References and Notes

(1) (a) This research was supported by the Office of Graduate Research, Southern Illinois University at Edwardsville. (b) Taken in part from the M.S. Thesis of Tai-Teh Wu, Southern Illinois University at Edwardsville, 1976.

(2) E. Buchner, *Chem. Ber.*, **28**, 215 (1895).

(3) O. P. Strausz, G. J. A. Kennepohl, F. X. Garneau, T. DoMinh, B. Kim, S. Valenty, and P. S. Skell, *J. Am. Chem. Soc.*, **96**, 5723 (1974), and references cited therein.

(4) T. B. Patrick and G. H. Kovitch, *J. Org. Chem.*, **40**, 1527 (1975).

(5) R. M. Acheson, "An Introduction to the Chemistry of Heterocyclic Compounds", 2nd ed, Interscience, New York, N.Y., 1967, pp 62–140.

(6) Carbene reactions, on the contrary, show less discrimination of reaction sites as many carbon–hydrogen and carbon–heteroatom insertion reactions have been reported. W. Kirmse, "Carbene Chemistry", 2nd ed, Academic Press, New York, N.Y., 1971, Chapter 11.

(7) See S. J. Valenty and P. S. Skell, *J. Org. Chem.*, **38**, 3937 (1973), for the synthetic utility of this type of reaction.

(8) T. Saegusa, Y. Ito, S. Kobayaski, K. Hirota, and T. Shimizu, *Tetrahedron Lett.*, 6131 (1966).

(9) Drs. P. S. Skell and S. J. Valenty have independently concluded that the diazomercury carbene (B) is the major intermediate formed in the photolysis of **1**. Private communication from Professor Skell.

(10) Mercury-containing carbenes do not undergo carbon–hydrogen insertion into ordinary hydrocarbons: P. S. Skell and S. J. Valenty, *J. Am. Chem. Soc.*, **95** 5042 (1973).

(11) A. P. Marchand and N. M. Brockway, *Chem. Rev.*, **74**, 431 (1974).

(12) All temperature readings are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn., and were within ±0.3% of the theoretical values. A Varian T-60 spectrometer was used for ^{1}H NMR analyses with tetramethylsilane as the internal reference. A Varian MAT-111 spectrometer was used for mass spectral analyses at 80 eV. A Perkin-Elmer Model 337 spectrometer calibrated with polystyrene was used for infrared analyses.

(13) See, R. E. Sievers, Ed., "Nuclear Magnetic Resonance Shift Reagents", Academic Press, New York, N.Y., 1973, for a review.

Carbon-13 Chemical Shift Response to Substituent Effects in Arylmethyl and Arylhydroxy Carbenium Ions. Evidence for Substituent Interaction in Disubstituted Ions Depending upon the Carbenium-like Character at the Trigonal Carbon

B. Ancian, F. Membrey, and J. P. Doucet*

Laboratory of Physical Organic Chemistry, The University of Paris VII (Associated with CNRS), 75005 Paris, France

Received September 16, 1977

The interrelations between the ^{13}C NMR shielding effects of para substituents and electronic structure have been investigated in diphenylmethyl and diphenylhydroxy carbenium ions 1 and 2. The prime dependence of the ^{13}C shieldings upon π charge delocalization effects is established. It is shown that a general description of the chemical shifts, valid on all sites, requires using both π-electron density and π-bond order terms, as illustrated by the correlation obtained at ca. 120 ppm. While for the substituted ring carbons the SCS remain nearly the same as for neutral monosubstituted benzenes, the substituent shifts at C_α are increased by 2.7 in ions 1 as compared to 2, thus showing that electronic effects at this position are strongly dependent on the withdrawing power of the carbenium center (as confirmed by the unusually small effects of acceptor substituents). Nonadditivity of the C_α SCS in some 4,4′-disubstituted ions demonstrates the existence of important interactions between substituent electron effects. These interactions can be accounted for with the concept of a concerted π-inductive-mesomeric effect: the electron transfer from a substituent to the carbenium center depends upon the demand of this center and therefore upon all the other groups present. The susceptibility of the substrate to these interactions is estimated by a I_{XY} term (expressed with a $\sigma_X{}^+\sigma_Y{}^+$ product) and related to the carbenium character. Long range effects at the unsubstituted ring result from a π-inductive effect without π-electron transfer from the substituent. The C_α bridge acts only as a relay whose efficiency is directly related to the magnitude of its positive charge.

A great deal of attention has been focused over the last years on carbenium ions as they are key intermediates in many organic reactions. In this field, NMR spectroscopy, especially ^{13}C NMR, appears to be one of the most suitable techniques for a charge-delocalization investigation in cations,[1] although Brown[2a] and Kramer[2b] have pointed out that some problems may occur in relating ^{13}C shifts and carbenium ion stabilities. Much of the literature is devoted to the study of substituent effects on the chemical shifts of aryl carbenium ions for which the unusual stabilities have been ascribed to delocalization of positive charge throughout the π-electron system of the aromatic rings. Substituent chemical shifts[3] (SCS) have been chosen as a probe of the ability of groups to disperse the positive charge and have been compared to substituent parameters (generally Brown or Taft constants) deduced from solvolytic reactions in which the transition state is postulated to approximate the character of these ions.[4-6]

The relationships between shieldings and semiempirical MO have been extensively investigated by Olah et al.[7] The fact that, for carbons remote from the carbenium center, the π charge densities are as good as total charge densities in correlating the observed shifts is a definite proof that the dominant influences on screenings are π-system resonance and polarization interactions; moreover, the slope of their regression line[7a] is very close to the usual proportionality constant of 160 ppm/electron density obtained in a large variety of aromatic systems.[1,8] Farnum's point of view[1a] is slightly different, since he uses the total charge density with the questionable assumption of no charge dispersion to the hydrogens. Ray, Kurland, and Colter[5] have also shown that carbon chemical shifts in trityl cations are well correlated with CNDO/2 charges, whereas the crude HMO electron densities poorly reflect the trends. However, a great dispersion of quaternary ipso and α carbons can usually be observed, while an impossibility to describe all the shifts by a general expression using only electron density, whatever the carbons, is also evident.[2] This situation has prompted us to reexamine the possible contribution of other terms—like π-bond orders—to the carbon shielding in aryl carbenium ions. The important question of the additivity of substituent effects in ions is also open to challenge. If saturation of their electronic influences is now a fairly well-documented experimental phenomenon,[6,9-14] its interrelation with the extent of a positive charge at the relevant nuclei is not yet elucidated. Con-

Table I. Carbon-13 Chemical Shifts in Diphenylmethyl Carbenium Ions[a]

X	Y	Registry no.	C_α	C_β	C_1	C_2	C_3	C_4	$C_{1'}$	$C_{2'}$	$C_{3'}$	$C_{4'}$	Other carbons
H	H	16805-85-9	173.8	−23.3	86.8	87.1	77.2	92.70					
Och_3	H	60665-78-3	153.5	−26.2	80.1	92.6	65.31	125.5	85.9	81.1	76.1	84.9	OCH_3: 5.2
CH_3	H	41912-34-9	168.3	−24.2	84.9	88.2	79.0	111.5	86.7	85.2	76.9	90.1	CH_3: −30.0
F	H	56519-30-3	170.0	−23.5	83.3	91.5	65.75	121.1	86.6	86.1	77.1	91.8	
Cl	H	41912-38-3	170.9	−23.5	84.9	86.7	78.1	102.9	86.8	87.8	77.5	92.9	
CF_3	H	60665-79-4	178.0	−23.2	89.3	85.0	72.7	87.7	88.3	87.4	77.7	96.9	CF_3: 69.3
NO_2	H	60665-80-7	177.5	−22.8	93.5	87.3	70.6	100.3	88.1	91.6	77.9	97.7	
OCH_3	OCH_3	25836-80-0	148.0	−27.4	79.2	88.2	63.4	119.5					OCH_3: 3.8
CH_3	OCH_3	60665-82-9	152.8	−26.6	83.5	82.6	77.2	100.6	79.7	91.3, 95.8	64.4, 65.3	123.2	OCH_3: 4.5 CH_3: −31.6
CF_3	OCH_3	64999-88-8	149.4	−26.1	88.3	79.2	72.3	82.3	80.3	91.3, 95.9	63.9, 66.2	127.8	OCH_3: 6.0 CF_3: 69
NO_2	OCH_3	60065-83-0	146.5	−26.1	91.4	79.0	70.9	96.5	80.5	92.0	67.9	129.6	OCH_3: 6.7
CH_3	CH_3	41912-36-1	164.7	−25.1	84.5	86.5	78.3	107.4					
F	F	39769-49-8	166.4	−23.8	83.2	90.5	65.7	120.5					
Cl	Cl	41912-40-7	167.5	−23.9	84.6	87.1	78.1	102.2					
Br	Br	64999-89-9	167.9	−23.8	85.0	86.5	81.3	93.2					
CF_3	CF_3	60665-81-8	184.8	−21.7	89.5	88.0	73.8	91.6					CF_3: 69.2

[a] Positive downfield values in ppm from internal CH_2Cl_2.

versely, the extent of the dependence of the electronic power of a given substituent with the electron deficiency at the carbenium center is not yet clear. In a ^1H NMR work on diarylmethyl carbenium ions[6] we have anticipated such a dependence of substituent–substituent interactions upon the electron demand by the deficient system, an early recognized fact for successive methyl substitution at a carbenium center.[15,16]

In view of these problems, a comparison of charge delocalization in a number of systems with distinct demands for electron stabilization is needed. Substituted diphenylmethyl and diphenylhydroxy carbenium ions have been chosen, as these two families have closely similar geometry and electronic structure, but the methyl and hydroxy groups clearly generate distinct electron demand at the carbenium center. The data are discussed with respect to INDO charge densities and compared with literature results on like ions. In an attempt to clarify the origin of nonadditivity, we also wished to analyze substituent–substituent interactions in these two disubstituted families with particular emphasis on their dependence upon the electron demand by the carbenium center. An electronic effect transmission from the substituted ring to the other via the positive trigonal carbon will also be examined.

