strongly electron-withdrawing oxygen atom now has a formal positive charge. The differences in the electron donating properties of phenyl and cyclopropyl groups, therefore, should be reflected to an even greater extent by the carbonyl carbon resonances. The chemical shifts in Table IV show that this is the case, with a difference of approximately 20 ppm in the carbonyl carbon resonances of protonated methylcyclopropyl ketone and protonated acetophenone, whereas for the corresponding nonprotonated species the difference is only 11.6 ppm. In the parent ketone, it is conceivable, although unlikely, that this latter difference reflects only a difference in substituent effects for phenyl and cyclopropyl groups, which is not a conjugative effect, but the possibility is quite remote that this is true for the protonated ketones. The methyl and cyclopropyl ring carbon shifts in protonated methylcyclopropyl ketone could not be assigned, even by off-resonance decoupling experiments, owing to their close proximity, so a comparison of the methyl shifts in protonated acetone, methylcyclopropyl ketone, and acetophenone was not possible. A comparison of the para carbon shifts in protonated phenylcyclopropyl ketone and benzophenone is not significant because of the small differences involved.

The carbonyl carbon shieldings in protonated acetone, dicyclopropyl ketone, and benzophenone occur at $\delta_{^{13}C}$ −55.7, −43.6, and −15.4, respectively, indicating again that in carbocations the phenyl group is more effective than the cyclopropyl group in its charge delocalizing ability.

This conclusion, based mainly on the relative positions of carbonyl carbon shieldings, rests on the assumption that the carbonyl carbon shift reflects the π-electron densities at the carbonyl carbon. A linear relationship has been found between the ^{13}C shieldings of some simple hydroxycarbenium ions, the corresponding ketones and esters as well as dimethyl carbonate, and the π-electron densities calculated by the simple HMO method.[26]

The total cmr spectra of the ions in Table IV reveal some interesting features about their structure. The nonequivalence of the methyl shieldings in protonated acetone has already been discussed.[6e] Similarly the seven signals between $\delta_{^{13}C}$ 48.3 and 63.2 in protonated

(26) G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **90**, 1884 (1968).
(27) P. H. Weiner and E. R. Malinowski, *J. Phys. Chem.*, **71**, 2791 (1967).
(28) I. J. Wilk, *J. Mol. Struct.*, **2**, 420 (1968).

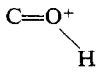
Table V. Carbon-13 Chemical Shifts in Methyl-, Phenyl-, Isopropyl-, and Cyclopropylbenzene[a]

Compd	CH_3	Phenyl C-1	Phenyl C-2	Phenyl C-3	Phenyl C-4	CH	CH_2
Toluene[b]	171.4	55.8 (55.0)	64.0 (63.5)	64.8 (64.3)	67.6 (67.2)		
Cyclopropylbenzene		49.5	67.2	64.8	67.6	177.4	184.0
Isopropylbenzene[b]	168.7	44.7 (44.1)	66.7 (66.2)	64.7 (64.2)	67.0 (66.7)	168.6	
Biphenyl		51.6	65.8	64.4	65.8		
		51.1[c]	65.2[c]	63.6[c]	65.1[c]		
		51.0[d]	65.0[d]	63.8[d]	65.0[d]		

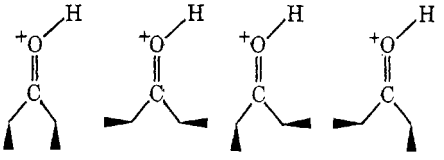
[a] 2.0 *M* solutions in CCl_4 (10% TMS) at probe temperature (37°). Chemical shifts in parts per million from $^{13}CS_2$. Experimentally measured from internal TMS and converted using δ_C^{TMS} 192.8. [b] Values in parentheses from ref 14. Data converted using δ_C^{TMS} 192.8 (also for footnotes *c* and *d*). [c] T. D. Alger, D. M. Grant, and E. G. Paul, *J. Amer. Chem. Soc.*, **88**, 5397 (1966). [d] H. L. Retcofsky, J. M. Hoffman, and R. A. Friedel, *J. Chem. Phys.*, **46**, 4545 (1967).

benzophenone indicate that the signals for each phenyl group are nonequivalent. The only shieldings that could be definitely assigned (by "off-resonance" decoupling) were the two ipso carbon signals at $\delta_{^{13}C}$ 62.3 and 63.2. The signal at $\delta_{^{13}C}$ 61.3 of approximately double the intensity of the others is probably the meta carbon shielding, since this should be the least shifted signal (by the presence of positive charge on the ring) from that of benzene.[14c,24]

The cmr spectrum of protonated dicyclopropyl ketone[10] can be accounted for by one of the following conformations in which the



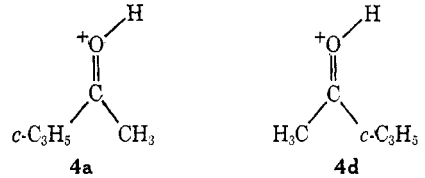
plane is orthogonal to and bisects the plane of the cyclopropane rings. We prefer conformation **3a**, since that



3a **3b** **3c** **3d**

was shown by us, from proton–proton coupling data, to be the preferable conformation for the analogous dicyclopropylcarbenium ion.[11]

The cmr spectrum of the unsymmetrically substituted protonated methylcyclopropyl ketone shows, by the total number of absorptions, that it consists of unequal amounts of the following two forms (**4a** and **4b**).



4a **4d**

The five absorptions between $\delta_{^{13}C}$ 160.4 and 172.4 could not be assigned by "off-resonance" decoupling experiments. The number of signals in the cmr spectrum of protonated acetophenone and cyclopropylphenyl ketone indicate that one of the structures analogous to **4a** and **4b** is significantly more stable than the other.

