Stable Carbocations. CXLIV.[1a,b] The Structure of Benzoyl Cations Based on Their Carbon-13 Nuclear Magnetic Resonance Spectroscopic Study. The Importance of Delocalized, "Ketene-Like" Carbenium Ion Resonance Forms

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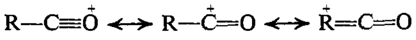
Abstract: The proton decoupled carbon-13 nuclear magnetic resonance spectra of benzoyl hexafluoroantimonate and a series of its substituted derivatives show there is significant charge delocalization into the aromatic ring and a large contribution from "ketene-like" mesomers. This conclusion is supported by cmr studies of ketenes as model compounds and is consistent with observed substituent effects.

Acyl cations[3] (acylium ions) are of interest as intermediates in Friedel–Crafts acylation reactions[4] and as powerful acylating agents in their own right. Their structure has been studied by a variety of spectroscopic methods since Seel[5] prepared the first stable acyl salt from the reaction of acetyl fluoride with boron trifluoride. It has been possible on the basis of infrared spectral data to distinguish between the polarized covalent complexes formed from acyl halides and some Lewis acid halides and the acyl cations formed by others.[6–8] The structure of an acyl cation can be considered as a resonance hybrid of the oxonium I, oxocarbenium II, and "ketene-like" III forms. It is generally agreed,[9,10] despite one claim to the contrary,[11] that the contribution of form III is not important for acetyl salts. Boer[9] and Le Carpentier and Weiss[10a] have summarized evidence which shows that most of the positive charge on the acetyl cation is located at the carbonyl carbon atom.



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

I II III

The structure of the benzoyl cation has been studied by infrared,[8] ultraviolet,[12] and nmr spectroscopy.[8,13–15] In this ion, structures of type III can play an important role, because the phenyl group is capable of carrying considerable positive charge. The pmr data indeed indicate[14] that there is considerable charge delocalization into the aromatic ring in the benzoyl cation. Ring proton shifts, however, are not sufficiently informative to give a true indication of the charge distribution in aroyl cations.

Recently with Mateescu[16] we obtained the X-ray electron spectra of several acyl and aroyl cations. The difference between the C_{1s} binding energies of the carbonyl and additional carbon atoms in the molecule is smaller for aroyl cations than for acyl cations, and this was attributed to charge delocalization into the ring in the aroyl cations.

The carbon-13 chemical shifts of the carbonyl carbon in both acyl and aroyl cations were found by Olah and White[13] to be in the range $\delta_{^{13}C}$ 39.0–44.3. The small range suggests that (a) either the acyl carbon chemical shift is insensitive to the electronic features of the molecule, (b) there is little structural difference between acyl and aroyl cations, or (c) the observed shifts are coincidental because differences in structure are offset by other factors.

We wish to report now complete cmr data for the benzoyl cation, and some of its substituted derivatives, which indicate substantial charge delocalization into the aromatic ring. The advantage of using cmr is that it is possible to observe the C_1 resonance (the ipso carbon) and base structural arguments on its chemical shift. It has been noted that this shift in monosubstituted benzene derivatives is quite sensitive to structural variations in the molecule.[17]

Results and Discussion

The preparation of acyl and aroyl salts was reported

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[1] (a) Part CXLIII: L. A. Paquette, M. J. Broadhurst, P. Warner, G. A. Olah, and G. Liang, *J. Amer. Chem. Soc.*, in press. (b) Presented in part at the ^{13}C NMR Spectroscopy Symposium of the Rocky Mountain Regional Meeting of the American Chemical Society, Colorado State University, June 30–July 1, 1972.

[2] Postdoctoral Research Fellow 1971–1973.

[3] It became obvious to us while writing this paper that as acyl cations (acylium ions) are always resonance hybrids of the oxonium, oxocarbenium and "ketene-like" carbenium ions forms (*i.e.*, $RC{\equiv}O^+ \leftrightarrow R{-}{}^+C{=}O \leftrightarrow {}^+R{=}C{=}O$) they can not be named as oxocarbenium ions, which would denote only one of the resonance forms. Therefore, it seems most appropriate to call them the corresponding acyl cations or acylium ions.

[4] For a review on this subject, see G. A. Olah, "Friedel-Crafts and Related Reactions," Vol. 1, Interscience, New York, N. Y., 1963, pp 91–95, 665–680, 790–812.