Experimental Section

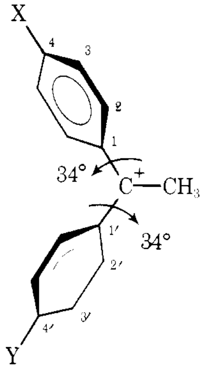
Preparation of Ions. All the carbenium ion samples were formed directly in a 10-mm o.d. Wilmad NMR tube at ca. 0.5 mol/L in three distinct media depending upon the studied ions. Most of the diphenylmethyl carbenium ions **1**—except when attracting groups substitute the aromatic ring—were formed from a 2-mL CD_2Cl_2 solution of the olefin precursor by slowly adding about 0.2–0.3 mL of FSO_3H at −50 °C (method a). As we observed that diphenylmethyl carbenium ions with attracting substituents (NO_2,CF_3) are not stable in CD_2Cl_2 solutions, they were generated by dissolving the proper olefin into FSO_3H at −50 °C (method b). Owing to the greater basicity of the carbonyl group, the more stable diphenylhydroxy carbenium ions **2** were prepared by protonation of substituted benzophenones in 98% H_2SO_4 at room temperature (method c), except for the mono- and dinitro-substituted ions which were obtained by method b. Complete protonation of benzophenone was checked by a study of its cation generated by both methods b and c.

Carbon-13 Nuclear Magnetic Resonance Spectra. The carbon-13 NMR spectra were recorded at 25.03 MHz on a JEOL PS-100 spectrometer equipped with a PFT-100 Fourier transform system, JEC-100 computer, ^2D field frequency lock, and noise-modulated proton-decoupling system. The observed free-induction decay after a 30° pulse width of 9 μs was sampled in 8192 data points with a spectrum width of 6250 Hz and a repetition time of 2 s (digital resolution 1.53 Hz). Either a deuteron signal from internal CD_2Cl_2 (method a or c) or an external 4-mm o.d. CD_2Cl_2 tube held concentrically inside the standard 10-mm tube (method b) was employed for the locking signal, depending on the three distinct media used in the preparation of ions. All spectra were run in the complete noise-decoupling mode.

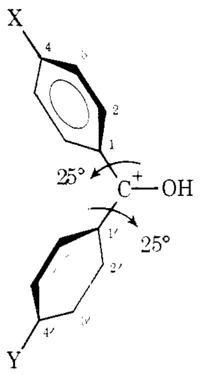
In methods a and c, chemical shifts were measured from 0.2 mL of internal CH_2Cl_2 dissolved in the solution; in method b, they were obtained from external CH_2Cl_2 contained inside the 4-mm o.d. CD_2Cl_2 tube and were corrected for the bulk magnetic susceptibility using the experimentally determined conversion factor $\delta_{\text{internal } CH_2Cl_2/\text{external } CH_2Cl_2} = -0.80$ ppm. Spectra of diphenylmethyl carbenium ions **1** were recorded at −30 °C, whereas the more stable protonated benzophenones were studied at room temperature. No significant temperature dependence of the chemical shifts was observed in this range. Minor solvent effects are also apparent from an examination of some spectra obtained by each method a, b, or c, and from a comparison of our results on unsubstituted cations with Olah's data.[17]

Results

The ^{13}C chemical shifts of substituted diphenylmethyl carbenium **1** and of substituted diphenylhydroxy carbenium ions **2** are respectively listed in Tables I and II. Specific peak assignments were made primarily by analogy with SCS on substituted benzenes[18] and protonated benzaldehydes and acetophenones.[17b] Typically, ortho and meta carbons can be distinguished from other resonances by a consideration of the relative peak intensities involved in the nuclear Overhauser



1



2

1a, **2a**, Y = H; X = OCH_3, CH_3, F, Cl, H, CF_3, NO_2
1b, **2b**, Y = X = OCH_3, CH_3, F, Cl, H, CF_3, NO_2
1c, **2c**, Y = OCH_3; X = OCH_3, CH_3, H, CF_3, NO_2

Table II. Carbon-13 Chemical Shifts in Diphenylhydroxy Carbenium Ions[a]

X	Y	Registry no.	C_α	C_1	$C_{2(6)}$	$C_{3(5)}$	C_4	$C_{1'}$	$C_{2'(6')}$	$C_{3'(5')}$	$C_{4'}$	Other carbons
H	H	16805-82-6	154.3	75.7	82.5	76.7	88.1					
OCH_3	H	10472-80-7	147.0	67.9	87.6	63.3	118.8	76.3	80.0	76.3	85.3	OCH_3: 3.6
CH_3	H	64999-75-3	152.1	72.9	83.4	77.8	103.7	75.9	81.1	76.4	87.1	CH_3: −31.4
F	H	64999-76-4	152.2	72.1	86.6	64.7	117.8	75.6	81.7	76.6	87.7	
Cl	H	64999-77-5	153.0	74.0	83.8	77.3	96.5	75.6	82.0	76.8	88.2	
Br	H	64999-78-6	153.4	74.5	83.4	80.5	86.3	75.7	82.1	76.9	88.4	
CF_3	H	64999-79-7	154.9	79.2	81.6	73.2	86.2	75.5	83.2	77.0	89.7	
NO_2	H	64999-80-0	154.6	82.1	81.8	71.1	98.5	75.7	83.4	77.2	90.5	
OCH_3	OCH_3	10487-81-7	143.5	68.7	85.1	62.7	115.8					OCH_3: 3.3
CH_3	OCH_3	10487-82-8	146.2	73.3	81.0	77.4	100.0	68.2	86.7	63.0	117.6	OCH_3: 3.5; CH_3: −31.8
CF_3	OCH_3	64999-81-1	145.5	79.2	79.2	72.9	84.1	67.5	88.2	63.9	120.6	OCH_3: 3.8
NO_2	OCH_3	64999-82-2	143.7	82.6	79.7	71.2	97.4	65.5	88.6	64.2	121.6	OCH_3: 4.1
CH_3	NO_2	64999-83-3	151.3	72.7	84.5	78.5	107.6	82.2	81.2	71.2	98.3	CH_3: −30.8
NO_2	NO_2	64999-84-4	157.4	81.2	84.0	71.7	100.0					
F	F	64999-85-5	150.3	72.1	85.9	64.7	117.5					
Cl	Cl	39787-21-8	151.7	74.1	83.4	77.5	96.6					
CH_3	Cl	64999-86-6	150.7	72.8	82.9	77.8	103.9	74.2	82.9	77.1	95.0	CH_3: −31.3
CH_3	CH_3	64999-87-7	150.5	73.1	82.5	77.6	102.1					CH_3: −31.5

[a] Positive downfield values in ppm from internal CH_2Cl_2.

enhancement. In some cases, assignments were also aided by running off-resonance decoupled spectra, which allowed differentiation of carbons bearing hydrogens.

Ortho and meta carbon nonequivalence,[7,17,19] as well as syn–anti isomerism in protonated benzophenone,[20] was generally not observed here because at the experimental temperature $C^+–C_{ipso}$ and $C^+–OH$ rotations are still fast in view of the NMR time scale. Among all the ions, the only two exceptions to this nonequivalence occur in ions **1c**, where X = CF_3 and NO_2; this is because of an increased electron demand by the carbenium center, which in turn reduces the free rotation about the $C^+–C_{ipso}$ bond of the anisyl ring.[7a]

All valence electron MO calculations were performed using the INDO method with the standard parametrization of Pople et al.[21] INDO approximation was preferred over CNDO/2, since it is known to give results as good as with ab initio STO-3G approach in cations.[22] Unless otherwise stated, standard bond lengths and angles as recommended in ref 21a, page 111, were used; this is a current trend in electronic structural studies of ions for which reliable experimental geometries are not available.[7,16] Moreover, we think that this choice has the merit of providing a consistent basis for comparison of charge delocalization in substituted families 1 and 2.

Owing to their structural analogy, diphenylmethyl and diphenylhydroxy ions can be predicted to have extremely similar conformations, i.e., symmetrical propeller conformations with two equally twisted aryl rings in respect to the nodal plane of the carbenium center.[6,10a] The geometry of ions 1 which has been determined in an earlier ^1H NMR work was retained without further modifications.[6] But a less stringent sterical hinderance between ortho positions in benzophenones has been postulated,[23] so that a twist angle of only 25° was assumed for the aryl rings and 1.47 Å was chosen for the bond length $C_1–C_\alpha$ to allow for an increase in conjugation between the phenyls and the positive carbon. Since only minor conformational changes occur with substituent changes, the geometry of ions 1 and 2 was held constant and independent from the electronic power of substituents.[6,10a] The value of 1.27 Å obtained by Ros[24] in a nonempirical calculation of protonated acetaldehyde was used. This distance just lies between the standard values of 1.36 (C–O bond) and 1.22 Å (C=O bond). Syn–anti positions of the hydrogen bonded to the oxygen were considered in our calculations on ions **2**, but only the average values of the results were used and reported in Table V (supplementary material).