The largest downfield shift of the methylene carbons compared with the methine carbons, which occurs on protonation of the cyclopropyl ketones in Table IV, suggests a conjugative effect which is more effective in delocalizing charge onto the β carbons relative to the closer α carbon. A comparison of the relative magnitudes of the changes in the β-carbon shifts of the cyclopropyl ring and the ortho and para carbon shifts of the phenyl rings, in protonated cyclopropyl and phenyl ketones, is not valid for determining the relative abilities of these two groups to delocalize charge on an adjacent carbon atom. It has been found for a large number of substituents that cyclopropyl and phenyl ring carbon shifts show differing sensitivities to the same substituent,[27] a difference which most likely is composed of more than two contributing factors[27] and does not simply reflect the relative polarizabilities of cyclopropyl and phenyl rings.

(c) Monosubstituted Benzenes. A further approach available for examining the relative electron donating abilities of phenyl and cyclopropyl groups is to make use of the observed relationship between para carbon shieldings in monosubstituted benzenes and the calculated electron densities at the para carbon.[23-25] Although some interesting deviations from this correlation are apparent, they are usually associated with a carbonyl or carbonitrile substituent. We have recorded the complete proton decoupled cmr spectra of methyl-, isopropyl-, cyclopropyl-, and phenyl-substituted benzenes under *identical* conditions (Table V). The second compound was included since the isopropyl substituent is a model of an alkyl group with approximately the geometry of the cyclopropyl ring. The para carbon resonance in biphenyl is 1.8 ppm deshielded of the corresponding resonance in both toluene and cyclopropylbenzene, and the meta carbon resonance, which has been observed to be the least sensitive of the ring carbon shifts to substituent electronic effects, is approximately the same in all four compounds ($\delta_{^{13}C}$ 64.6 ± 0.2). The ortho carbons absorb over a wider range than either the meta or para carbons, possibly indicating the operation of additional perturbations in addition to electronic effects. Perhaps the shielded ortho carbon in cyclopropylbenzene arises partly from an anisotropic shielding effect of the cyclopropyl ring.

The above difference of 1.8 ppm, although small, is in the expected order for phenyl having a greater electron delocalizing ability than cyclopropyl. This is the case, even though π-electron conjugative overlap is limited in the biphenyl molecule by the phenyl rings being noncoplanar, in solution.[28]

(B) Competitive Stabilization of Carbenium Centers by Methyl, Phenyl, and Cyclopropyl Groups. 1,2-Hydrogen and alkyl shifts in carbenium ions are well known.[29] The driving force for such shifts is usually

(29) (a) G. A. Olah, C. U. Pittman, Jr., E. Namanworth, and M. B. Comisarow, *J. Amer. Chem. Soc.*, **88**, 5571 (1966); (b) M. Saunders, P. v. R. Schleyer, and G. A. Olah, *ibid.*, **86**, 5680 (1964), and other papers in the Carbocation series by G. A. Olah, *et al.*

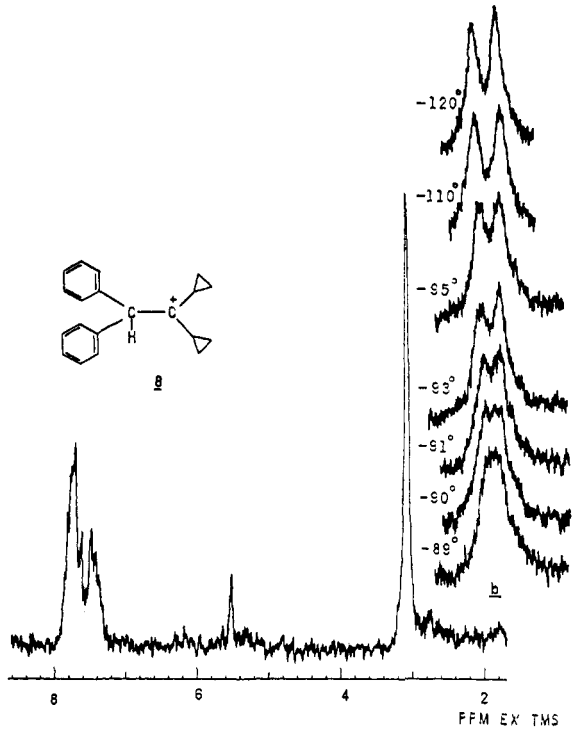


Figure 3. (a) ^1H nmr spectrum (100 MHz) of the dicyclopropylbenzhydrylcarbenium ion **8** in FSO_3H–SO_2ClF at −60°. (b) Cyclopropyl proton signals of carbocation **8** at several temperatures.

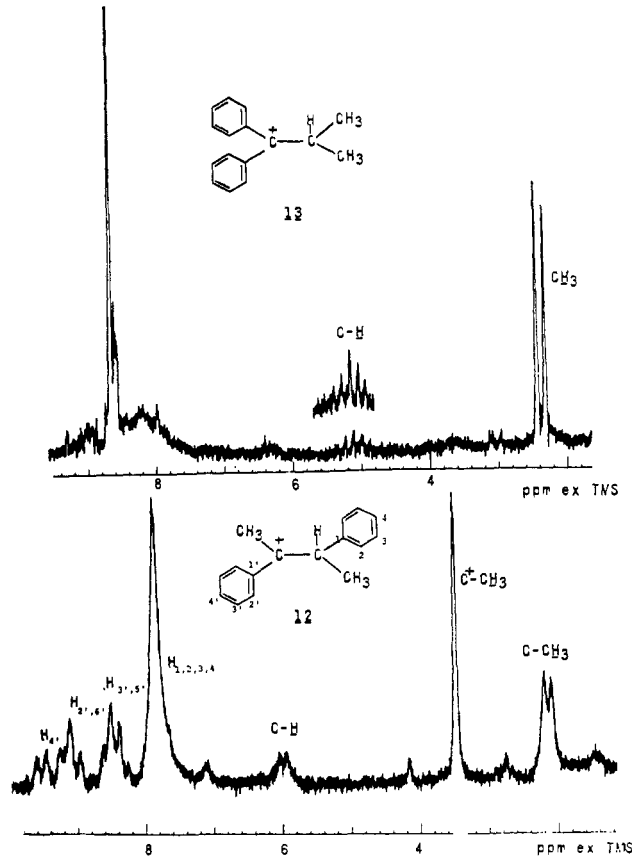
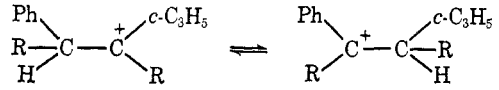


Figure 4. (a) Proton decoupled carbon-13 nmr spectrum (25.16 MHz) of the dicyclopropylbenzhydrylcarbenium ion **8** in FSO_3H–SbF_5–SO_2ClF at −60°. (b) Cyclopropyl carbon region at −95°. (c) Off-resonance decoupled spectrum at −60°.