[5] F. Seel, *Z. Anorg. Allg. Chem.*, **250**, 331 (1943).

[6] D. Cook, *Can. J. Chem.*, 37, 48 (1959).

[7] B. P. Susz and J. Wuhrmann, *Helv. Chim. Acta*, **40**, 722 (1957).

[8] G. A. Olah, S. J. Kuhn, W. S. Tolgyesi, and E. B. Baker, *J. Amer. Chem. Soc.*, **84**, 2733 (1962).

[9] F. B. Boer, *J. Amer. Chem. Soc.*, **90**, 6706 (1968).

[10] (a) J. M. Le Carpentier and R. Weiss, *Acta Crystallogr., Sect. B*, **28**, 1430, 1437, 1442 (1972); (b) B. Chevrier, J. M. Le Carpentier, and R. Weiss, *J. Amer. Chem. Soc.*, **94**, 5718 (1972); (c) *Acta Crystallogr., Sect. B*, **28**, 2673 (1972).

[11] (a) D. Cassimatis and T. Theophanides, *Can. J. Spectrosc.*, 17, 17 (1972); (b) D. Cassimatis, J. P. Bonnin, and T. Theophanides, *Can. J. Chem.*, **48**, 3860 (1972).

[12] G. A. Olah, C. U. Pittman, Jr., R. Waáck, and M. Doran, *J. Amer. Chem. Soc.*, **88**, 1488 (1966).

[13] G. A. Olah and A. M. White, *ibid.*, **89**, 7072 (1967).

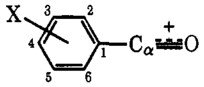
[14] D. A. Tomalia, *J. Org. Chem.*, **34**, 2583 (1969).

[15] G. A. Olah, J. Lukas, and E. Lukas, *J. Amer. Chem. Soc.*, **91**, 5319 (1969).

[16] G. D. Mateescu, J. L. Riemenschneider, J. J. Svoboda, and G. A. Olah, *ibid.*, **94**, 7191 (1972).

[17] G. L. Nelson, G. C. Levy, and J. D. Cargioli, *ibid.*, **94**, 3089 (1972).

Table I. Carbon-13 Chemical Shifts[a] of Substituted Benzoyl Cations at 20° in SbF_5



X	C+	C_1	C_2	C_3	C_4	Other shift
H	38.9	106.0	52.4	60.8	44.3	
p-CH_3	37.2	110.9	53.4	60.2	27.4	CH_3, 169.2
p-F	39.1	110.3	48.3 (13)[c]	71.8 (23)	18.0 (289)	
p-Cl	37.6	106.6	47.8	55.7	32.8	
p-CH_3O[b]	32.3	116.6	48.9	73.5	17.3	CH_3O, 133.9
m-CH_3	37.0	105.4	52.5	47.8	41.7	C_5, 60.8; C_6, 53.5
o-CH_3	36.4 (34.9)[d]	104.8	34.9 (36.4)[d]	58.8	43.8	C_5, 62.6; C_6, 52.4
p-CO^+ [e]	48.5	85.3	52.1			
p-$CO_2H_2^+$	43.9	92.3	50.6	59.3	57.1	CO_2H_2, 12.9

[a] In parts per million from $^{13}CS_2$ ($\delta_{TMS}^{CS_2}$ 193.7). [b] At −60° in SO_2ClF. [c] Carbon–fluorine coupling constants in hertz. [d] (Alternate assignment.) [e] At −20° in SO_2ClF.

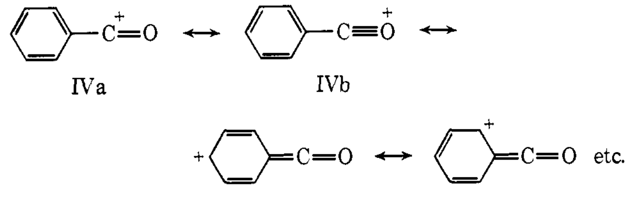
previously.[8,14,18] The present preparation of aroyl salts represents improvements of the methods previously employed and is described in the Experimental Section.

