Stable Carbonium Ions. LVIII.[1] Carbon-13 Resonance Investigation of Protonated Carboxylic Acids (Carboxonium Ions) and Oxocarbonium Ions (Acyl Cations)[2]

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Abstract: The carbon-13 resonance of protonated formic, acetic, propionic, and benzoic acids and their corresponding acyl cations (methyl, ethyl, and phenyloxocarbonium ions) was investigated in FSO_3H–SbF_5 solution of the acids and in HF solution of the isolated oxocarbonium hexafluoroantimonate complexes. Data are in accordance with linear sp hybridization of the acyl cations (oxocarbonium ions) leading to more shielded nmr absorptions than the sp^2-hybridized protonated acids (carboxonium ions).

Considerable interest centers on the elucidation of the structure of stable carbonium and oxocarbonium ions.[4] Carbon-13 magnetic resonance offers a unique possibility of directly observing the carbonium carbon atom of these ions in solution.

We have reported previously[5] the observation of the carbon-13 resonance of the methyloxocarbonium ion by investigating methyloxocarbonium hexafluoroantimonate ($CH_3C^{13}O^+SbF_6^-$) using liquid hydrogen fluoride as solvent. The carbonyl carbon atom showed a quartet at about 0 ppm from $C^{13}S_2$ ($J_{C^{13}-CH} = 6.3$ Hz) which was assigned to the methyloxocarbonium ion. A higher field peak at about +40 ppm was also observed and was assigned to a minor hydrolysis product.

The proton spectra of acyl fluoride–antimony pentafluoride complexes in HF or SO_2 solution generally show two species.[5] The lower field species was assigned to the oxocarbonium ion and the second species was tentatively assigned to a polarized coordination complex (donor–acceptor complex). More recently it has been found possible to eliminate the higher field peaks by the complete exclusion of moisture from the system.[6] It has further been noted that the chemical shifts of protonated carboxylic acids in FSO_3H–SbF_5 solution correspond closely to those of the higher field peaks in the proton nmr spectra of the corresponding acyl fluoride–antimony pentafluoride complexes.[7] It thus appears likely that oxocarbonium ion salts in either SO_2 or HF solution can react with trace amounts of water giving the protonated acid (alkylcarboxonium ion). Indeed it has recently been shown[7] that the methylcarboxonium ion can be isolated as a stable crystalline salt from solutions of acetic acid in 1:1 molar HF–SbF_5 solutions and that the proton nmr spectrum of this salt, when redissolved in SO_2, is identical with that of the "high-field species" observed in the spectra of the methyloxocarbonium ion salts.

Maciel and Traficante[8] investigated the carbon-13 resonance of acetic and benzoic acid in sulfuric acid and oleum. They reported two carbon-13 peaks for acetic acid at about 0 and +42 ppm and similarly for benzoic acid at +12 and +39 ppm. The low-field peaks were assigned to the protonated acids, but no assignment was offered for the "high-field species" which were observed in oleum solution. We wish now to report the carbon-13 resonance investigation of protonated acetic, propionic, and benzoic acids and their corresponding oxocarbonium ions under nonequilibrium conditions[7] which allows an unambiguous assignment of the carbon-13 resonances in both the carboxonium and oxocarbonium ions and clarification of the discrepancies in the previous work. Our studies also included the carbon-13 resonance investigation of protonated formic acid, the proton resonance spectrum of which was recently observed independently by Hogoveen, Mackor, and Maclean and their co-workers[9] and by ourselves.[7]

Results and Discussion

Acetic acid has been shown to be completely protonated at −40° in FSO_3H–SbF_5–SO_2 solution and can be dehydrated to the methyloxocarbonium ion by raising the temperature to about −10°.[7]

The C^{13} spectrum of acetic acid-1-C^{13} in FSO_3H–SbF_5 at −40° consisted of a single, although broad, absorption (Table I). The chemical shift of this peak, the mean of a number of sweeps in both directions, was +1.6 ppm. When the sample was warmed to −10°, a new peak at +44.3 ppm appeared, concurrently with the disappearance of the lower field peak. Monitoring of the proton spectrum of the sample showed that this change was a result of cleavage of the protonated acid to the methyloxocarbonium ion.

$$CH_3C^{13}O_2H \xrightarrow[-40^\circ]{FSO_3H-SbF_5-SO_2} CH_3C^{13}O_2H_2^+ \xrightarrow[-10^\circ]{} CH_3C^{13}O^+ + H_3O^+$$

Carrying out the same experiment with propionic acid-1-C^{13}, the resonance absorption of the ethylcar-

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(1) Part LVII: G. A. Olah and J. M. Bollinger, *J. Am. Chem. Soc.*, in press.