Discussion

(1) Expression of Carbon Chemical Shifts in Aryl Carbenium Ions. There is now considerable evidence that carbon screenings are dominated by charge-polarization effects,[1,7,8,16,25] so carbon shifts can be expected to constitute a quite sensitive probe for understanding charge distribution and substituent effects in aryl carbenium ions. This point will be first studied by a comparison of the carbon shifts in Tables I and II with π-electron parameters derived from INDO-MO calculations.[26] Rather than examining the correlation trends for certain types of carbons, leading to distinct correlations of variable slopes without physical justification of these variations, a general fit was sought for all carbons: systematic deviations would then be attributed to specific influences or properties of the relevant positions. This approach also allows charge-distribution effects to be separated from other factors.

From the carbon shifts (Tables I, II) and π charge densities (Tables IV and V, supplementary material) a rough correlation is observed for all the positions of ions **1a, 2a** (except where X = OCH_3) and **1b, 2b** (eq 1).

$$\delta = -(173 \pm 6)q_\pi + 256 \quad (r = 0.943;\ SD = 9.8). \qquad (1)$$

Ions **1a, 2a** (where X = OCH_3) and **1c, 2c** have been excluded, since we previously showed the failure of the INDO method to correctly describe the charge delocalization induced by a methoxy group in some methoxyaryl-substituted ions.[28]

The major deviations are observed for α and substituted carbons (C_1 and C_4), a not unusual comportment given the important structural change they undergo (hybridization, substitution, neighboring effects).[1b,7,16] A great improvement is obtained by inclusion of the bond order term according to the Karplus–Pople evaluation of the dominant paramagnetic terms in carbon screening.[29] Using π charge densities and the sum of the π-bond orders with adjacent carbons, since non-nearest-neighbor terms contribute very little (<2%) and can be omitted,[29-30] in a linear least-squares analysis, eq 2 is obtained

$$\delta = -(207 \pm 4)q_\pi + (72 \pm 4)p_\pi + 187 \quad (r = 0.984;\ SD = 5.3) \qquad (2)$$

Equation 2 leads to a much better agreement with the observed shifts, particularly for the nonhydrogenated ipso carbons (which have a largely different bond order than those of the tertiary ortho, meta, or para carbons) and appears very satisfactory in view of the covered scale (i.e., 122 ppm for 122 points). Such an agreement is further proof of the generality of the relationships between carbon-13 shifts, π-electron density, and π-bond order.[30] It also establishes that carbon-13 SCS in diphenylmethyl or diphenylhydroxy carbenium ions can definitively be used as a probe of charge delocalization induced by substituents onto distinct carbons.

(2) SCS in Diphenylmethyl and Diphenylhydroxy Carbenium Ions. Although the greatest SCS are observed at the cationic center, other valuable information can be obtained by examination of ring carbons. It is thus interesting to examine SCS with great emphasis on each type of carbon. Due to the strong interactions between the two substituents in para, para′-disubstituted ions, and in an attempt to clarify the causes and origins of such interactions, the discussion will unfold as follow: (i) the substituted aromatic ring of monosubstituted ions **1a** and **2a,** (ii) the α-carbon of mono- and disubstituted ions **1** and **2,** and (iii) the unsubstituted aromatic ring of monosubstituted ions **1a** and **2a.**

(i) Substituted Aromatic Ring of Ions 1a and 2a. In these ions, SCS are very small at C_2 but greater at C_1 and C_3 (as expected from the crude scheme of resonance) and greater at the C_4-substituted carbon.

The agreement between the shifts calculated by eq 2 and the experimental results is quite good for the C_1 para carbons, but nonnegligible deviations (~5 ppm) are observed for the C_4-substituted carbons and, to a lesser extent, for C_3 ortho carbons. Indeed, this fact is not surprising and was also noticed in correlations between carbon-13 shifts and π (or total) electron densities in substituted benzenes[18,30c] and aryl carbenium ions.[1,5,7] The better agreement for C_1 para carbons has been rightly attributed to the predominance of electronic effects over secondary effects in their shieldings, whereas this is not as true at the C_4 and C_3 positions for which neighboring and magnetic anisotropy effects are important. INDO calculations reveal that π-bond orders of other positions are nearly insensitive to the substituent in contrast to C_4 carbons for which large variations of the X–C_4 π-bond order term are observed. As a result, the neglect of the π-bond order contribution in the usual simplified δ vs. q_π (or q_t) correlations on the substituted benzenes[7,18] can partially explain the shift of the two regression lines of the substituted and para carbons; small deviations of ortho and meta points from the line of the para carbons also certainly originate[7,18] from such a neglect. Inclusion of the π-bond order allows the most general comparison between distinct families of substituted derivatives, e.g., benzenes or other neutral aromatic compounds and aryl carbenium ions. A good linear relationship with a slope near 1 is obtained when all the SCS of the substituted aromatic ring of ions **1a** are correlated with those of ions **2a.** A similar relationship has also been observed with the analogue carbons of substituted protonated benzaldehydes and acetophenones[31] and even, to some extent, with the substituted benzenes[1c,18] from which substituent parameters are often defined by workers. The only apparent deviations are for the C_4-substituted carbons. This means that, except for the C_4 positions, the various groups para to the substituent X [i.e., $-C^+(CH_3)C_6H_5$, $C^+(OH)C_6H_5$, C^+HOH, $C^+(CH_3)OH$] do not significantly perturb the SCS on the substituted aromatic ring with respect to the substituted benzenes and are independent of the specific electron demand by the relevant group.

However, these conclusions break down in the case of the C_4 points for which nonconstancy of the SCS is clear [e.g., 7.6 ppm for ion **1a** (X = NO_2) and 10.4 ppm in **2a** (X = NO_2)], while a shift of 20 ppm is observed from the nitrobenzene; other substituents give smaller variations. The nonconstancy in the SCS of the C_4 points was attributed either to a modulation of the σ-electron density at C_4 by the π-polarization of the group para to X[32] or to local variation in the excitation energy.[33] Nevertheless, the fact that the C_1 points of ions **1a** and **2a** are well correlated seems contradictory to the first explanation but rather in agreement with the hypothesis of a local variation in the excitation energy. Indeed, the SCS at the C_1 carbons in ions **1a** and **2a** are well described by a Taft dual-substituent parameter analysis[34] [eq 3 and 4 respectively], using the $\sigma_R°$ resonance parameters instead of the σ_R^+ set:

$$\delta_{C_1} = 86.8 + 5.5\sigma_I + 18.6\sigma_R° \ (r = 0.992;\ SD = 0.7) \qquad (3)$$

for ions **1a** and

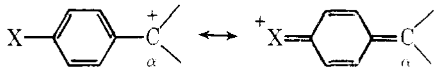
$$\delta_{C_1} = 75.4 + 6.7\sigma_I + 20.0\sigma_R° \ (r = 0.994;\ SD = 0.6) \qquad (4)$$

for ions **2a.**

Despite the strong electron demand by the carbenium center which can be expected to increase electron transfer from the substituent by resonance, the effects at the C_1 carbons do not increase, since the $\sigma_R°$ set works better than the σ_R^+ set. Furthermore, the susceptibilities to inductive and resonance effects are nearly identical with those reported for substituted benzenes, i.e., 5.7 and 21.2, respectively.

(ii) Substituent Effects at C_α. Examination of the SCS induced at C_α in both series of 4-substituted ion **1a** and **2a** shows that the electron-releasing groups generate major upfield shifts, as they can attenuate the electron deficiency at C_α (20.3 and 7.4 ppm, respectively, for the 4-OCH_3 ions **1a** and **2a**). In contrast, the variations remain small with electron-withdrawing groups (for NO_2: 4.2 and 0.4 ppm). These results are strikingly different from the substituent effects observed in parent neutral molecules;[31] as shown by various examples[35] for such carbons in the α position with respect to a phenyl ring in conjugated systems, the SCS remain small and inverted in accordance with Pople's prediction of as alternation of charges,[21a] while the essential part of the influences is developed at C_β.

The exaltation of effects for releasing groups is consistent with an important transmission of substituent influences by conjugative π-resonance interaction between donor X groups



and the carbenium center, since this "through conjugation" increases in importance because of the greater electron demand at C_α.

More puzzling are the small influences of acceptor groups, particularly in view of the fact that these groups are quite effective at C_1. This is illustrated in Figure 1 where C_α has been plotted vs. C_1 for ions **1** and **2;** thus, while the chemical shifts are proportional for releasing substituents, discrepancies are evident for the attracting NO_2 and CF_3 groups. This minor importance of withdrawing groups on the C_α shifts can be interpreted by the decrease of mesomeric interactions between, for instance, the 4-NO_2-substituted phenyl ring and C_α. This decrease little affects the electron density at this position inasmuch as it can be balanced by a further release from the other fragments bonded to C_α, i.e., the second phenyl ring or the OH group. In accordance with this scheme, it may be observed that the substituent shifts of the CF_3 or NO_2 groups are quite small for protonated benzophenones, where the carbonyl oxygen can conjugate the C_α empty orbital, whereas for enium ions (where hyperconjugative donation from Me is limited), these groups are more efficient. However, such an analysis would indicate more important C_α shifts in styryl or cumyl cations where no group can accommodate the

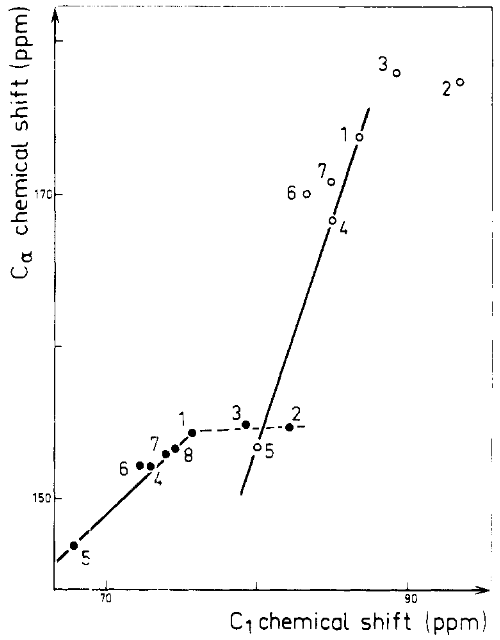


Figure 1. Plot of C_α chemical shifts vs. C_1 chemical shifts: (○) diphenylmethyl carbenium ions, (●) diphenylhydroxy carbenium ions. See ref 52 for the meaning of the numbers.