The proton decoupled carbon-13 nmr spectra of solutions of aroyl cations in SbF_5 solvent were obtained by the fast Fourier transform method[19] on a modified Varian HA-100 nmr spectrometer, and subsequently some of the studies also used a Varian XL-100. The results obtained are summarized in Table I. The carbon resonances for C_1 and C_4 and those for $C_{2,6}$ and $C_{3,5}$ can be distinguished by "off-resonance" decoupling experiments. The C_4 resonance of the benzoyl salt will also be split by "off-resonance" decoupling experiments, but it can readily be assigned to the signal with approximately half the intensity of the $C_{2,6}$ and $C_{3,5}$ peaks (assuming similar spin–lattice relaxation times and NOE factors for C_4 and $C_{2,3,5,6}$). Without the spectra of specifically labeled derivatives it is not possible to directly distinguish between the $C_{2,6}$ and $C_{3,5}$ resonances. It has been shown, however, that the shifts of the meta carbons in monosubstituted benzene derivatives are little affected by the substituents[20] even when the molecule carries a formal positive charge.[17] Therefore, the signal at 60.8 ppm in the cmr spectrum of the benzoyl salt is assigned to $C_{3,5}$.

The relative magnitude of the carbon–fluorine coupling constants[21] in the p-fluorobenzoyl cation enable the assignment of the signals in the p-fluoro derivative. Additive variations in aryl carbon shieldings, caused by methyl substitution in the monosubstituted benzene derivatives, have been observed by Lauterbur.[22,23] Assuming that these additive relationships also apply to methyl-substituted benzoyl cations, we have used them together with the chemical shifts of the benzoyl cation to make assignments in the o-, m-, and p-toluoyl cations.

Data for monosubstituted benzenes show a good linear relationship between para-carbon chemical shifts and calculated π-electron densities.[24] The large deshielding of the para-carbon resonance in the benzoyl cation therefore (approximately 21 ppm from benzene) implies that substantial positive charge is located on that carbon[18] and that mesomeric form IVc is of considerable importance. For other carbon atoms, where anisotropic field effects arising from the substituent and from local ordering of solvent molecules around the substituent may be more significant, a good linear relationship has still been found between the chemical shifts in a number of substituted benzenes and the total charge densities.[17] The deshielded C_2 resonance, therefore, implies a considerable contribution from IVd. If the sum of the observed changes from benzene for the $C_{2,6}$, $C_{3,5}$, and C_4 resonances is multiplied by the slope of the above plot (5.5×10^{-3} e/ppm),[17] a value of 0.312 charge unit is obtained. The large positive value indicates that the "ketene-like" mesomers are major contributors to the structure of the benzoyl cation. This figure, however, is approximate, since the calculated charge densities on which the measured slope is based are very sensitive to changes in ring geometry.[17] There may be distortion in the geometry of ion IV, particularly if the C_1–C_α bond has double bond character. There are also inherent inconsistencies in applying values calculated in the gas phase to data measured in solution.

The large contribution of forms IVc and IVd to the structure of the benzoyl cation is also strongly indicated by the shielded C_1 chemical shift. It is shielded from the corresponding resonance in its precursor, benzoyl fluoride, by 49 ppm. There is no satisfactory method of estimating the magnitude of field effects from the positively charged ion as well as the counterion, but they are most likely too small to account for the observed shift. The difference between the magnetic anisotropic effects of the -COF and -CO^+ groups may also account for part of the shielding, although



IVa IVb

IVc IVd

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(18) (a) G. A. Olah, *Rev. Chim., Acad. Repub. Pop. Roum.*, **7**, 1139 (1962); (b) G. A. Olah, W. S. Tolgyesi, S. J. Kuhn, M. E. Moffatt, I. J. Bastien, and E. B. Baker, *J. Amer. Chem. Soc.*, **85**, 1328 (1963); (c) H. Volz and M. J. Volz de Lecca, *Tetrahedron Lett.*, **36**, 3413 (1965); (d) G. A. Olah, D. H. O'Brien, and A. M. White, *J. Amer. Chem. Soc.*, **89**, 5694 (1967); (e) G. A. Olah and A. M. White, *ibid.*, **89**, 3591, 4752 (1967); (f) G. A. Olah and M. B. Comisarow, *ibid.*, **88**, 3313 (1966).

(19) (a) R. Ernst, *Advan. Magn. Resonance*, **2**, 108 (1966); (b) R. Ernst and W. A. Anderson, *Rev. Sci. Instrum.*, **37**, 93 (1966).