(2) Presented in part at the Pittsburgh Analytical Conference, Symposium of Carbon-13 Resonance, March 1967.

(3) National Institutes of Health Postdoctoral Research Investigator, 1966–1967.

(4) For a recent review, see G. A. Olah, *Chem. Eng. News*, **45**, 13, 77 (March 27, 1967).

(5) G. A. Olah, W. S. Tolgyesi, S. J. Kuhn, M. E. Moffatt, I. J. Bastien, and E. B. Baker, *J. Am. Chem. Soc.*, **85**, 1328 (1963).

(6) G. A. Olah and M. B. Comisarow, *J. Am. Chem. Soc.*, **88**, 4442 (1966).

(7) G. A. Olah and A. M. White, *ibid.*, **89**, 3591 (1967).

(8) G. E. Maciel and D. D. Traficante, *J. Phys. Chem.*, **69**, 1030 (1965); **70**, 1314 (1966).

(9) H. Hogoveen, A. F. Rieckel, C. W. Hilbers, E. L. Mackor, and C. MacLean *Chem. Commun.*, 898 (1966).

Table I. Carbon-13 Magnetic Resonance Shifts (in parts per million from External $C^{13}S_2$) of Carboxonium Ions (Protonated Acids) and Oxocarbonium Ions (Acyl Cations)

	Solvent	Temp, °C	$RC^{13}O_2H$	$RC^{13}O_2H_2^+$	$RC^{13}O^+$
$CH_3C^{13}O_2H$	. . .		15.6		
$CH_3CO_2H_2^+$	FSO_3H-SbF_5	−40		1.6	
CH_3CO^+	FSO_2H-SbF_5	−10			44.3
$CH_3CO^+SbF_6^-$	HF				41.5
$CH_3CO_2H_2^+SbF_6^-$	HF			−0.4	
$C_6H_5C^{13}O^2H$	$(C_2H_5)_2O$		19.7		
$C_6H_5C^{13}O_2H_2^+$	FSO_3H-SbF_5	−40		12.0	
$C_6H_5CO^+$	FSO_3H-SbF_5	0			40.0
$C_6H_5CO^+SbF_6^-$	HF				39.0
$C_6H_5CO_2^+H_2SbF_6^-$	HF			10.3	
$CH_3CH_2C^{13}O_2H$	. . .		14.8		
$CH_3CH_2C^{13}O_2H_2^+$	FSO_3H-SbF_5	−40		1.6	
$CH_3CH_2C^{13}O^+$	FSO_3H-SbF_5	0			44.1
$HC^{13}O_2H$	88% aqueous soln[a]		27.0		
$HC^{13}O_2H_2$ I	FSO_3H-SbF_5	−65		17.0	
II	FSO_3H-SbF_5	−65		19.9	

[a] P. C. Lauterbur, *J. Chem. Phys.*, **27**, 217 (1957).

boxonium ion was observed at +1.6 ppm and that of the ethyloxocarbonium ion at +44.1 ppm.

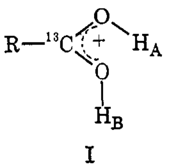
$$CH_3CH_2C^{13}O_2H \xrightarrow[-40^\circ]{FSO_3H-SbF_6-SO_2} CH_3CH_2C^{13}O_2H_2^+ \xrightarrow[-10^\circ]{} CH_3CH_2C^{13}O^+ + H_3O^+$$

Repetition of the experiment at −40° with 56% enriched benzoic acid gave an absorption peak at +12.0 ppm. On raising the temperature, a new peak appeared at +40.0 ppm. Again, simultaneous study of the proton magnetic resonance spectrum showed this change corresponded to conversion of the protonated acid (phenylcarboxonium ion) to the phenyloxocarbonium ion.