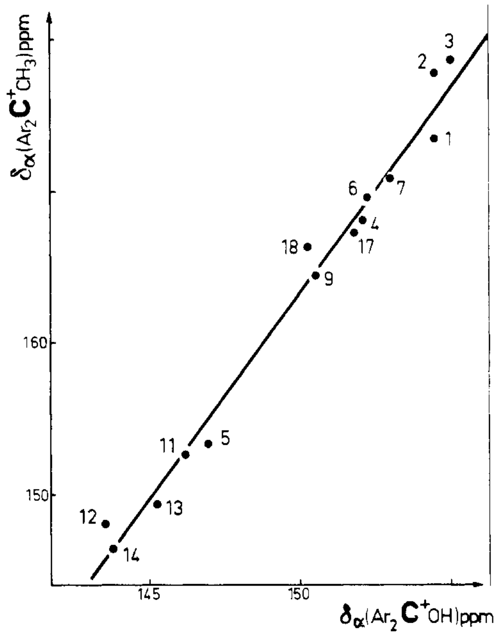


Figure 2. Plot of ^{13}C chemical shifts at C_α in diphenylmethyl carbenium ions **1** vs. ^{13}C chemical shifts at C_α in diphenylhydroxy carbenium ions **2**. See ref 52 for the meaning of the numbers.

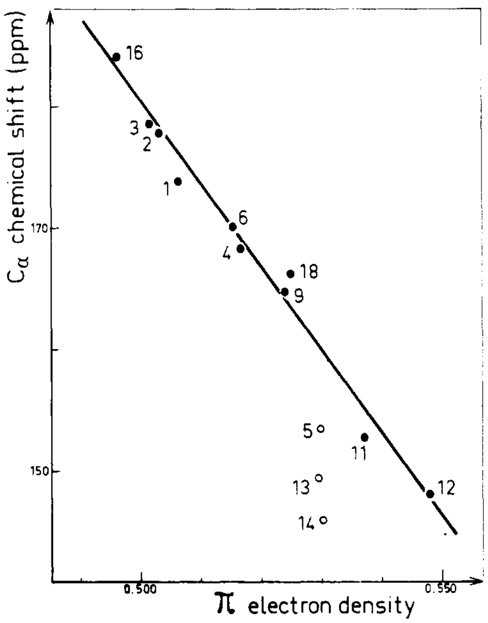


Figure 3. Plot of δ vs. INDO π-electron density for C_α in substituted diphenylmethyl carbenium ions (δ ppm downfield from internal CH_2Cl_2). Points noted (○) are excluded from the correlation; cf. text. See ref 52 for the meaning of the numbers.

positive charge. The available data (4-CF_3-cumyl cation[4c]) suggest a slightly greater shift than expected from a comparison with diphenylmethyl carbenium ions or protonated acetophenones, in accordance with our point of view. INDO calculations on substituted styryl ions also indicate a slightly increased effect for a NO_2 group on the C_α π-electron density with respect to that estimated for ions **1**. This unusual response pattern to substituent effects is clearly exemplified when one attempts to correlate the C_α shifts with the Brown σ^+ constants of the X groups,[36] which have led to some success in the interpretation of the α-carbon shifts of styryl,[4a] cumyl,[4a] or trityl[5] cations. Our results show, however, that, although this is valid for donor groups, any attempt to correlate all the data (including halogens or acceptors) has failed.[37]

Another important point is that the observed trends are very similar in the two families, as illustrated in Figure 2 by the good linear correlation obtained for 14 points, including disubstituted ions, by plotting δC_α in ions **1** vs. the corresponding values in ions **2**[38] (eq 5).

$$\delta_{C_{\alpha(1)}} = (2.7 \pm 0.1)\delta_{C_{\alpha(2)}} - 250 \; (r = 0.993;\ SD = 1.33) \quad (5)$$

The slope, which is much greater than 1, indicates that the sensitivity to substituent perturbations is greater for diphenylmethyl carbenium ions. This is consistent with a more developed carbenium character in **1**, where the positive charge can only be partly delocalized on the phenyl rings, whereas in protonated benzophenones the carbonyl oxygen can accomodate some fraction of this charge; i.e., the greater the electron demand at C_α, the greater the π interactions between this position and the releasing groups through the phenyl ring, and therefore the greater the sensitivity of C_α to substituent effects.

Turning now to eq 2, it appears that the INDO method gives a fairly good estimation of the shifts, although the deviations are larger than for the other positions. Such a general representation (although of prime interest to confirm that the δ are a good experimental probe of electron distribution) is not the best suited one for an accurate investigation of substituent shifts on a given position where the immediate environment of the carbon remains constant. So, for a discussion restricted to the C_α position, for the series of ions **1** or **2**, a simplified δ vs. q_π plot is very convenient (insofar as the variations of the p_π and q_π terms are proportional). As seen in Figures 3 and 4, good correlations are also obtained (eq 6 and 7) for all disubstituted ions except ions **1b** and **2b**, where X = CF_3, and **1c** and **2c**, where X = H, CF_3 and NO_2:
for ions **1**:

$$\delta_{C_\alpha} = -(677 \pm 38)q_\pi + 519 \; (r = 0.987;\ SD = 1.8) \quad (6)$$

and for ions **2**:

$$\delta_{C_\alpha} = -(528 \pm 18)q_\pi + 481 \; (r = 0.995,\ SD = 0.12) \quad (7)$$

Nevertheless, the slopes are far higher than the commonly accepted value (~170 ppm/electron), suggesting that the INDO method underestimates substituent-induced charge

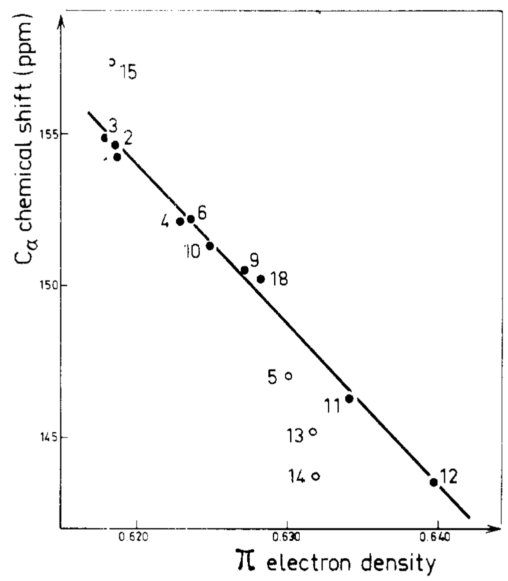


Figure 4. Plot of δ vs. INDO π-electron density for C_α in substituted diphenylhydroxy carbenium ions **2**. The symbols are the same as in Figure 5. See ref 52 for the meaning of the numbers.

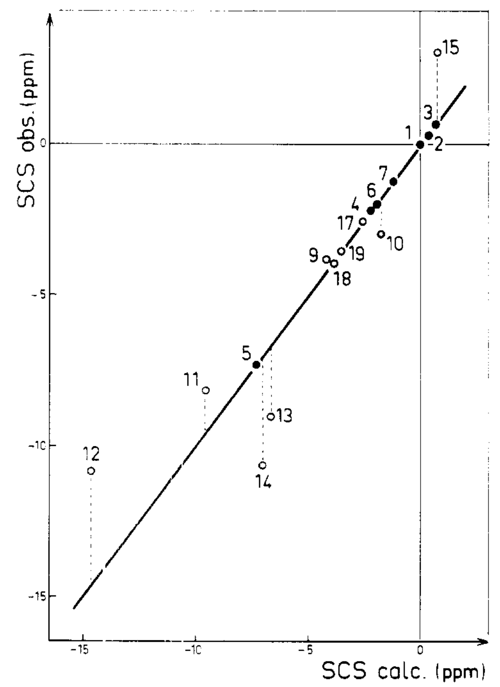


Figure 5. Deviations to additivity of substituent shifts in ions **1**: plot of observed SCS for disubstituted ions **1b** and **1c** (○) vs. calculated values assuming additivity of the SCS observed in monosubstituted ions **1a** (negative SCS correspond to upfield shifts). To provide a scaling of the deviations observed when interactions appear, SCS observed in monosubstituted ions have also been plotted (●): by definition they lie on the theoretical line of unit slope. See ref 52 for the meaning of the numbers.

variations at C_α, whereas it correctly reflects the perturbations induced on C_1 (the neglect of the p_π term, whose variations counteract those of q_π, is certainly quite insufficient to account for these discrepancies). These shortcomings suggest that the method does not equally scale the perturbations at the various carbons. Streitwieser[27a] has already pointed out that CNDO calculations bear similar limitations when comparing electron-density changes in polycyclic aromatic ions and in substituted benzyl cations. Larsen and Bouis[39] have also noted an unusually high slope in correlating ^{13}C NMR shifts of benzoyl cations with CNDO charges and have questioned the validity of the CNDO method to accurately express substituent effects in charged species. An alternate explanation would be that the proportionality constant between δ and q_π may be different for C_α and the phenyl carbons; indeed, the possibility of local distortions to the excitation energy has been proposed by Karplus and Pople.[29b] The deviations appearing for ions bearing OCH_3 substituents are very important to the understanding of substituent interactions and will be the topic of a subsequent discussion after an examination of SCS in disubstituted ions.