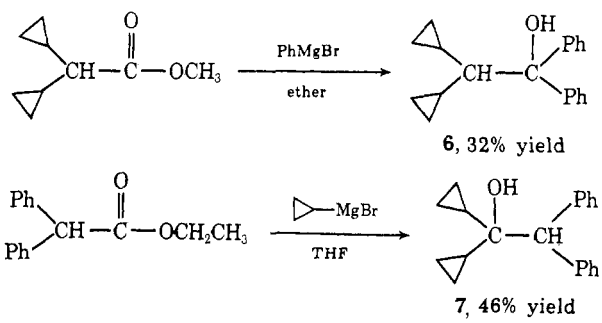
the greater stability of the product ion compared with the initially formed ion and the low energy barrier required for interconversion.

In order to further study the relative ability of methyl, phenyl, and cyclopropyl groups to delocalize charge in carbocations, we have attempted to prepare ions of the type **5** in which phenyl and cyclopropyl groups compete with each other to stabilize an adjacent carbenium center. The ratio of **5a** to **5b** at equilibrium should reflect the relative stabilizing abilities of phenyl and cyclopropyl.



5a **5b**

Two precursors to ions of this type, 1,1-diphenyl-2,2-dicyclopropylethanol (**6**) and 1,1-dicyclopropyl-2,2-diphenylethanol (**7**), were prepared by the Grignard reactions of methyl dicyclopropylacetate with phenylmagnesium bromide and of ethyl diphenylacetate with a large excess of cyclopropylmagnesium bromide, respectively. The pmr and cmr spectra of compounds **6** and **7** in CCl_4 are as expected apart from the nonequivalence of the methylene carbon signals in the cmr spectrum of **6**. This is not asymmetrically induced and must result from some type of restricted rotation in the highly crowded molecule or from some type of intramolecular interaction between the hydroxyl group and the cyclopropane ring.[30]



Ionization of 1,1-dicyclopropyl-2,2-diphenylethanol with FSO_3H in SO_2ClF at −110° gave a light brown solution whose pmr spectrum showed a multiplet at δ 7.2–8.0 (10 H), a singlet at δ 5.5 (1 H), and two broad signals between δ 2.6 and 3.4 (10 H). On warming the sample, these latter signals became a broad singlet at δ 3.0 at −85° and a sharp singlet at −60°. These observed changes in the cyclopropane proton signals with temperature are reversible and are shown in Figure 3, together with the complete pmr spectrum at −60°. At −120°, spectral integration shows that the more intense of the two methylene proton signals (Figure 3) is coincident with the methine proton signals.

The cmr spectrum at −60° (Figure 4) showed a very broad signal between $\delta_{^{13}C}$ 148 and 162, which became three signals at $\delta_{^{13}C}$ 146, 150, and 157 on cooling the solution to −95°. The remaining signals at $\delta_{^{13}C}$ −80.9, 56.9, 63.7, 64.3, 64.6, and 133.9 were independent of temperature between −100 and −40° and were assigned as shown in Figure 4. Assignments were made

(30) (a) M. Oki, H. Iwamura, T. Murayama, and I. Oka, *Bull. Chem. Soc. Jap.*, **42**, 1986 (1969); (b) L. Joris, P. v. R. Schleyer, and R. Gleiter, *J. Amer. Chem. Soc.*, **90**, 327 (1968).

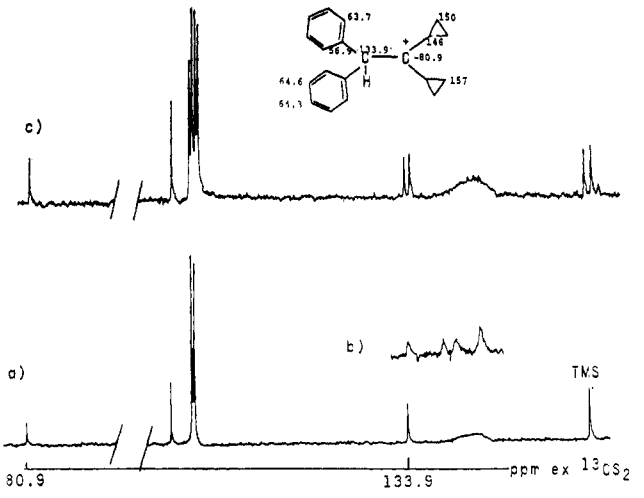
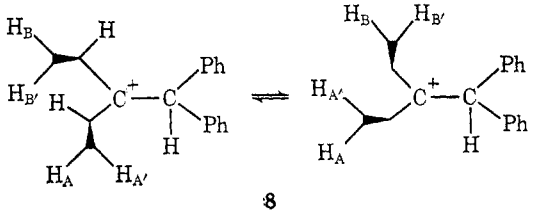


Figure 5. (a) ^1H nmr spectrum (100 MHz) of carbocation **12** in FSO_3H–SO_2ClF at −80°. (b) Pmr spectrum of product formed on raising temperature to −40°.

from "off-resonance" decoupling experiments as well as from a comparison between the cyclopropyl ring carbon shifts of this ion and the related dicyclopropylmethylcarbenium ion. The cyclopropyl ring carbon shifts and the phenyl ring carbon shifts (similar to those of uncharged alkyl monosubstituted benzenes)[15e] indicated that the ion had structure **8**, with the carbenium

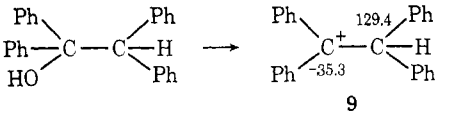


8

center α to the substantially charged cyclopropyl rings. The observed temperature dependence above can be attributed to the following equilibrium, which at −120° is slow on the nmr "time scale." The bulk of the $-CHPh_2$ group must be responsible for the observed temperature variation in the nmr spectrum of this ion, as the same behavior was not observed in the nmr spectrum of the related dicyclopropylmethylcarbenium ion.

