Stable Carbonium Ions. CXI.[1] The Styryl (1-Phenylethyl) Cation and Substituted Styryl Cations

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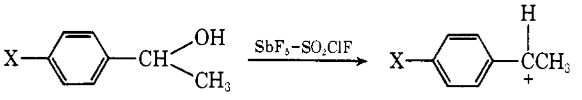
Abstract: The styryl cation and a series of para-X-substituted styryl cations (**1**-X) where X = OCH_3, [2,4,6-$(CH_3)_3$], CH_3, H, and CF_3 have been generated from their alcohol precursors (**2**-X) in SbF_5–SO_2ClF solution. The pmr data of these ions are reported and show the expected deshielding trend due to electron withdrawal from the aromatic ring. The carbon-13 nmr chemical shifts of the carbonium ions were obtained *via* the indor technique and are shown to follow a linear relationship with σ^+ substituent constants.

The study of cationic polymerization of styrene played a major role in the understanding of the mechanism of cationic polymerizations and also is of substantial practical importance. The intermediate styryl cation **1**-H is thus of prime importance but its direct observation proved to be difficult and has been one of the long-standing challenges of carbonium ion chemistry. The *p*-methoxystyryl cation **1**-OCH_3 and the 2,4,6-trimethylstyryl cation **1**-[2,4,6-$(CH_3)_3$] were obtained previously in our work,[2] but these are strongly stabilized styryl cations. We would like now to report our success in the observation of the parent styryl cation **1**-H as well as some monosubstituted styryl cations by pmr and carbon-13 nmr (cmr) spectroscopy.

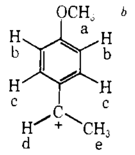
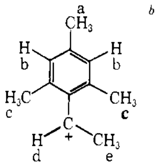
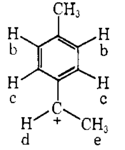
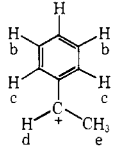
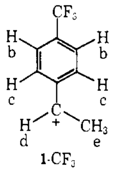
The **1**-*p*-X-phenylethyl (styryl) cations **1**-X, where X = H, CH_3, OCH_3, and CF_3, as well as the 1-mesitylethyl **1**-[2,4,6-$(CH_3)_3$] cation were prepared from their respective alcohol precursors **2**-X in antimony pentafluoride–sulfuryl chloride–fluoride solution at −78°. Table I gives the pmr spectral parameters of these ions.



2-X 1-X

As the para-X substituents in the series **1**-X become less able to delocalize positive charge, the chemical shifts of the methyl and methine protons show the expected deshielding trend, indicative of an increasing amount of the positive charge residing on the benzylic carbon. The directly attached methine protons are, of course, more sensitive to substituent effects than the methyl protons. Ions **1**-H and **1**-CF_3 could be observed only together with their precursor alcohol–SbF_5 complexes. Raising the temperature of the solution to −30° to complete ionization in the case of **1**-CF_3 resulted in the conversion of most of the **2**-CF_3–SbF_5 complex to **1**-CF_3. Figure 1 shows a 60-MHz spectrum of **1**-CF_3 and **2**-CF_3–SbF_5 at −40°. Arrows denote peaks due to the ion, the complex **2**-CF_3–SbF_5, H_3O^+, and acid peaks being also observed. Only dilute solutions could be obtained with this ion as well as with **1**-H, making indor experiments difficult (*vide infra*). The same attempt at warming in the case of the styryl ion **1**-H was not successful, resulting in little change in the ratio of **1**-H to the complex and substantial polymerization. The proton spectrum of the styryl cation **1**-H together with some of the **2**-H–SbF_5 complex present is

Table I. Proton Magnetic Resonance Data of *p*-X-Styryl Cations[a]

Cation	H_a	H_b	H_c	H_d	H_e
 1-OCH_3 [b]	4.50	7.48	9.4	8.86	2.98
 1-2,4,6-$(CH_3)_3$ [b]	2.59	7.40	2.76[c] 2.78[c]	9.77	3.02
 1-CH_3	3.25	8.25 ($J_{b,c}$ = 8)	8.70[c] 9.12[c]	10.07	3.61
 1-H	8.7	8.4	9.2	10.50 ($J_{d,e}$ = 7)	3.73
 1-CF_3		8.48	9.29	10.90	3.93

[a] Chemical shifts in parts per million from TMS capillary; coupling constants in hertz. [b] Pmr spectrum previously reported in ref 2. [c] Nonequivalent.

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(1) (a) Part CX: G. A. Olah, J. R. DeMember, C. Y. Lui, and R. D. Porter, *J. Amer. Chem. Soc.*, in press; (b) postdoctoral research associate, 1969. Currently at University of Melbourne, Australia.