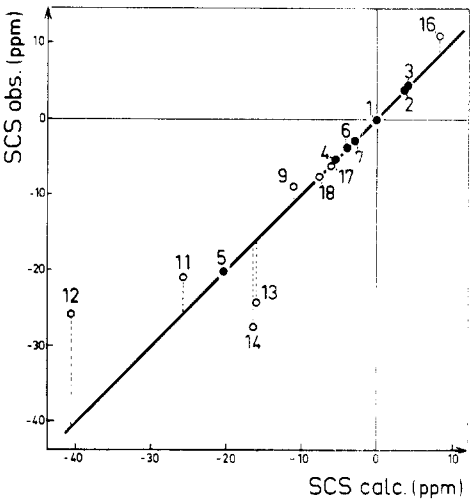


Figure 6. Deviations to additivity of substituent shifts in ions **2**. The symbols are the same as in Figure 7. See ref 52 for the meaning of the numbers.

Substituent–Substituent Interactions in Some Disubstituted Compounds. The SCS observed at C_α for 4,4′-disubstituted ions can be approached by referring to the corresponding shifts in monosubstituted derivatives. This is illustrated in Figures 5 and 6 where we have plotted the δ measured vs. the δ calculated by assuming an additivity of the shifts derived from monosubstituted ions. When this hypothesis of additivity works, the points do fall on lines of unit slopes obtained from the unsubstituted ions **1a** and **2a**. This is indeed observed for groups F, Cl, and CH_3, i.e., groups with weak electronic effects. However major discrepancies are noticed when a strongly conjugating group (like OCH_3) is present: deviations are downfield when the other group is also an electron donor but upfield with a second attractor group (as in 4-OCH_3,4′-NO_2 ions) thereby corresponding to shifts larger than expected, a so-called "exaltation effect". In the same way, downfield deviations are also observed with the electron-withdrawing substituents, i.e., CF_3 and NO_2.

Among the most striking features of these plots, it can be noticed that the 4-OCH_3,4′-NO_2 and the 4-OCH_3,4′-OCH_3 ions roughly correspond to the same δC_α value (143.5 and 143.7 for ions **1c**; 148.0 and 146.5 for **2c**), an evidently surprising fact meaning that NO_2 and OCH_3 would both induce a shielding variation of comparable magnitude on C_α. It can be also seen, going from the monosubstituted ion **1a** to its 4-OCH_3 and 4,4′-dimethoxy derivatives, that the second OCH_3 group exerts on C_α a shift of −5.5 ppm, whereas the first methoxy substitution corresponds to a shift as large as −20.3 ppm. These results extend and substantiate our earlier conclusions[6] derived from the ^1H NMR study of ions **1** where nonadditivity of the β-proton diamagnetic shifts was observed between the diphenylmethyl carbenium ions and its mono and dimethoxy derivatives. This result is in clear contrast with the additive behavior of the shifts in the parent neutral 1,1-diphenylethylenes.[40]

Inasmuch as variations of geometry remain small, whatever the para substituents,[6] the origin of these deviations must be understood in terms of electronic effects. The remark that deviations to additivity appear larger in methyl carbenium ions **1** than in hydroxy carbenium ions **2**, where the electron demand at C_α is reduced, as well as the fact that there is additivity in neutral parents suggest that the extent of electron deficiency at the α-carbenium center is a determining factor in these effects. All of these results lead to the concept that π-electron transfer by a substituent to a carbenium empty orbital is not an intrinsic characteristic of the group but, on the contrary, that it depends on the electron demand of the positive center and therefore on the electronic power of all the other substituents already present. These mutual perturbations in the influences of substituent groups can be accounted for by the Mulliken and Godfrey concepts of π-inductive mesomeric-concerted action.[41,42]

The electron-releasing power of a group such as OCH_3 may be divided into two parts: a mesomeric charge-transfer donation bringing π electrons from the substituent to the conjugated system and a π-inductive effect I_π which redistributes the electrons in the conjugated system without any neat transfer from the substituent. According to the Mulliken and Godfrey points of view, the electron transfer depends upon the I_π effects of all the other substituents; it decreases, for instance, when the I_π effects of the other groups increase.

The existence of such substituent–substituent interactions based on the concept of a concerted π-inductive mesomeric action has been previously demonstrated by the works of Taft et al.[13] or Freedman et al.[10,43] Taft and McKeever[13c] have shown that the donor effects of 4-OCH_3 and $N(CH_3)_2$ on the stabilization energy of trityl anions are nearly the same, while in successive NO_2 substitutions a saturation of electronic influences appears. Conversely, for the stabilization energies of substituted trityl cations, a similar saturation occurs with donor groups.[13b] Saturation is also evident in the ^{19}F NMR spectra of 4-F trityl cations bearing two OCH_3 or $N(CH_3)_2$ groups.[13b] Moreover, Freedman et al.[43] have shown that in para′-substituted *p*-dimethylaminotrityl cations the rotational barrier about the N–aryl bond is substituent dependent and is related to π delocalization: the π bond order and the extent of the electron transfer from $\overline{N}$ to the ring are weakened if the releasing power of the others groups is greater.

The existence of these two π effects is largely illustrated by our results. For example, regarding the 4-OCH_3,4′-OCH_3 ions **1b** and **2b**, it can be ascertained that the strong I_π effect of each methoxy opposes an appreciable electron migration from the other OCH_3. This is felt to be an overall reduction of the electron transfer attributed to each methoxy group as compared to the transfer taking place in the monosubstituted 4-OCH_3 ions **1a** and **2a**. Such a saturation of donor influences does not occur in the disubstituted ions bearing F, Cl, or CH_3 substituents: the π interactions of these groups with the carbenium center act mainly via an I_π effect for which additivity undoubtedly occurs. Conversely, an electron-withdrawing group such as CF_3 or NO_2 exerts an I_π effect which, if a strong releasing substituent is present, leads to an increased electron migration from this last group to the C_α empty orbital: thus, a 31-ppm upfield shift appears from ion **1a** (X, NO_2) to **1c** (X = NO_2) as compared to the 20.3-ppm upfield SCS of ion **1a** (X = OCH_3).

The same type of arguments can be invoked to explain the sequence of the shifts in the 4-NO_2,4′-NO_2 ion and in the 4-NO_2 and the unsubstituted ion **2**. The small mesomeric effect of the NO_2 group in the monosubstituted ion results from an increase in the electron migration from the unsubstituted ring to the α-carbon, as evidenced by large SCS on this ring (see Tables I and II); in contrast, the greater variations between the di- and mononitro ions **2** correspond to an increased effect in the disubstituted ion, since the attracting influence of the NO_2 group cannot now be counterbalanced by any other donating mesomeric effect at the C_α; then, the overall effect of the two NO_2 groups in ions **2b** appears as more than twice the effect of one NO_2 group in ion **2a.**

Table III. Interaction Term I_{XY} (ppm)

Ions	OCH_3, OCH_3	OCH_3, CH_3	OCH_3, CF_3	OCH_3, NO_2	CH_3, NO_2	CH_3, CH_3	NO_2, NO_2	CF_3, CF_3
1	14.8	4.8	−8.3	−10.7		3.9		2.6
2	3.8	1.4	−2.3	−3.6	1.1	0.6	2.5	

Another confirmation of the proposed interpretation is based on the observation of the magnetic nonequivalence of the 2′,6′ and 3′,5′ positions in the spectra of ions **1c** where X = NO_2 and CF_3, whereas only time-averaged spectra are recorded at the same temperature for ions **1c** where X = H and OCH_3. As already evidenced by other authors in similar aryl carbenium ions,[7a,10,19,43] the height of the rotational barrier of the C_α–C_1 bond in ions **1c** or **2c** is substituent-dependent: the greater the attracting effect of the X group, the greater the electron donation by electron transfer from the OCH_3 group to the C_α and thus the greater the π-bond order and rotational barrier of the C_α–C_1 bond. However, as already pointed out, the π charge at the α-carbon of ions **1** is clearly greater than in the analogue ions **2** because of the mesomeric electron donation by the oxygen in the latter. Therefore, π-electron demand from the aryl rings for stabilization is smaller in ions **2** and leads to a smaller rotational barrier for the C_α–C_1 bond in ions **2** than in ions **1**; the time-averaged magnetic equivalence for the two ortho and meta anisyl ring carbons in the range −50 to +25 °C substantiates this interpretation.

Definite proof for this dependence of π-electron transfer from a methoxy group upon the electronic structure of ions can be gained by examination of the chemical shifts of the OCH_3 carbons in ions **1c** and **2c.** With respect to the parent monosubstituted 4′-OCH_3 ions, the downfield shifts observed in the disubstituted 4-NO_2,4′-OCH_3 ions (1.5 ppm for **1c** while 0.5 ppm for **2c**) as well as in the disubstituted 4-CF_3,4′-OCH_3 ions (0.8 ppm for **1c** while 0.2 ppm for **2c**) also suggest an increased π-electron transfer from the methoxy when the more attracting groups are present. In contrast, Tables I and II show a reverse trend in the case of disubstituted 4-CH_3,4′-OCH_3 and 4-OCH_3,4′-OCH_3 ions **1c** and **2c,** i.e., an upfield shift of the methoxy group.[44] Moreover, INDO π-electron densities on the oxygen atom (Tables IV and V, supplementary material) parallel the methoxy carbon shifts in ions **1c** and **2c,** and a rough correlation between these two quantities can be obtained ($m = -308 \pm 46$; $i = 576 \pm 85$; $r = 0.922$; $s = 0.5$).