$$C_6H_5C^{13}O_2H \xrightarrow[-40^\circ]{FSO_3H-SbF_6-SO_2} C_6H_5C^{13}O_2H_2^+ \longrightarrow C_6H_5C^{13}O^+ + H_3O^+$$

We conclude from these studies that the "high-field species" observed for acetic, propionic, and benzoic acids corresponds to the oxocarbonium ions and the low-field species to the protonated acids (carboxonium ions). In going from the carboxylic acids to their protonated forms (carboxonium ions) a deshielding of 14.0 ppm is observed for acetic acid, 13.2 ppm for propionic acid, but only 8.9 ppm for benzoic acid.[10] Since there is no change in the state of hybridization of the sp^2 C-1 atoms, this deshielding effect is primarily caused by the positive charge. This positive charge is better delocalized in the benzoyl than in either the acetyl or propionyl systems. The carbon-13 resonance of the corresponding oxocarbonium ions (acyl cations) is at considerably higher field than either that of the starting carboxylic acids or their protonated forms. This is despite the fact that the proton resonance spectra of the oxocarbonium ions show substantial deshielding effects. We propose that this observation is in accordance with the sp hybridization of the oxocarbonium carbon atom in these ions[11] and a substantial magnetic anisotropy effect causing the upfield shift. More suitable compounds for evaluation of the deshielding data of the oxocarbonium ions are the corresponding nitriles. Compared with these compounds, the oxocarbonium ions indeed show substantial deshielding due to the positive charge. Thus the C^{13} chemical shift of the nitrile carbon in acetonitrile is +75.4 ppm,[12] which is 33.1 ppm to higher field of the absorption peak of the methyloxocarbonium ion.[13]

The long-range coupling constants, $J_{C^{13}-C-H}$, were determined in the proton spectra of protonated acetic and propionic acids and the corresponding oxocarbonium ions (Table II). This coupling is 7.0 Hz for neat acetic acid, 6.5 Hz for protonated acetic acid, and 9.3 Hz for the methyloxocarbonium ion. The latter coupling constant compares well with the 9.8 Hz coupling observed in the isoelectronic acetonitrile molecule[14] emphasizing the validity of the choice of this compound for evaluation of the chemical shift data for the methyloxocarbonium ion. A striking feature of the proton spectrum of protonated acetic acid is that the two hydroxyl protons are unequally coupled to the C^{13} nucleus. In the major form of the protonated acid (I, R = Me), the higher field OH resonance is a triplet (Figure 1) with a $J_{C^{13}-OH}$ coupling of 7.5 Hz, while the lower field OH resonance shows only a small coupling (<0.5 Hz). The small peak at −12.85 ppm (from external TMS) which is attributed to structure II (R = Me)[7,15] also shows only a small coupling (<0.5 Hz). This difference demonstrates the well-known sensitivity of long-range C^{13}–H coupling constants to small structural variations as illustrated by the 16-Hz difference in the $J_{C^{13}-C-H}$ coupling constant between *cis*-dichloroethylene and the *trans* isomer.[16]



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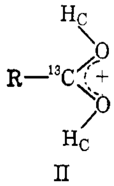

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[10] The chemical shifts for the C^{13}-carboxylic acids are for either the neat liquids or concentrated solutions in which the acids exist in their dimeric form. Taking this into account, the appropriate deshieldings noted are increased by 7 ppm (J. B. Stothers and P. C. Lauterbur, *Can. J. Chem.*, 42, 1563 (1964)).

[11] F. P. Boer (*J. Am. Chem. Soc.*, 88, 1572 (1966)) found from X-ray studies that the CCO bond angle in the CH_3CO^+ ion is close to 180°.

[12] K. Frei and J. H. Bernstein, *J. Chem. Phys.*, **38**, 1216 (1963).

[13] Chemical shifts for nitriles lie between 70 and 90 ppm: J. B. Stothers, *Quart. Rev.* (London), **19**, 144 (1965), and references therein.

[14] D. R. McAdams, *J. Chem. Phys.*, **36**, 1948 (1962).

[15] M. Brookhart, G. C. Levy, and S. Winstein, *J. Am. Chem. Soc.*, **89**, 1735 (1967).

[16] N. Muller, *J. Chem. Phys.*, **37**, 2729 (1962).