Ion **8** is stable up to −10°, whereupon decomposition occurs to, as yet, unidentified products. Even at this temperature there is no evidence in the nmr spectra for a 1,2-hydride shift. Attempts to ionize 1,1-diphenyl-2,2-dicyclopropylethanol with FSO_3H, HF–SbF_5, FSO_3H–SbF_5 or SbF_5 in SO_2, or SO_2ClF only gave polymeric materials.

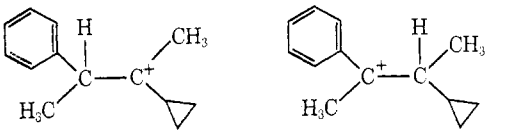
Furthermore, in ions such as **8**, cyclopropyl groups delocalize charge so effectively that the ground state energy of the ion compared with that of the transition state leading to the rearranged ion is sufficiently lowered to make the 1,2-hydride shift a very slow reaction. Phenyl groups, however, have the same effect, which prevents this method from being used to determine the relative effectiveness of cyclopropyl and phenyl delocalization. This is shown by nmr spectral studies of ion **9**, where no hydride shift was observed between −80 and 37°. Ionization of tetraphenylethanol with FSO_3H in SO_2ClF at −80° gave a solution whose pmr



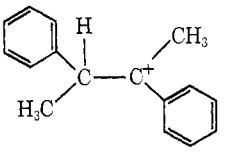
9

spectrum showed multiplets at δ 7.3–7.9 (10 H) and 8.0–8.6 (10 H) and a singlet at δ 5.5 (1 H). On the basis of these data and the cmr spectrum ($\delta_{^{13}C}$ −35.3, 46.8, 50.9, 53.3, 56.9, 62.7, 62.8, 63.6, 64.7, and 129.4; assignments except for phenyl ring carbons are shown on structure **9**), we assign the above nonequilibrating structure to this ion.[31] No change occurred in the methine proton or carbon shifts of this ion from −80 to 37°, indicating that the ion maintained its static ion form. The phenyl ring proton signals were unchanged up to −10° but then decreased in intensity and changed in appearance suggesting that electrophilic attack by FSO_3H might be occurring.

We have also attempted to prepare ions **10** and **11**, which should have a lower activation for the 1,2-hydride shift and therefore should show more readily the competition between phenyl and cyclopropyl groups to stabilize an adjacent carbenium center. To see if such a rearrangement can occur in ions **10** and **11**, we have studied the closely related ion **12**. Ionization of 2,3-

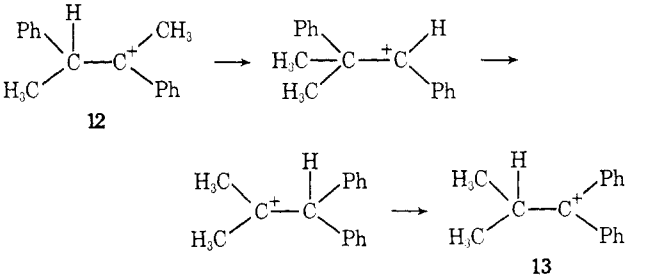


10 **11**



12

diphenyl-2-butanol with FSO_3H in SO_2ClF at −120° gave a solution whose pmr spectrum at −80° showed absorptions at δ 9.55 (1 H), 9.13 (2 H), 8.50 (2 H), 7.87 (5 H), 6.0 (q, 1 H), 3.45 (3 H), and 2.16 (d, 3 H) (Figure 5). These data indicated that ion **12** was obtained (the assignments are shown in Figure 5). On warming to −40°, **12** rearranges *via* successive methyl, phenyl, and hydride shifts to the diphenylisopropylcarbenium ion **13**. We prepared independently the diphenyliso-



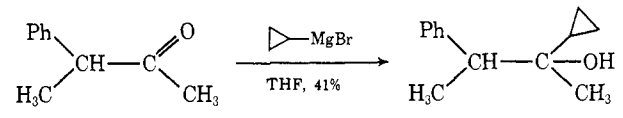
12 **13**

propylcarbenium ion **13** from 1,1-diphenyl-2-methylpropanol and 1,1-diphenyl-1-propanol and found it to have identical pmr and cmr spectra as the ion formed

(31) This contrasts with our earlier pmr studies of the ion in FSO_3H–SbF_5–SO_2 solution, where the methine proton was not observed and the only incompletely resolved aromatic region was interpreted as the equilibrating ion. The detailed reinvestigation of the tetraphenylethyl (as well pentaphenylethyl) cations by their cmr studies will be reported separately.

by the above rearrangement[29a] (Figure 5). In the cmr spectra of ion **13**, signals were observed at $\delta_{^{13}C}$ −48.4 (C^+), 48.0 (C_p), 53.0 (C_o), 62.8 (C_m), 64.3 (C_{ipso}), 149.3 (CH), and 169.0 (CH_3).

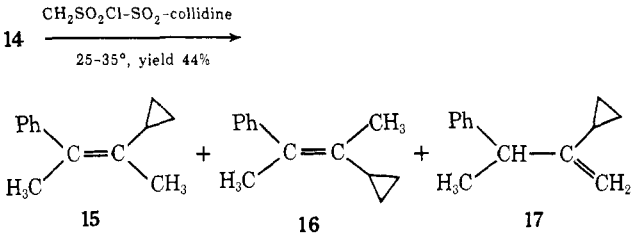
2-Cyclopropyl-3-phenyl-2-butanol (**14**), the precursor



14

of ion **10**, was prepared by treating α-methylphenylacetone with cyclopropylmagnesium bromide in tetrahydrofuran.