(2) G. A. Olah, M. B. Comisarow, E. Namanworth, and B. Ramsey, *J. Amer. Chem. Soc.*, **89**, 5259 (1967).

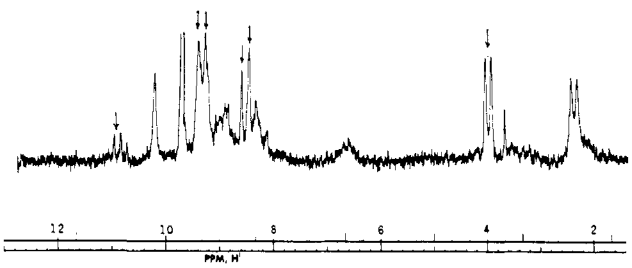

Figure 1. 60-MHz nmr spectrum of *p*-trifluoromethylstyryl cation ion (**1**-CF_3) along with its precursor **2**-CF_3–SbF_5 complex at −40° in SbF_5–SO_2ClF (arrows denote absorptions due to **1**-CF_3).

shown in Figure 2. The methyl doublet δ 3.73 (J = 7 Hz) and the methine quartet δ 10.50 (J = 7 Hz) of ion **1**-H are characteristic of a secondary carbonium ion.

Pmr chemical shifts of the aromatic regions of **1**-X (X = CH_3, H, CF_3) are considerably deshielded from those observed for the dimethyl-*p*-X-phenylcarbonium ions (**3**-X), indicating substantially greater positive charge delocalization into the aromatic ring.[3]

An empirical relationship between carbon-13 chemical shifts and charge density in carbonium ions was established in previous work.[4] It was, therefore, of practical interest to obtain the carbonium carbon atom shifts in ions **1**-X. ^{13}C chemical shifts for the benzylic carbons of the ions **1**-X were obtained by the indor method of main peak enhancement previously described.[5] We have found in many cases that time averaging is a helpful and necessary addition to the technique. Many of the ions studied were obtained in concentrations too low to observe either the ^{13}CH satellite or the ^{12}CH enhancements upon satellite decoupling (and possibly Overhauser effect) in a single sweep. The use of a time-averaging computer (Varian Associates Model C-1024) connected to the nmr spectrometer (Varian HA-100) allowed us to carry out the indor experiment in these cases. The voltage ramp is used to drive the frequency synthesizer. The time-averaging computer is internally triggered, the indor spectra being then accumulated in the memory. It can be seen in both Figures 1 and 2 that the signal-to-noise ratio is low and precludes obtaining indor spectra by any technique other than time averaging. Figure 3 shows part of such a time-averaged spectrum for **1**-CF_3. This was obtained by monitoring the low-field peak of the methyl doublet and sweeping irradiating 25.1-MHz frequency 50 passes over the region shown, each pass taking 25 sec. We have found that the speed of the passes over this range (1600 Hz) causes very little error (less than 2 ppm) when 10-sec sweeps are used. The ^{13}C spectrum of the **1**-H styryl cation was obtained in a similar fashion and required 600 sweeps of 10-sec duration; **1**-[2,4,6-$(CH_3)_3$] required 175 sweeps.

The ^{13}C data of the studied styryl cations are shown in Table II, together for comparison with those of the analogous carbonium ^{13}C chemical shifts found in the *p*-X-cumyl cations **3**-X, reported previously,[4b] as well as the carbonium ion shifts of dimethylcyclopropylcarbonium ion **4**,[4a] and of *tert*-butyl cation **5**.[4a]

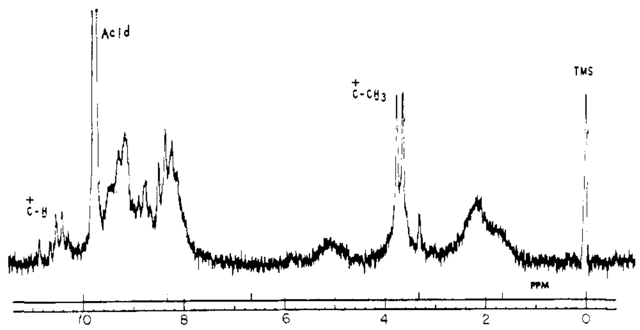

Figure 2. 60-MHz nmr spectrum of the styryl cation (**1**-H) at −78° in SbF_5–SO_2ClF.