(20) H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35**, 722 (1961).

(21) E. F. Mooney and P. H. Winson, *Annu. Rev. NMR (Nuclear Magnetic Resonance) Spectrosc.*, **2**, 153 (1969).

(22) P. C. Lauterbur, *J. Amer. Chem. Soc.*, **83**, 1846 (1961).

(23) P. C. Lauterbur, *J. Chem. Phys.*, **38**, 1406, 1415, 1432 (1963).

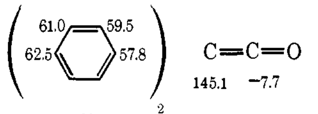
(24) T. K. Wu and B. P. Dailey, *ibid.*, **41**, 2796 (1964).

distant contributions (σ') to the shielding tend to be relatively small for the carbon-13 nucleus.[25] The large difference may be partly the result of the different effects of substituents bearing conjugated double and triple bonds on the diamagnetic screening constant (σ_d) for C_1.[26] The importance of this effect may be reflected in that the C_1 resonances of ethynylbenzene and benzonitrile are the most shielded of the ring carbon resonances, while in many monosubstituted benzenes, bearing a conjugated carbonyl group, the C_1 resonance is the most deshielded. As there is little difference in the other carbon shifts, for these two classes of compounds, the above difference in C_1 shifts is most likely not a charge polarization effect. Furthermore, as noted by Nelson, Levy, and Cargioli,[17] a plot of total charge density *vs.* ^{13}C chemical shifts for the aromatic carbons in substituted cyano- and ethynylbenzenes gives a straight line for the carbons bearing the substituent which is parallel to the line determined by the other ring carbons yet is shifted 0.050 charge unit to lower electron density. A similar shift, only 0.105 charge unit to higher electron density, was found for the C_1 carbons in substituted acetophenones. However, we do not believe that this is the entire effect because the C_1 shift in the benzoyl cation is still shielded by 23 ppm compared with the corresponding resonance in the isoelectronic benzonitrile. It seems that additional effects must be invoked.

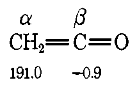
If the local screening constant for a carbon nucleus is treated as the sum of several terms,[27] then the dominant[25] paramagnetic shielding term can be shown to be affected by principally three factors.[28] These are: (a) charge polarization, (b) variations in the π-bond order, and (c) the average energy excitation (ΔE) required for the magnetic field to mix higher energy paramagnetic levels into the ground-state description of the molecule. If factor b contributes at all,[29] calculations for aromatic molecules[30] and protonated pyridine[31] show that it is small. From a consideration of ultraviolet absorption data, the difference between ^{13}C chemical shifts in related compounds has been accounted for in terms of factor c.[17,28,32] It is difficult, however, to explain the different C_1 chemical shifts in the benzoyl cation and benzonitrile by such considerations. Replacement of the nitrogen in benzonitrile by a positively charged oxygen results in the shift of the absorption maxima at 224 nm (ϵ 13,000) and 271 (1000)[33] to 259 (16,000) and 308 (3,700), respectively.[12] The excitation energy for these two transitions is therefore lowered implying greater delocalization and a consequent downfield shift in the carbon resonances.

The third factor which could account for the C_1 chemical shift in the benzoyl cation is the total electron density at that carbon. The observed shielding from benzonitrile would therefore be a result of an increase in the total electron density at C_1. That this factor is important is implied by the results of Nelson, Levy, and Cargioli.[17] Wehrli, *et al.*,[34] have also found a linear relationship between LCAO–MO π-electron densities at C_1 and C_1 chemical shifts in a series of para-substituted benzonitriles. Regardless of the relative importance of factors a and c, the large difference in the C_1 chemical shift from that of related monosubstituted benzenes suggests a rather large disturbance of the electronic structure of the benzene ring by the positively charged carbonyl group. We propose that the combined data for the C_1 and C_4 shifts, and to a lesser extent the $C_{2,6}$ shift, indicate a large contribution from resonance forms IVc and IVd. This is in agreement with the conclusion reached by Tomalia[14] on the basis of the pmr data.