A quantitative description of these substituent–substituent interactions has been carried out by considering the interaction terms I_{XY}. These terms, listed in Table III, are defined in the 4,4′-disubstituted ions as the deviations to a strict additivity of the SCS corresponding to the monosubstitution:

$$I_{XY} = (\delta_{X,Y} - \delta_{H,H}) - [(\delta_{X,H} - \delta_{H,H}) + (\delta_{Y,H} - \delta_{H,H})]$$

where $\delta_{X,Y}$ is the C_α chemical shift in the 4-X,4′-Y ion.

From the above discussion it results that I_{XY} would depend on the charge-transfer effect of the substituent and on its I_π effect which both modulate the transfer from other groups. Before making an accurate separation of these contributions, the success of the models that we have previously proposed to traduce substituent–substituent interactions in the bromination rate constants of polysubstituted benzenes[12b] and in the protonation equilibrium constants of polysubstituted benzophenones[12c] leads us to use an σ^+ representation as an exploratory tool. With a symmetrical model, chosen so as not to introduce an artificial dis-

tinction between the substituents, we obtained for the interaction term:[45]
ions **1**:

$$I_{XY} = 20.4\sigma_X{}^+\sigma_Y{}^+ + 0.9\ (r = 0.989;\ SD = 1.3) \qquad (8)$$

ions **2**:

$$I_{XY} = 5.8\sigma_X{}^+\sigma_Y{}^+ + 0.1\ (r = 0.996;\ SD = 0.2) \qquad (9)$$

Although the use of σ^+ constants is certainly an oversimplification, these correlations appear to give a quite satisfactory evaluation of substituent–substituent interactions on the ^{13}C chemical shifts. Since the coefficient of the $\sigma_X{}^+\sigma_Y{}^+$ term depends only on the structure of the substrate, no matter what the substituents,[46] it may be considered as an estimation of the sensitivity to these interactions and would thereby permit discussing the variations of the sensitivity in connection with the electronic structure of the ions. From the first results obtained here, it is suggested that (for systems of similar geometry) this sensitivity increases with the interactions of the substituted phenyl rings with the carbenium center, i.e., with the electron demand on this position.

As anticipated in our earlier work,[6] Figures 5 and 6 clearly indicate that the INDO method fails in describing the strong π-electron releasing effect of the OCH_3 in the ions **1c** where X = H, CF_3 and NO_2, while it is adequate for ions **1c** and **2c** where X = OCH_3; the CNDO/S approximation[28] is not more successful. On these grounds, we have invoked[6] some inadequacies in the standard parametrization of resonance integrals or atom valence-state ionization potentials. However, we have seen before that π-electron densities at the substituted ring carbons are always well pictured by INDO calculations, a fact which apparently seems contradictory to this assertion. Actually, π-electron density at the substituted ring carbons is mainly developed by π-inductive and polarization effects without important electron transfer from the substituent, whereas the charge at the positive α-carbon is favored by a possible electron migration from the substituent into the empty $2p_z$ orbital; in this last event, it is clear that the adequacy of the C_1–C_α bond is crucial to a good picture of the charge transfer to the aromatic ring. The similar trends in SCS of anisole and ions **1a** and **2a** where X = OCH_3 (see above) give further evidence of the predominance of π-inductive and polarization effects at the anisyl ring carbons, whatever the electron demand by the α-carbon may be. The higher rotational barrier of the C_1–C_α bond in ions **1c** where X = NO_2 and CF_3 suggests that this π-electron migration is governed by the magnitude of the C_1–C_α π-resonance integral as well as by the magnitude of the C_4–OCH_3 π-resonance integral.

(iii) Long Range Substituent Effects. The existence of a transmission of the X substituent electronic effects to the second aromatic ring has been previously investigated by ^{19}F NMR in 4-F,4′-substituted protonated benzophenones[47] and other closely related neutral molecules or ions.[47,48] We very recently pointed out[49] that ^{13}C is a very powerful technique for following the propagation of these influences along the carbon framework.

Tables I and II show that the $C_{1'}$ and $C_{3'}$ positions undergo very small variations, ~2 ppm, while $C_{2'}$ and $C_{4'}$ signals move up to 13.4 ppm in ions **1a** from X = OCH_3 to X = NO_2. These results are easily explained by the existence of π-conjugation between the $C_{2'}$, $C_{4'}$, and C_α positions but are in contrast with the trends observed in the parent hydrocarbons; for example, in the substituted 1,1-diphenylethylenes there is no transmission of the substituent π-electronic effects to the other aromatic ring, particularly at the $C_{2'}$ or $C_{4'}$ positions. The simplified π molecular orbital theory has demonstrated that this results from an absence of electronic interactions between the two distinct sets of carbons (namely starred or unstarred) in an even-alternant hydrocarbon like 1,1-diphenylethylene.[50] In line with this formalism, we can notice that unsubstituted ions **1** and **2** belong to the class of the odd-alternant hydrocarbons[50] for which our data, as well as literature results,[48] show the reverse situation, i.e., that electronic perturbations at the C_4 position strongly affect C_α, $C_{2'}$, and $C_{4'}$ carbons of the same set. It is clear that the C_α bridge acts as a transmitter for such electronic interactions from one ring to the other, probably through the nonbonding orbital centered at the C_α carbon, since the transmission is greater when the energy of this orbital is greater.[51]

In addition, from an extensive comparison of substituent effects across bridged ring systems, Phillips et al.[48] have concluded that, for most of the bridges, there is no π-electron transfer from one ring to the other, since the bridge acts as a relay rather than a transmitter. For the protonated benzophenones, however, they recognize that the situation is not as obvious and question the various contributions of π-inductive and π-electron transfer at the $C_{4'}$ carbon; indeed, due to the absence of direct conjugation between the C_4 and $C_{4'}$ carbons, they are inclined to think that the second effect is absent. Our results allow us to make more precise conclusions.

From our data in Tables I and II, rather good correlations between SCS at the $C_{4'}$ and C_1 carbons can be obtained for each series of ions **1a** and **2a** (eq 10 and 11)

$$\delta_{C_{4'}} = 0.91\delta_{C_1} + 13.6\ (r = 0.922;\ SD = 1.8) \qquad (10)$$

for ions **1a** and

$$\delta_{C_{4'}} = 0.35\delta_{C_1} + 61.7\ (r = 0.972;\ SD = 0.4) \qquad (11)$$

for ions **2a.**

Since π-electron densities at the C_1 carbons are mainly developed by the π-inductive effect, eq 10 and 11 mean that this is also true at the very remote $C_{4'}$ positions. It is then ascertained that C_α acts only as a relay without electron transfer from the substituent to the unsubstituted ring; hence, π electron density at the C_α carbon is the only one developed by π-electron migration from the substituents in ions **1** and **2,** but π-electrons at the C_α carbon in turn polarize the second aromatic ring by a π-inductive effect. Moreover, we have shown above that the magnitude of the π-inductive effect at C_1 is independent of the π-electron demand by C_α, since it is nearly the same in ions **1a** and **2a;** thus, the ratio of the slopes of eq 10 and 11 indicates that the π-polarization at the unsubstituted aromatic ring is greater, by a factor of 2.6, in ions **1a** than in ions **2a.** It is extremely noteworthy that this value is nearly identical with the ratio of the C_α susceptibilities in ions **1a** and **2a,** namely, 2.7 (eq 5). These observations clearly confirm that the C_α bridge acts as a relay for the electronic interactions and that the greater the positive charge at C_α the greater will be the relay efficiency; in other words, the magnitude of the π-inductive effect at the unsubstituted ring is directly related to the π-electron deficiency at the C_α position (q = 0.5063 in diphenylmethyl carbenium and q = 0.6188 in protonated benzophenone), i.e., to the energy of the empty orbital of the π-carbon. This conclusion is in full agreement with the results obtained for various bridges by Phillips and co-workers[48] and with the theoretical predictions of Murell.[51]

Conclusion

^{13}C NMR has been used to investigate the electronic structure of diphenylmethyl and diphenylhydroxy carbenium ions. The ability of the chemical shifts in a range of ~120 ppm as a probe of electronic distribution is demonstrated by general correlations with π-electron density and π-bond order for para, para′-substituted ions **1** and **2.** The importance of the

π-bond order term is borne out when comparing shifts of sites differing in their environment or their substitution degree.

The distinct SCS on the C_α carbenium center are interpreted on the basis of the electron demand at this position, whereas on the substituted ring the shifts remain near the values observed in neutral monosubstituted benzenes, regardless of the electron demand. Nonadditivity of the SCS points out substituent–substituent interactions and substantiate the concept that the π-electron donation from a releasing group (such as OCH_3) is strongly dependent on the electron deficiency at the carbenium center, in accordance with the notions of concerted π-inductive mesomeric action.

Long-range substituent effects from one phenyl ring to the other are observed and interpreted by means of a relay influence of C_α whose electron density does not directly contribute to the observed shifts.

Finally, our results show that ^{13}C chemical shifts are an extremely good means for studying the structure of carbocations inasmuch as specific electronic effects at each carbon are singled out; thus, some insight concerning the nature of transmission of substituent perturbations in the ion framework becomes possible.

Acknowledgments. During a ^1H NMR study of some of these ions, Professor J. E. Dubois, through his discussions and suggestions, prompted the present work. We gratefully acknowledge his constant help and encouragement.