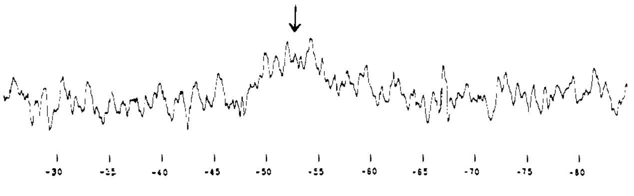

Figure 3. Computer time-averaged indor enhancement of the low-field peak of the methyl doublet in **1**-CF_3. Chemical shifts of decoupling frequency are relative to $^{13}CS_2$.

Table II. Carbon-13 Chemical Shifts[a] of the Carbonium Ion Carbon Atoms in Styryl and Cumyl Cations and Related Methyl and Cyclopropyl Carbonium Ions

Secondary ion	$\delta_{^{13}C^+(sec)}$	Tertiary ion	$\delta_{^{13}C^+(tert)}$	$\Delta\delta_{^{13}C^+(tert-sec)}$
1-OCH_3	−5	**3**-OCH_3	−25[b]	20
1-2,4,6-$(CH_3)_3$	−18			
1-CH_3	−28	**3**-CH_3	−49[b]	21
1-H	−40	**3**-H	−61[b]	21
1-CF_3	−53	**3**-CF_3	−75[b]	22
6	−59[d]	**4**	−87[c]	28
7	−125[c]	**5**	−135[c]	10

[a] All chemical shifts relative to $^{13}CS_2$ in parts per million. [b] Shown here for comparison; see ref 4b. [c] See ref 4a. [d] See ref 4c.

The carbonium ion ^{13}C chemical shifts in the cumyl cations have been shown to correlate well with σ^+ substituent constants.[4b] As shown in Table II, $\Delta\delta_{^{13}C(tert-sec)}$ for ions **1**-X compared with **3**-X remains essentially the same (20–22 ppm) as X is varied and amounts to a methyl substituent effect as compared to hydrogen. The continued relationship of the ^{13}C chemical shift of the styryl cations to σ^+ is expected in these benzylic systems.[6–9]

The styryl ion **1**-H was also of interest for comparison with the secondary methylcyclopropylcarbonium ion **6** and the isopropyl cation (dimethylcarbonium ion **7**), relating the stabilizing effects of the phenyl, methyl, and

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(3) Pmr chemical shifts for the aromatic regions of the **3**-X ions have been reported by G. A. Olah, M. B. Comisarow, and C. J. Kim, *J. Amer. Chem. Soc.*, **91**, 1458 (1969). For comparison with those shown in Table I, they are given here: (a) for **5**-CH_3 (ortho = 8.75, meta = 7.86); for **5**-H (ortho = 8.73, meta = 7.82, para = 8.42); for **5**-CF_3 (ortho = 8.90, meta = 8.08).

(4) (a) G. A. Olah and A. M. White, *ibid.*, **91**, 5801 (1969), and references contained therein; (b) G. A. Olah, C. L. Jeuell, and A. M. White, *ibid.*, **91**, 3961 (1969); (c) G. A. Olah, D. P. Kelly, C. L. Jeuell, and R. D. Porter, *ibid.*, in press; (d) G. A. Olah, J. R. DeMember, C. Y. Lui, and R. D. Porter, *ibid.*, in press.

(5) A. M. White and G. A. Olah, *ibid.*, **91**, 2943 (1969).

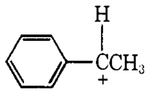
(6) E. A. Hill, M. L. Gross, M. Stasiewicz, and M. Marion, *ibid.*, **91**, 7381 (1969).

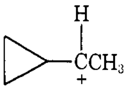
(7) R. Taylor, G. G. Smith, and W. H. Wetzel, *ibid.*, 87, 4817 (1962).

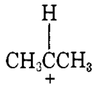
(8) Y. Okamoto and H. C. Brown, *J. Org. Chem.*, **22**, 485 (1957).

(9) A. Streitwieser, *Chem. Rev.*, **56**, 571 (1956).

cyclopropyl substituents by their ability to delocalize positive charge. The reported carbonium ion carbon chemical shifts of ions **6** and **7** are also shown for comparison in Table II.