For comparison as a model compound, we studied the proton decoupled carbon-13 nmr spectrum of diphenylketene. It is a suitable model of the "ketene-like" mesomers IVc and IVd because the conjugative effect of the phenyl groups should be similar to that of the double bonds of structures IVc and IVd. Six carbon resonances were observed, and "off-resonance" decoupling experiments enabled their assignment (see structure V). To confirm that the highly shielded resonance ($\delta_{^{13}C}$ 145) arose from the terminal carbon and not the carbonyl carbon, we also studied the cmr spectrum of ketene at −80°. Two signals were observed at $\delta_{^{13}C}$ 191 and $\delta_{^{13}C}$ −1 and these are assigned to C_α and C_β, respectively (structure VI), by "off-resonance" decoupling experiments. As in the case of the C_1 resonance of the benzoyl cation, we can only speculate on the reasons for the highly shielded terminal carbon resonance in ketenes. Hehre and Pople[35] in an *ab initio* molecular orbital calculation found that somewhat in excess of half a negative charge was located on the terminal carbon atom in ketene.



V



$$\overset{\alpha}{\underset{191.0}{CH_2}}=\overset{\beta}{\underset{-0.9}{C}}=O$$

VI

The above results show that associated with a ketene functionality is a highly shielded shift for the terminal carbon atoms, compared with that of an olefinic carbon. Therefore, we rationalize that the shielded C_1 shift in the benzoyl cation arises from a substantial contribution of the "ketene-like" mesomers IVc and IVd. The terminal and carbonyl carbon shifts are still 39 ppm deshielded and 41 ppm shielded, respectively, from the corresponding carbons of the model compound, diphenylketene. Indeed, if diphenylketene is a suitable model, there is a substantial difference of the benzoyl cation from its "pure" ketene form.

The observed substituent effects of electron-donating groups such as the methyl and methoxy groups are consistent with outlined structural views. These groups increase the contribution of the "ketene-like" forms by

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

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

(27) A. Saika and C. P. Slichter, *J. Chem. Phys.*, **22**, 26 (1954).

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

(29) J. E. Bloor and D. L. Breen, *J. Amer. Chem. Soc.*, **89**, 6835 (1967).

(30) T. D. Alger, D. M. Grant, and E. G. Paul, *ibid.*, **88**, 5397 (1966).

(31) R. J. Pugmire and D. M. Grant, *ibid.*, **90**, 697 (1968).

(32) P. V. Demarco, D. Doddrell, and E. Wenkert, *Chem. Commun.*, 1418 (1969).

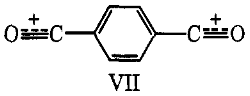
(33) A. E. Gillam and E. S. Stern, "An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry," 2nd ed, Edward Arnold Ltd., London, 1957.

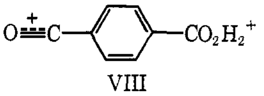
(34) F. W. Wehrli, J. W. de Haan, A. I. M. Keulemans, O. Exner, and W. Simon, *Helv. Chim. Acta*, **52**, 103 (1969).

(35) W. J. Hehre and J. A. Pople, *J. Amer. Chem. Soc.*, **92**, 2191 (1970).

accommodating positive charge, and a shielding of the C_1 resonance in the aroyl cations, compared with the parent compound, is observed. An electron donating group in the meta position, however, should have little effect on the C_1 chemical shifts of the benzoyl cation, and this was found to be the case for the *m*-toluoyl cation. The shielded methyl carbon resonance of the meta isomer compared with that of the para isomer may also be an indication of the decreased electron donating role of the methyl group in the former compound. Interpretation of the results for the ortho isomer (Table I) is difficult because steric interactions between the two ring substituents most likely affect several chemical shifts in this molecule.[36] The shielding at C_1 caused by the *p*-fluorine substituent in the *p*-fluorobenzoyl cation is consistent with the fluorine-19 nmr data[37] for the *o*-, *m*-, and *p*-fluorobenzoyl cations. A much smaller deshielding in the fluorine resonance of *p*-fluorophenacyl chloride occurs on ionization with SbF_5 than for the ortho and meta isomers. This has been attributed to substantial "back-donation" of electrons from the fluorine in the *p*-fluorobenzoyl cation.[37]

The observed substituent effects on the C_1 resonance of para-substituted benzoyl cations, caused by electron-withdrawing groups, is also consistent with outlined structural views. The chemical shift results (Table I) for the terephthaloyl dication (VII) show that the $C_{1,4}$ resonance is deshielded by 21 ppm from the corresponding resonance in the benzoyl cation. The difference can be interpreted in terms of the relative importance of the "ketene-like" forms. In the dication the contribution from such a structure should be negligible. The deshielded C_1 chemical shift in ion VIII ($\delta_{^{13}C}$ 92.3) also indicates a decreased contribution, compared with the parent IV, of a "ketene-like" form.