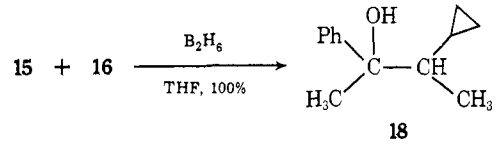
Dehydration of 2-cyclopropyl-3-phenyl-2-butanol was carried out with $SOCl_2$–pyridine, $POCl_3$–pyridine, or CH_3SO_2Cl–collidine to give a mixture of *cis*- and *trans*-2-cyclopropyl-3-phenyl-2-butene (**15** and **16**) and 2-cyclopropyl-3-phenyl-1-butene (**17**). The best yield



15 **16** **17**

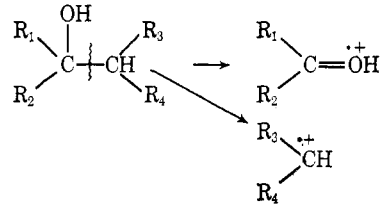
of 2-cyclopropyl-3-phenyl-2-butene was obtained with the latter reagent.

Hydroboration of olefins **15** and **16** afforded 3-cyclopropyl-2-phenyl-2-butanol (**18**), the precursor to ion **11**,



18

in quantitative yield. The mass spectra of alcohols **6**, **7**, **14**, and **18** showed that fragmentation occurred exclusively at the C_1–C_2 bond in dicyclopropyldiphenylethanols or at the C_2–C_3 bond in compounds **14** and **18**.



Ionization of 2-cyclopropyl-3-phenyl-2-butanol (**14**) with FSO_3H in SO_2ClF at −120° gave a solution whose pmr spectrum showed broad signals at δ 7.9 (5 H), 5.0 (1 H), 3.5–4.5 (5 H), 2.8 (3 H), and 1.6–2.2 (3 H). These data suggest that ion **10** is present in solution. However, it is quite unstable, decomposing to, as yet, unidentified products at −90°. On the other hand, 3-cyclopropyl-2-phenyl-2-butanol (**18**), in FSO_3H–SO_2ClF and in other superacid systems, even at −120°, gave only polymeric material, and ion **11** could not be observed.

There is therefore no evidence for a 1,2-hydrogen shift in the ions of type **5** that could be prepared, and consequently this approach cannot be used in determining the relative abilities of phenyl and cyclopropyl groups to delocalize charge on an adjacent carbenium center. Furthermore, even if ion **11** and the diphenyl(dicyclopropylmethyl)carbenium ion could be prepared, the results for ion **12** suggest that a 1,2-hydrogen shift may not be the preferred migration in these ions.

In similar experiments involving possible intermolecular rather than intramolecular hydrogen shifts we found that the triphenylcarbenium ion does not react with tricyclopropylmethane in SO_2, nor does the tricyclopropylcarbenium ion abstract hydride ion from triphenylmethane. The reason that neither reaction occurs under these conditions is probably the same as for intramolecular hydride shifts are not observed in ion **8**.

(C) Addition Reactions to Cyclopropyl- and Phenyl-Substituted Olefins. As a third approach to investigate the relative abilities of phenyl and cyclopropyl groups to delocalize positive charge, we have studied some electrophilic addition reactions, such as oxymercuration and hydrochlorination, to 1-phenyl-2-cyclopropyl-substituted olefins **15** and **16**. (The synthesis of these olefins has already been outlined in the preceding discussion.)

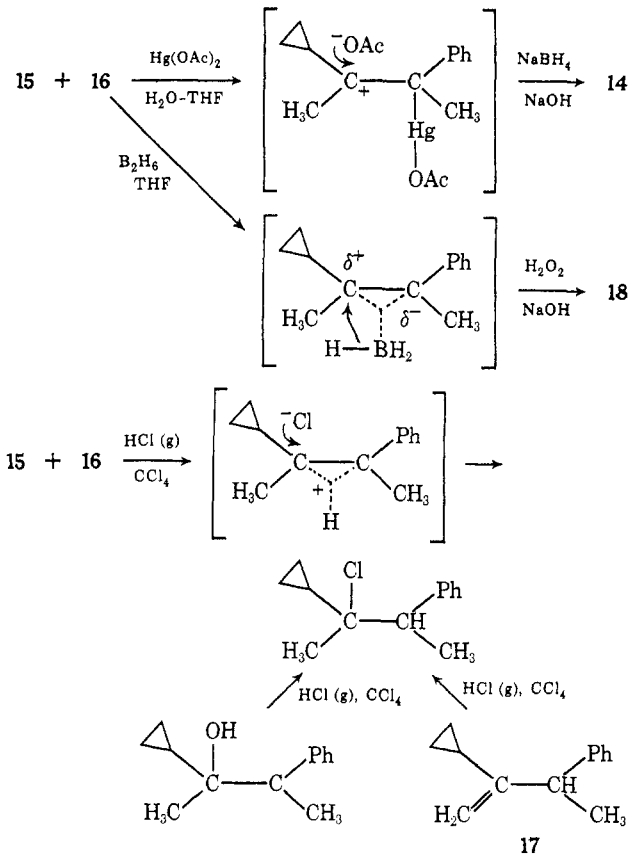
Oxymercuration of 2-cyclopropyl-3-phenyl-2-butene **15** + **16** gave exclusively 2-cyclopropyl-3-phenyl-2-butanol (**14**), while hydroboration produced exclusively 3-cyclopropyl-2-phenyl-2-butanol (**18**). Hydrochlorination of the olefins **15** and **16** afforded 2-chloro-2-cyclopropyl-3-phenylbutane, the same product as that obtained by chlorination of 2-cyclopropyl-3-phenyl-2-butanol (**14**) or hydrochlorination of 2-cyclopropyl-3-phenyl-1-butene (**17**). The pmr spectrum of the reaction mixture from hydrochlorination of **15** and **16** showed no significant amount of the other isomer or any product was formed, when the reaction was carried out at 0°, using a Brown hydrogenation apparatus to avoid the presence of excess HCl.