Supplementary Material Available. INDO total and π-electron densities and π-bond orders for diphenylmethyl carbenium ions **1** (Table IV) and diphenylhydroxy carbenium **2** (Table V) (2 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) G. Fraenkel and D. G. Farnum in "Carbeniums Ions", Vol 1, G. A. Olah and P. V. R. Schleyer, Ed, Wiley, New York, N.Y., 1973, p 237; (B) D. G. Farnum, *Adv. Phys. Org. Chem.*, **11,** 123 (1975); (c) J. B. Stothers, "Carbon 13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972, chapters 3, 4, 6, and 7.

(2) (a) H. C. Brown and E. N. Peters, *J. Am. Chem. Soc.*, **95,** 2400 (1973); (b) H. C. Brown, "The Nonclassical Ion Problem", Plenum Press, New York, N.Y., 1977, p 244–247; (c) G. M. Kramer, *Adv. Phys. Org. Chem.*, **11,** 177 (1975).

(3) Substituent chemical shift (SCS) as defined by M. J. S. Dewar and A. P. Marchand, *J. Am. Chem. Soc.*, **88,** 3318 (1956), represents the difference in chemical shifts between the observed nucleus and the corresponding nucleus in the unsubstituted species.

(4) (a) G. A. Olah, C. L. Jeuell, and A. M. White, *J. Am. Chem. Soc.*, **91,** 3961 (1969); (b) G. A. Olah, R. D. Porter, and D. P. Kelly, *ibid.*, **93,** 464 (1971); (c) G. A. Olah, R. D. Porter, C. L. Jeuell, and A. M. White, *ibid.*, **94,** 2044 (1972).

(5) G. J. Ray, R. J. Kurland, and A. K. Colter, *Tetrahedron,* **27,** 735 (1971).

(6) B. Ancian, J. P. Doucet, and J. E. Dubois, *J. Am. Chem. Soc.*, **98,** 4764 (1976).

(7) (a) G. A. Olah, P. W. Westerman, and D. A. Forsyth, *J. Am. Chem. Soc.*, **97,** 3419 (1975); (b) D. A. Forsyth, R. J. Spear, and G. A. Olah, *ibid.*, **98,** 2512 (1976).

(8) (a) H. Spiesecke and W. G. Schneider, *Tetrahedron Lett.*, 468 (1961); (b) P. C. Lauterbur, *J. Am. Chem. Soc.*, **83,** 1846 (1961); (c) G. A. Olah and G. D. Mateescu, *ibid.*, **92,** 1430 (1970).

(9) J. Hine, "Physical Organic Chemistry", McGraw-Hill, New York, N.Y., 1962, p 100.

(10) (a) H. H. Freedman an "Carbonium Ions", Vol. 4, G. A. Olah and P. v. R. Schleyer, Ed., Wiley, New York, N.Y., 1973, p 1501; (b) S. V. McKinley, J. W. Rakshys, A. E. Young, and H. H. Freedman, *J. Am. Chem. Soc.*, **93,** 4715 (1971).

(11) S. Nishida, *J. Org. Chem.*, **32,** 2697 (1967).

(12) (a) A. F. Hegarty, J. S. Lomas, W. V. Wright, E. D. Bergmann, and J. E. Dubois, *J. Org. Chem.*, **37,** 2222 (1972); (b) J. E. Dubois, J. J. Aaron, P. Alcais, J. P. Doucet, F. Rothenberg, and R. Uzan, *J. Am. Chem. Soc.*, **94,** 6823 (1972); (c) G. Goethals, J. P. Doucet, P. Bauer, and R. Uzan, *Spectrochim. Acta, Part A,* **31,** 1501 (1975).

(13) (a) E. D. Jenson and R. W. Taft, *J. Am. Chem. Soc.*, **86,** 116 (1964); (b) R. W. Taft and L. D. McKeever, *ibid.*, **87,** 2489 (1965); (c) L. D. McKeever and R. W. Taft, *ibid.*, **88,** 4544 (1966).

(14) F. G. Bordwell and G. J. McCollum, *J. Org. Chem.*, **41,** 2391 (1976).

(15) L. Radom, J. A. Pople, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **94,** 5935 (1972), and references therein.

(16) G. A. Olah and D. A. Forsyth, *J. Am. Chem. Soc.*, **97,** 3137 (1975), and references therein.

(17) (a) G. A. Olah and P. W. Westerman, *J. Am. Chem. Soc.*, **95,** 7530 (1973); (b) G. A. Olah, P. W. Westerman, and J. Nishimura, *ibid.*, **96,** 3548 (1974).

(18) (a) Reference 2, p 197; (b) G. C. Levy and G. L. Nelson, "Carbon 13 Nuclear Magnetic Resonance for Organic Chemists", Wiley, New York, N.Y., 1972, p 81; (c) G. L. Nelson, G. C. Levy, and J. D. Cargioli, *J. Am. Chem. Soc.*, **94,** 3089 (1971).

(19) (a) R. Jost, P. Rimmelin, and J. M. Sommer, *J. Chem. Soc., Chem. Commun.*, 879 (1971); (b) J. M. Sommer, R. Jost, and T. Drakenberg, *J. Magn. Reson.*, **21,** 93 (1976).

(20) (a) M. Brookhart, G. C. Levy, and S. Winstein, *J. Am. Chem. Soc.*, **89,** 1735 (1967); (b) G. A. Olah, H. O'Brien, and M. Calin, *ibid.*, **89,** 3582, 3585 (1967); (c) H. Brouwer, *Recl. Trav. Chim. Pays–Bas,* **86,** 879 (1967).

(21) (a) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory", McGraw-Hill, New York, N.Y., 1969; (b) Quantum Chemistry Program Exchange, program no. 141, Department of Chemistry, Indiana University, Bloomington, Ind. 47401.

(22) (a) W. C. Danen, *J. Am. Chem. Soc.*, **94,** 4835 (1972); (b) L. D. Kispert, C. U. Pittman, D. L. Allison, T. B. Patterson, C. W. Gilbert, C. F. Hains, and J. Prather, *ibid.*, **94,** 5979 (1972); (c) E. M. Evleth and P. M. Horowitz, *ibid.*, **93,** 5636 (1971).

(23) (a) H. Suzuki, "Electronic Absorption Spectra and Geometry of Organic Molecules", Academic Press, New York, N.Y., 1967, chapters 13 and 21; (b) F. Zuccarello, S. Trovato, and S. Millefiori, *Z. Phys. Chem.*, **79,** 103 (1972); **86,** 27 (1973).

(24) P. Ros, *J. Chem. Phys.*, **49,** 4902 (1968).

(25) G. J. Martin, M. L. Martin, and S. Odiot, *Org. Magn. Reson.*, **7,** 2 (1965), and references therein.

(26) Using Olah's results and values for this study, we observed that for parent ions $C_6H_5C^+(R)R'$ where R, R′ = H, OCH_3, OH, or C_6H_5, a definite trend to correlation is obtained when plotting δ vs. q_π, whereas a δ vs. q_t plot leads to a great scatter and, even for C_α, to an inverted trend (i.e., deshielding while increasing the charge at this position). The reasons for the better agreement observed using q_π rather than q_t, in contrast to various observations on neutral compounds,[18c,25,29] are not clear. Several defects of semiempirical MO calculations for ions may be invoked as a rough estimation of some resonance integrals or Coulomb integrals or overestimation of σ effects.[27]

(27) (a) A. Streitwieser and R. G. Jesaitis, in "Sigma Molecular Orbital Theory", O. Sinanoglu and K. B. Wiberg, Ed., Yale University Press, New Haven, Conn., 1970, p 197; (b) A. Streitwieser, P. C. Mowery, R. G. Jesaitis, J. R. Wright, P. H. Owens, and D. M. E. Reuben in "The Jerusalem Symposia on Quantum Chemistry and Biochemistry", E. D. Bergmann and B. Pullman, Ed., The Israel Academy of Sciences and Humanities, Jerusalem, 1970, p 160.

(28) A CNDO/S calculation using the Pariser approximation for the electronic repulsion integrals does not give a better electron density at the α-carbon of ions **1a** ($X = OCH_3$), i.e., $q_\pi = 0.4594$, whereas for the unsubstituted ion $q_\pi = 0.4329$.

(29) (a) J. A. Pople, *J. Chem. Phys.*, **37,** 53, 60 (1962); *Discuss. Faraday Soc.*, **34,** 7 (1962); *Mol. Phys.*, **7,** 301 (1964). (b) M. Karplus and J. A. Pople, *J. Chem. Phys.*, **38,** 2803 (1963).

(30) (a) P. C. Lauterbur, *J. Chem. Phys.*, **43,** 360 (1965); (b) T. D. Alger, D. M. Grant, and E. G. Paul, *J. Am. Chem. Soc.*, **88,** 5397 (1966); (c) J. E. Bloor and D. L. Breen, *J. Am. Chem. Soc.*, **89,** 6835 (1967); *J. Phys. Chem.*, **72,** 716 (1968).

(31) F. Membrey and J. P. Doucet, unpublished results.

(32) J. Bromilow, R. T. C. Brownlee, R. D. Topsom, and R. W. Taft, *J. Am. Chem. Soc.*, **98,** 2020 (1976).

(33) B. M. Lynch, *Can. J. Chem.*, **55,** 541 (1977).

(34) S. Ehrenson, R. T. C. Brownlee, and R. W. Taft, *Prog. Phys. Org. Chem.*, **10,** 1 (1973).

(35) (a) F. Membrey and J. P. Doucet, *J. Chim. Phys., Phys.–Chim. Biol.*, **73,** 1024 (1976), and references therein; (b) B. Ancian, to be published.

(36) H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80,** 4979 (1958).