VII


VIII

The results in Table I indicate that the carbonyl carbon shift is also sensitive to structural changes. As the relative importance of resonance forms I and II decreases, a progressive deshielding of this resonance occurs, until in diphenylketene, where contributions from structures analogous to I and II are small, it is at −7.7. At the other extreme, in dication VII, resonance forms analogous to III are insignificant and the carbonyl carbon shift is observed at 48.5.

Experimental Section

The precursors of all ions prepared in this study were commercially available materials or were prepared by standard methods. Solutions of benzoyl hexafluoroantimonate and its *p*-chloro derivative were prepared by the reaction of the appropriate acyl fluoride, at room temperature, with an excess of antimony pentafluoride. Other salts were prepared in the same way from the acyl chlorides. The pmr spectrum of the *p*-methoxy salt prepared in this manner indicated the presence of an impurity (most likely sulfonation product[14]) which could only be avoided if the salt was prepared from the acyl chloride and 1:1 *M* FSO_3H-SbF_5 in SO_2ClF at −60°. The pmr spectra for the seven salts were consistent with the data[14] reported. In several cases the ions were also prepared by warming to room temperature a sulfur dioxide solution of the corresponding benzoic acid in 1:1 *M* FSO_3H-SbF_5.[18e]

The terephthaloyl dication VII was obtained by the treatment of terephthaloyl fluoride with excess SbF_5 in SO_2ClF at −60°. The resulting solution [pmr: δ 9.78 (s)] gave terephthalic acid on quenching with water. Reaction of terephthaloyl fluoride with 1:1 *M* FSO_3H-SbF_5 in SO_2 at −60°, and subsequent warming at room temperature, gave a mixture of diprotonated terephthalic acid [pmr: δ 9.20 (s, 4) and 13.52 (s, 4)] and dication VIII [pmr: δ 9.41 (d, 2 H, J = 9 Hz), 9.62 (d, 2 H, J = 9 Hz), and 12.93 (s, 2 H)]. Further warming resulted in the complete conversion of ion VIII to protonated terephthalic acid. Quenching with water at any stage yielded terephthalic acid exclusively. The cmr data for ions VII and VIII are shown in Table I. The proton decoupled cmr spectrum of diprotonated terephthalic acid shows signals at $\delta_{^{13}C}$ 11.0 ($CO_2H_2^+$), 59.3 ($C_{2,3,5,6}$), and 62.8 ($C_{1,4}$).

Diphenylketene and ketene were prepared by the described procedure,[38-40] and the pmr spectrum of ketene was consistent with the reported data.[41]

Proton Magnetic Resonance Spectroscopy. Proton magnetic resonance spectra were obtained using a Varian Associates Model A56/60A nmr spectrometer equipped with a variable-temperature probe. External TMS (capillary tube) was used as reference.

Carbon-13 Nuclear Magnetic Resonance Spectroscopy. Cmr spectra were obtained on a Varian Associates Model HA-100 spectrometer equipped with a FT-100 Fourier transform accessory (V-4357 Pulsing and Control unit), a broad band proton decoupler (V-3512), and a variable-temperature probe. Details of the instrumentation and the procedure used to determine chemical shifts are provided elsewhere.[42]

The chemical shifts for the last four entries in Table I were obtained using a Varian Associates XL-100 nmr spectrometer.

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

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(36) D. M. Grant and B. V. Cheney, *J. Amer. Chem. Soc.*, **89**, 5315 (1967).

(37) G. A. Olah and Y. K. Mo, *J. Org. Chem.*, in press.

(38) E. Horning, Ed., "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 356.

(39) J. W. Williams and C. D. Hurd, *J. Org. Chem.*, **5**, 122 (1940).

(40) S. Andreades and H. D. Carlson, *Org. Syn.*, **45**, 50 (1965).

(41) E. L. Allred, D. M. Grant, and W. Goodlett, *J. Amer. Chem. Soc.*, **87**, 673 (1965).

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