Oxymercuration[32a,b] and hydrochlorination[32c] of olefins are considered to be electrophilic addition reactions passing through a classical carbenium ion. Product analysis of the above reactions showed that in electrophilic additions to 2-cyclopropyl-3-phenyl-2-butenes **15** and **16**, the major product arises from the carbenium ion intermediate, which bears positive charge on the carbon substituted by the cyclopropyl group. We conclude, therefore, that in the transition state leading to the intermediate the cyclopropyl group participates to stabilize the electron deficient site more effectively than phenyl.

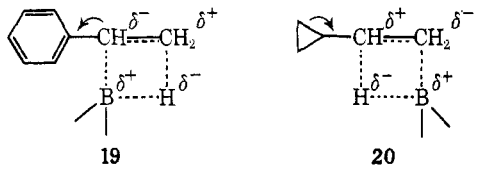
The previously discussed results for the hydroboration of olefins **15** and **16** may not necessarily indicate the relative donating abilities of phenyl and cyclopropyl groups, since it was found[33] in the hydroboration of vinylcyclopropane that the cyclopropyl group had a β-directing effect, whereas in β-methylstyrene the phenyl group was α directing. The ability of the phenyl group to stabilize transition state **19** by absorbing electron density was the reason given for the latter result, while the cyclopropyl group is β directing

(32) (a) H. C. Brown and P. Geoghegan, *J. Amer. Chem. Soc.*, **89**, 1522 (1967); (b) H. C. Brown and P. J. Geoghegan, *J. Org. Chem.*, **35**, 1844 (1970); (c) J. March, "Advanced Organic Chemistry: Reactions, Mechanisms, and Structure," McGraw-Hill, New York, N. Y., 1968, Chapter 15.

(33) S. Nishida, I. Moritani, K. Ito, and K. Sakai, *J. Org. Chem.*, **32**, 939 (1967).



because it stabilizes transition state **20** by supplying electron density.



Conclusion

We feel that there is no discrepancy in the conclusions that can be reached regarding the relative charge delocalizing abilities of phenyl and cyclopropyl groups from ^{13}C chemical shift data, from solvolytic rate data, from the study of equilibrium constants of the related ions and their alcohol or olefin precursors in acid media,[4,34] and our results from the oxymercuration and hydrochlorination of 1,2-cyclopropyl- and phenyl-substituted olefins.

The fact that cyclopropylcarbinyl esters solvolyze faster than the related phenyl esters clearly shows that cyclopropyl is a better participating group in solvolysis than phenyl. A contributing factor can be that the significant strain in the bent, electron-rich cyclopropyl groups in covalent cyclopropylcarbinyl esters is partially relieved upon reaching the carbenium ion like transition state, thus greatly facilitating the reaction. The fact that cyclopropyl is a better participating group than phenyl in the transition state of these reactions does not necessarily mean that it also delocalizes charge better in the intermediate ions. In other words, phenyl can remove charge further, spreading it out over a larger system without necessarily meaning that the stability of phenylcarbenium ions is greater than that of cyclopropylcarbenium ions. Similar considerations explain the equilibrium data between ions and their alcohol or olefin precursors. pK_{R^+} values show only the stabilities of the ions relative to their covalent precursors, with which they are in equilibrium. If, for example, cyclopropylcarbinyl esters release more strain upon ionization than related phenylcarbinyl esters this could affect the solvolysis rates and pK_{R^-} data. Spectroscopic data, particularly the cmr study of related long-lived ions, give, in contrast, direct information on the structure of the carbenium ion intermediates. Spectroscopic properties are solely a function of the carbenium ion species, and, therefore, unlike solvolysis data or equilibrium constant measurements, can be expected to be correlatable with theoretical assessments of the R^+ structure. Carbon-13 chemical shifts, therefore, if used with proper consideration of all the factors involved, are a very powerful tool in studying the structure of carbocations, including the trend of charge distribution.

Finally it should be emphasized that no single, uniform sequence of the delocalizing ability of phenyl *vs.* cyclopropyl groups can be predicted for all systems. Whereas in the presently studied series of structurally closely related carbenium ions phenyl is indicated to be the better delocalizing group than cyclopropyl, it easily can be that in other systems, such as allylic cations, this sequence is reversed (we will report our continuing studies separately). Of possible neighboring electron donors σ-donor alkyl groups (as C–H or C–C donors) are clearly the weakest and π donors (as in allyl cations) the strongest electron donors. Aromatic π systems and bent σ-bond donors (such as cyclopropyl groups) are intermediate and their relative effectiveness may depend on the specific systems. This of course has no bearing on the fact that the study of stable, long-lived carbocation intermediates is now firmly established and their structural study by spectroscopic methods, such as cmr spectroscopy, enables the trend of charge delocalization in these ions, to be established.

Experimental Section

Most of the alcohols in Table II and ketones in Table IV were commercially available and were used without further purification. 1,1,2,2-Tetraphenylethanol,[35] *threo*- and *erythro*-2,3-diphenyl-2-butanol,[36] 1,1-diphenyl-2-methyl-1-propanol,[37] and α-methylphenylacetone[38] were prepared by reported methods.