(37) For example: ions **1a,** $\delta_{C_\alpha} = 14.2\sigma^+ + 169.6$ ($r = 0.916$; SD = 3.6); ions **2a,** $\delta_{C_\alpha} = 4.5\sigma^+ + 152.4$ ($r = 0.876$; SD = 1.4).

(38) The fact that the regression line also fits well the disubstituted ions is not in conflict with the existence of substituent–substituent interactions of different magnitudes in ions **1** and **2.** This results from a greater sensitivity to substituent effects and hence from greater interactions in ions **1** than in **2.**

(39) J. W. Larsen and P. A. Bouis, *J. Am. Chem. Soc.*, **97,** 4418 (1975).

(40) B. Ancian and J. P. Doucet, *J. Chim. Phys.. Phys. Chim. Biol.*, **69,** 1211 (1972).

(41) R. S. Mulliken, *Tetrahedron,* **5,** 253 (1959).

(42) M. Godfrey, *J. Chem. Soc. B,* 799 (1967); 751 (1968); 1534, 1537, 1540, 1545 (1971).

(43) H. H. Freedman, J. W. Rakshys, and S. V. McKinley, *J. Chem. Soc., Chem. Commun.*, 180 (1969).

(44) By contrast, in parent 1,1-diphenylethylenes or benzophenones the OCH_3 signal does not significantly move, indicating no modification of the electron donation by this group.

(45) (a) For ions bearing two acceptor groups, i.e., 4-NO_2,4′-NO_2 and 4-CF_3,4′-CF_3, the estimation of I_{XY} is less satisfactory, although reproduced; thus, these two points have been excluded from eq 8 and 9. (b) As the C_α chemical shifts cannot be expressed by σ^+ constants in monosubstituted ions, a more simple formulation of δ_{C_α} (X,Y) with $\sigma_X{}^+\sigma_Y{}^+$ cannot be attained in contrast with the parent models of ref 12b and 12c.

(46) In a study of the stabilization energies of trityl cations, Freedman (ref 10a, p 1553) defined a saturation ratio "SR" which is the ratio of the substituent effect observed in disubstituted compounds vs. the value calculated assuming additivity of the perturbations observed in monosubstitution; he pointed out that SR is dependent on the nature of the group and is roughly correlated to its σ^+. Our I_{XY} term is more useful for unsymmetrical disubstitution and leads via the $\sigma_X{}^+\sigma_Y{}^+$ representation to a measure of the

sensitivity to interactions depending only on the substrate and not on the substituents.

(47) (a) R. G. Pews, Y. Tsuno, and R. W. Taft, *J. Am. Chem. Soc.*, **89**, 2391 (1967); (b) S. K. Dayal, S. Ehrenson, and R. W. Taft, *ibid.*, **94**, 9113 (1972); (c) J. Fukunaga and R. W. Taft, *J. Am. Chem. Soc.*, **97**, 1612 (1975).

(48) (a) P. J. Mitchell and L. Phillips, *J. Chem. Soc., Perkin Trans. 2*, 109 (1974); (b) I. R. Ager, L. Phillips, and S. J. Roberts, *ibid.*, 1988 (1972).

(49) F. Membrey and J. P. Doucet, *C. R. Hebd. Seances Acad. Sci., Ser C*, **262**, 149 (1976).

(50) (a) A. Streitwieser, "Molecular Orbital Theory for Organic Chemists", Wiley, New York, N.Y., 1961, chapter 2; (b) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry", McGraw-Hill, New York, N.Y., 1969, chapter 6.

(51) J. N. Murrell, "The Theory of the Electronic Spectra of Organic Molecules", Methuen, London, 1963, chapters 9 and 10.

(52) For all figures, the numbers refer to the following substituents: 1, H, H; 2, H, NO_2; 3, H, CF_3; 4, H, CH_3; 5, H, OCH_3; 6, H, F; 7, H, Cl; 8, H, Br; 9, CH_3CH_3; 10, CH_3NO_2; 11, CH_3OCH_3; 12, OCH_3, OCH_3; 13, OCH_3, CF_3; 14, OCh_3, NO_2; 15, NO_2, NO_2; 16, CF_3, CF_3; 17, Cl, Cl; 18, F, F; 19, CH_3, Cl.

1-Phenylallyl Cations and Their Rearrangement to Indanyl Cations in Superacidic Media[1a]

George A. Olah,* Gregorio Asensio,[1b] and Herbert Mayr[1b,c]

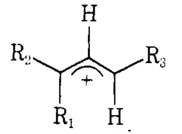
Hydrocarbon Institute, Department of Chemistry, University of Southern California, Los Angeles, California 90007, and the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106

Received July 25, 1977

The 2-phenyl-2-penten-4-yl cation (4) has been prepared in magic acid solution at −120 °C from 2-phenyl-3-penten-2-ol. Upon raising the temperature, a cyclic ion 12 was observed at −80 °C, which finally rearranged to the indanyl cation 14 at −70 °C. Methyl and deuterium substitution of the phenyl ring allowed identification of the structure of the intermediate ions and determination of the mechanism of the cyclization process.

A large number of stable alkyl-substituted allyl cations have been prepared and investigated[2] in superacidic media, but very few phenylallyl cations[3] are known as stable species at low temperature. At first glance this seems to be surprising since phenyl groups in most other carbocations have been shown to exhibit a greater stabilizing ability than alkyl groups.[4] However, in contrast to alkylated allyl cations, phenylallyl cations can easily undergo intramolecular cyclization to the corresponding indanyl cations, which explains the difficulty in obtaining them as stable species.[3a,b]

While ions **1**, **2**, and **3** were reported to be observable from −50 to −70 °C in FSO_3H–SO_2 or SO_2ClF, **4** could not be detected under these conditions since it rearranged to **14** (Scheme I). A deprotonation–reprotonation sequence was suggested to cause this rearrangement.[3b] Since deprotonation should be less favored in more acidic media, phenylallyl cations are expected to be more stable in FSO_3H-SbF_5-SO_2ClF than in FSO_3H-SO_2. Therefore, we attempted to prepare **4** in magic acid solution and to study its rearrangement under these conditions.

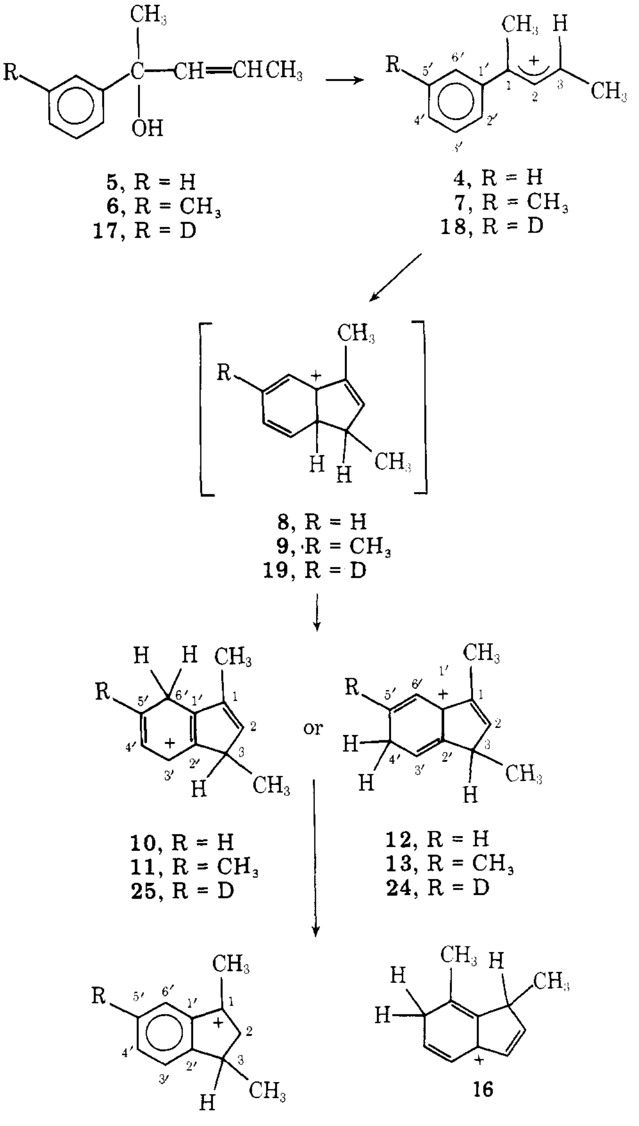


1, $R_1 = CH_3$; $R_2 = R_3 = Ph$
2, $R_1 = R_2 = R_3 = Ph$
3, $R_1 = H$; $R_2 = Ph$; $R_3 = CH_3$
4, $R_1 = R_3 = CH_3$; $R_2 = Ph$

Results and Discussion

When a precooled solution of 2-phenyl-3-penten-2-ol (**5**) in SO_2ClF was slowly added with good stirring to an excess of FSO_3H-SbF_5 in SO_2ClF at −120 °C, the 2-phenylpentenyl cation **4** was obtained. It is stable below −90 °C but starts to rearrange at this temperature (Scheme I). Ion **4** was characterized by its ^1H NMR and ^{13}C NMR spectra (Tables I and II). Conversion of **4** into another ion was observed at −80 °C. This species, however, could not be obtained with complete purity since contamination resulting from rearrangement to the known indanyl cation **14** began to occur at −70 °C. Both

Scheme I



5, R = H
6, R = CH_3
17, R = D

4, R = H
7, R = CH_3
18, R = D

8, R = H
9, R = CH_3
19, R = D

10, R = H
11, R = CH_3
25, R = D

12, R = H
13, R = CH_3
24, R = D

16

14, R = H
15, R = CH_3

---

* Address correspondence to this author at the University of Southern California.

0022-3263/78/1943-1518$01.00/0