1-H


6


$CH_3\overset{H}{C}^{+}CH_3$

7

The ability of the phenyl groups to delocalize positive charge, from the values of ^{13}C chemical shifts in the ions compared followed the expected sequence p-$CH_3OC_6H_4 > [2,4,6\text{-}(CH_3)_3]C_6H_2\text{-} > p\text{-}CH_3C_6H_4 > C_6H_5 > p\text{-}CF_3C_6H_4$. The effect on ^{13}C chemical shift replacement of hydrogen in a secondary carbonium ion at the carbonium ion carbon by a methyl group is similar for all three types (phenyl, cyclopropyl, methyl) of substituents compared. The effect is greatest with cyclopropyl, and least with methyl substituents. It should be emphasized, however, that at this point we are comparing systems which place the carbonium carbon atom in different environments. The effect in terms of change of delocalization of these small $\Delta\delta_{^{13}C}$ values is difficult to estimate at the present time, as chemical shifts cannot be correlated with charge densities alone. Methyl groups attached to the carbonium ion center, however, seem consistently to be electron withdrawing compared to hydrogen.[4a]

Experimental Section

Preparation of Ions. The styryl ions were prepared in 3:1 v/v solution of SO_2ClF-SbF_5 at −78°. The precursor alcohol is frozen to the inside of the test tube above the surface of the liquid. It is then carefully washed with the ionizing solvent by means of a vortex mixer. In the cases of **1**-H and **1**-CF_3, attempts to build up the ion concentration to a high level resulted in polymerization.

2-H and **2**-CH_3 are commercially available and were used without purification. **2**-H was obtained from K & K Laboratories and **2**-CH_3 from Aldrich Chemical Co. **2**-[2,4,6-$(CH_3)_3$] was described in ref 2.

2-OCH_3 was prepared by treating 25 ml of p-methoxybenzaldehyde in 50 ml of diethyl ether with 70 ml of 3 M methylmagnesium bromide in ether (Arapahoe) at −5°. After addition was completed, they were refluxed 30 min and worked up in the usual way. A 14.8-g sample of **2**-OCH_3 (47%) was obtained, bp 93.5–95.0 (3.5 mm).

2-CF_3 was prepared by addition of acetaldehyde to the Grignard reagent made from 11.2 g of p-trifluoromethylbromobenzene and 1.3 g-atoms of magnesium, yield 4.0 g (42%) of **2**-CF_3, bp 72° (4 mm). Nmr parameter of all **2**-X precursor alcohols are given in Table III.

Table III. Pmr Parameters[a] for Alcohols **2**-X

	CH_3	CH	ortho	meta	X
2-OCH_3	1.28 (6.5)	4.61	7.13	6.69	3.64
2-[2,4,6-$(CH_3)_3$]	1.37 (6.7)	5.16	2.31	6.67	2.18
2-CH_3	1.26 (6.6)	4.59	7.04	7.04	2.25
2-H	1.25 (6.5)	4.60	7.15	7.15	7.15
2-CF_3	1.38 (6.5)	4.79	7.34	7.55	

[a] Chemical shifts relative to TMS in CCl_4. Coupling constants in hertz in parentheses.

Nmr Measurements. Precursor alcohols and styryl cations were run (pmr) on a Varian Associates Model A 56/60 spectrometer. Indor measurements were carried out on a Varian Associates Model HA-100 spectrometer with details described previously.[5] Time averaging was done with a C-1024 time-averaging computer; the method is described in the text.

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Internal Solvent Pressure. I. A Demonstration of the Effect of Internal Solvent Pressure on Conformational Equilibria[1]

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Abstract: The role of internal solvent pressure in controlling conformational equilibria is discussed. Conformational studies of 4,4-dimethyl-2-silapentane and 2,3-dimethyl-2-silabutane establish that internal solvent pressure increases the population of *gauche*-butane conformations with respect to *trans*-butane conformations. The differences in molar volumes for the trans $\rightleftharpoons$ gauche equilibria −3.7 and −4.1 cm^3/mol for 4,4-dimethyl-2-silapentane and 2,3-dimethyl-2-silabutane, respectively. It is suggested that internal solvent pressure may play a role in controlling equilibria and kinetics of systems in which solvent effects are usually considered negligible.

The terms used to describe the liquid state and its effects in organic chemistry range from measurable thermodynamic properties,[2–6] semiempirical parameters,[7–9] and intuitive qualitative generalizations.

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(1) The authors acknowledge Grant GP-9231 from the National Science Foundation in support of this research.

(2) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N. Y., 1963, pp 50–55, 147–155, 263–267.

(3) K. B. Wiberg, "Physical Organic Chemistry," Wiley, New York, N. Y., 1964, pp 253–272.

(4) S. W. Benson, "The Foundations of Chemical Kinetics," McGraw Hill, New York, N. Y., 1960, pp 504–510.

(5) L. L. Schaleger and F. A. Long, "Advances in Physical Organic Chemistry," Vol. 1, Academic Press, New York, N. Y., 1963, pp 1–31.

(6) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," Wiley, New York, N. Y., 1958, pp 113–146.

(7) J. Hine, "Physical Organic Chemistry," McGraw-Hill, New York, N. Y., 1962, pp 157–162.