1,1-Diphenyl-2-methyl-2-propanol was prepared in 93% yield by the addition of excess methylmagnesium iodide to ethyl diphenylacetate[39] in diethyl ether: bp 136–138° (5 mm).[29a]

1,1-Diphenyl-2,2-dicyclopropylethanol (6). Methyl dicyclopropylacetate (5.7 g, 0.037 mol), prepared by the method of Nierth, Ensslin, and Hanack,[40] was added dropwise to an ether solution of phenylmagnesium bromide (0.1 mol). After refluxing for 12 hr, the reaction mixture was worked up in the usual manner to give the crude alcohol **6** (3.35 g, 32%), which was recrystallized from ethanol: mp 94°; ir (Nujol) 3480 (OH), 1020 (cyclopropyl), and 685 cm^{-1} (phenyl); pmr (CCl_4) δ 7.5–8.0 (m, 10, phenyl), 3.27 (m, 1, OH), 2.35 (t, 1, J = 7.0 Hz, C*H*), and 0.2–1.4 (m, 10, cyclopropyl); cmr ($CDCl_3$) $\delta_{^{13}C}$ 189.6 (CH_2), 189.4 (CH_2), 182.0 (*C*H, cyclopropyl), 140.6 (*C*H), 109.6 (*C*OH), 65.5 ($C_{o,p}$), 64.3 (C_m), 45.3 (C_{ipso}); mass

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(35) A. Banchetti, *Gazz. Chim. Ital.*, 72, 74 (1942).
(36) J. Levy, *Bull. Soc. Chim. Fr.*, 29, 888 (1921).
(37) J. Levy, *Bull. Soc. Chim. Fr.*, 29, 882 (1921).
(38) C. M. Suter and A. W. Weston, *J. Amer. Chem. Soc.*, 64, 533 (1942).
(39) G. Heyl and V. Meyer, *Chem. Ber.*, 28, 2776 (1895).
(40) A. Nierth, H. M. Ensslin, and M. Hanack, *Justus Liebigs Ann. Chem.*, 733, 187 (1970).

spectrum (20 eV) *m/e* (rel intensity) 183 (100), 95 (31). *Anal.* Calcd for $C_{20}H_{22}O$: C, 86.29; H, 7.97. Found: C, 85.87; H, 7.93.

1,1-Dicyclopropyl-2,2-diphenylethanol (7). Ethyl diphenylacetate[39] (7.0 g, 0.029 mol) was treated with cyclopropylmagnesium bromide, prepared from 0.3 mol of cyclopropyl bromide and 0.3 mol of magnesium in 200 ml of freshly distilled tetrahydrofuran. The reaction mixture was kept at 60° for 20 hr. On working up in the usual manner, 10 g of crude product was obtained, which glpc analysis (3DS 3 ft, 200°) showed to be a mixture of two compounds in the ratio 54:46. The two products, diphenylmethyl cyclopropyl ketone and 1,1-dicyclopropyl-2,2-diphenylethanol (**7**) were separated by preparative gas chromatography (3DS 1 ft, 180°).

Diphenylmethyl cyclopropyl ketone: mp 40–42°; ir (Nujol) 1700 (C=O), 1603 (phenyl), 1040 (cyclopropyl), and 710 cm^{-1} (phenyl); nmr (CCl_4) δ 7.66 (s, 10, phenyl), 5.62 (s, 1, $(phenyl)_2CH$), 2.0–2.6 (m, 1, c-PrH(C=O)), 0.6–1.7 (m, 4, cyclopropyl). *Anal.* Calcd for $C_{17}H_{16}O$: C, 86.41; H, 6.82. Found: C, 86.34; H, 6.93.

1,1-Dicyclopropyl-2,2-diphenylethanol: ir (liquid film) 3570 (OH), 1600 (phenyl), 1020 (cyclopropyl), 705 cm^{-1} (phenyl); nmr (CCl_4) δ 7.7–8 (m, 10, phenyl), 4.69 (s, 1, Ph_2CH), 1.63 (s, 1, OH), 0.6–2.2 (m, 10, cyclopropyl); mass spectrum (20 eV) *m/e* (rel intensity) 167 (19), 111 (100), 69 (41). *Anal.* Calcd for $C_{20}H_{22}O$: C, 86.29; H, 7.97. Found: C, 86.25; H, 7.97.

2-Cylopropyl-3-phenyl-2-butanol (14). 3-Phenyl-2-butanone (29.6 g, 0.2 mol) was treated with 0.3 mol of cyclopropylmagnesium bromide in THF (200 ml). The reaction mixture was refluxed for 2 hr, allowed to stand at room temperature for 12 hr, and worked up in the usual manner. The crude product was distilled under reduced pressure to give 15.6 g (41%) of 2-cyclopropyl-3-phenyl-2-butanol (bp 87–89° (0.08 mm)): ir (liquid film) 3510 (OH), 1603 (phenyl), 1370 (methyl), 1010 (cyclopropyl), 890 and 690 cm^{-1} (phenyl); nmr (CCl_4) δ 7.77 (s, 5, phenyl), 3.41 (q, 1, J = 7.0 Hz, c-PrCHCH$_3$), 1.92 (d, 3, J = 7.0 Hz, CHCH_3), 1.57 (s, 3, C(OH)CH_3), 1.6–1.8 (m, 1, OH), 1.1–1.5 (m, 1, c-PrH), 0.6–1.0 (m, 4, cyclopropyl); cmr (neat) $\delta_{^{13}C}$ 191.3 (CH_2), 192.2 (CH_2), 177.0 ($CHCH_3$), 172.8 (CH), 168.5 (C(OH)CH_3), 142.3 (CH), 121.2 (COH), 50.2 (C_{ipso}), 64.8 and 66.3 (C_o and C_m), 67.7 (C_p); mass spectrum (20 eV) *m/e* (rel intensity) 105 (44), 85 (100). *Anal.* Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 82.13; H, 9.62.

Dehydration of 2-Cyclopropyl-3-phenyl-2-butanol (14). Methylsulfonyl chloride (12 ml) containing 5% sulfur dioxide was added dropwise at 25–35° to a mixture of 15 g (0.08 mol) of alcohol **14** and 24 ml of collidine in 90 ml of dimethylformamide. The reaction mixture was allowed to stand at room temperature for 20 min before being poured into water and extracted with light petroleum The combined petroleum ether extracts were washed with saturated aqueous sodium chloride solution and dried ($MgSO_4$). On evaporation of the solvent, the crude product was distilled over lithium aluminum hydride to give 6.1 g (44%) of olefins **15**, **16**, and **17**: (bp 60–70° (0.2 mm)); glpc analysis (Q 150 ft, 160°) showed that the ratio of 2-cyclopropyl-3-phenyl-1-butene (**17**):*cis*-2-cyclopropyl-3-phenyl-2-butene (**15**):*trans*-2-cyclopropyl-3-phenyl-2-butene (**16**) was about 50:25:25. The substituted 2-butenes were separated from the substituted 1-butene by preparative gas chromatography (SE-30 20 ft, 200°).

2-Cyclopropyl-3-phenyl-2-butene (cis and trans): nmr (CCl_4) δ 7.64 (m, 5, phenyl), 2.3–2.7 (m, 3, PhCCH_3), 1.6–2.0 (m, 3, c-PrCCH_3), 0.5–1.3 (cyclopropyl). *Anal.* Calcd for $C_{13}H_{16}$: C, 90.64; H, 9.36. Found: C, 90.53, H, 9.33.

2-Cyclopropyl-3-phenyl-1-butene: nmr (CCl_4) δ 7.63 (m, 5, phenyl), 5.15 (d, 2, J = 6.0 Hz, methylene), 3.62 (q, 1, J = 7.0 Hz, PhCHCH$_3$), 1.95 (d, 3, J = 7.0 Hz, PhCHCH_3), 0.6–1.7 (m, 5, cyclopropyl). *Anal.* Calcd for $C_{13}H_{16}$: C, 90.64; H, 9.36. Found: C, 90.62; H, 9.33.

2-Phenyl-3-cyclopropyl-2-butanol (18). To a mixture of 3.0 g (0.017 mol) of 2-cyclopropyl-3-phenyl-2-butene and 0.4 g of sodium borohydride in THF (20 ml) was added dropwise 4 ml of boron trifluoride etherate. The reaction mixture was allowed to stand at room temperature for 20 min before decomposing excess acid with water (1 ml). Aqueous 3 N sodium hydroxide solution (2 ml) was then added, followed by 2 ml of 30% hydrogen peroxide. The reaction mixture was extracted with ether and the combined ether extracts were washed with saturated aqueous sodium chloride solution and dried ($MgSO_4$). After the solvent was removed the crude product was distilled under reduced pressure (bp 90–93° (0.6 mm)) to give 2-phenyl-3-cyclopropyl-2-butanol in quantitative yield: ir (liquid film) 3510 (OH), 1603 (phenyl), 1365 (methyl), 1010 (cyclopropyl), 890 and 687 cm^{-1} (phenyl); nmr (CCl_4) δ 7.4–8.0 (m, 4, phenyl), 2.2 (m, 1, OH), 2.15 (s, 3, PhC(OH)CH_3), 1.30 (d, 3, J = 4.0 Hz, c-PrCHCH_3), 0.2–2.0 (m, 6, methine and cyclopropyl); mass spectrum (20 eV) *m/e* (rel intensity) 121 (100), 69 (4). *Anal.* Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 81.98; H, 9.48.

Oxymercuration of 2-Cyclopropyl-3-phenyl-2-butene. A mixture of olefins **15** and **16** (0.5 g) was treated with 1 g of mercuric acetate in aqueous THF, according to the described procedure.[32b,c] Glpc analysis of the reaction mixture showed that 2-cyclopropyl-3-phenyl-2-butanol was the sole product.

Hydrochlorination. 2-Cyclopropyl-3-phenyl-2-butene (0.5 g) in 6 ml of carbon tetrachloride was treated at 0° for 20 min with HCl gas, using a Brown apparatus.[31] The nmr spectrum of the resulting reaction mixture showed that the product was exclusively 2-chloro-2-cyclopropyl-3-phenylbutane (observed integral ratio of phenyl protons/methine proton = 4.7 (calcd 5.0)): nmr (CCl_4) δ 7.66 (s, 5, phenyl), 3.55 (q, 1, J = 7.0 Hz, PhCHCH$_3$), 1.95 (d, 3, J = 7.0 Hz, PhCHCH_3), 1.83 (d, 3, J = 2.0 Hz, c-PrC(Cl)CH_3), 0.6–1.8 (m, 5, cyclopropyl). The reaction of 2-cyclopropyl-3-phenyl-1-butene or 2-cyclopropyl-3-phenyl-2-butanol in carbon tetrachloride with hydrogen chloride gave the same product as above.

Preparation of Ions. Most of the ions discussed have been reported previously and procedures for their preparation, similar to those given in the references cited, were used throughout. In all cases the solutions had proton spectra identical with those described previously.

Most of the ions were prepared from carbinol precursors. Best results were obtained by freezing approximately 60 mg of the alcohol onto the wall of a test tube containing about 1.5 ml of the acid solution at −78° (~1:2 (v/v) FSO_3H, FSO_3H–SbF_5, or SbF_5 in SO_2ClF or SO_2). The alcohol is then gently washed into solution. Careful agitation at the start is usually required. Complete mixing is accomplished with a vortex mixer.

Proton Nuclear Magnetic Resonance Spectra. Pmr spectra were obtained using Varian Associates Model A56/60A and HA 100 spectrometers equipped with variable temperature probes. External tetramethylsilane (capillary) was used as reference.

Carbon-13 Nuclear Magnetic Resonance Spectra. The spectrometer used was a Varian Associates Model XL 100 spectrometer equipped with a broad-band proton 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 the 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 signal of an external sample of hexafluorobenzene. 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. They were converted to parts per million from $^{13}CS_2$ using the experimentally determined conversion factor: $\delta_{CS_2}^{TMS}$ 193.8.

Some spectra were obtained using a Varian Associates Model HA-100 equipped with a Fourier transform accessory (V-4357 pulsing and control unit), broad-band proton decoupler, and variable temperature probe. The instrument, lock, and referencing systems have been described in more detail elsewhere.[41]

Acknowledgment. Support of our work by the National Science Foundation is gratefully acknowledged.

(41) G. A. Olah, G. Liang, and P. W. Westerman, *J. Amer. Chem. Soc.*, **95**, 3698 (1973).