Table II. $J_{C^{13}H}$ Coupling Constants (in Hertz) Determined from the Proton Spectra of Carbonium Ions (Protonated Acids) and Oxocarbonium Ions (Acyl Cations)

	Solvent	Temp, °C	$J_{C^{13}-H}$	$J_{C^{13}-C-H}$	$J_{C^{13}-C-C-H}$	$J_{C^{13}-O-H}$
HCO_2H	SO_2	−40	225.1			
$HCOOH_2^+$ I	FSO_3H-SbF_5	−75	244.8			8.2
II	FSO_3H-SbF_5	−75	235.8			0.5 0.5
$CH_3CO_2H_2^+$	FSO_3H-SbF_5	−65		6.5		7.5 0.5
CH_3CO^+	FSO_3H-SbF_5	−10		9.3		
$CH_3CH_2CO_2H_2^+$	FSO_3H-SbF_5	−65		6.2	6.2	7.5 0.5
$CH_3CH_2CO^+$	FSO_3H-SbF_5	−10		9.3	8.2	
$C_6H_5CO_2H_2^+$	FSO_3H-SbF_5	−70				3.5

The proton spectrum of protonated propionic acid also shows this difference in the $J_{C^{13}-OH}$ coupling constants. Again the highest field OH resonance is coupled by 7.5 Hz to the C^{13} while the other $J_{C^{13}-OH}$ coupling is unresolved.

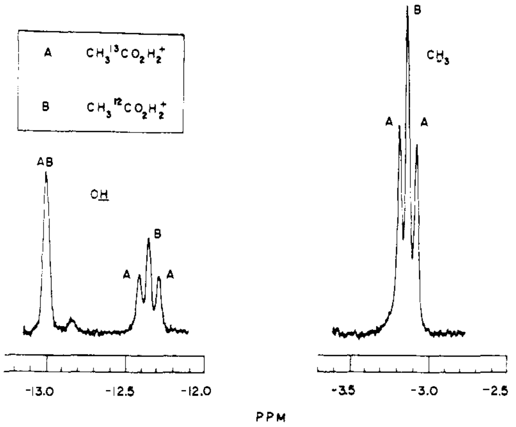

Figure 1. Proton magnetic resonance spectrum of C^{13}-enriched acetic acid in FSO_3H-SbF_5 at −65°.

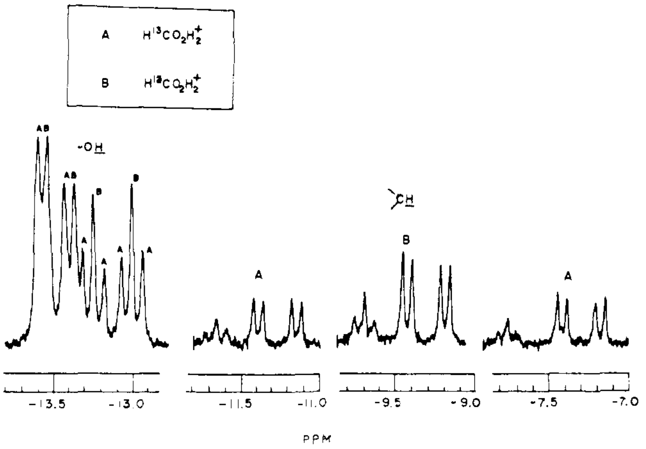

Figure 2. Proton magnetic resonance spectrum of C^{13}-enriched formic acid in FSO_3H-SbF_5 at −75°.

The spectrum of protonated formic acid (Figure 2), in which the OH resonances show the presence of two isomers (I and II, R = H), can be assigned unambiguously on the basis of coupling of the hydroxyl protons with the methine proton.[7,9] Using C^{13}-enriched formic acid it was established that the highest field OH resonance, which is assigned to H_A (I), is coupled by 8.2 Hz to the C^{13} whereas H_B and H_C (I and II) are coupled by less than 0.5 Hz. These results demonstrate that the highest field hydroxyl resonance in protonated acetic, propionic, and formic acids is due, in all cases, to the "inner" proton, H_A.

The C^{13} resonance of protonated formic acid was also observed and shows two doublets resulting from the two isomeric forms of the protonated acid. Chemical shifts were assigned (Table I) on the basis of the intensity of the peaks (structure I predominates over II by a factor of *ca.* 2:1) and from the 9-Hz difference in the $J_{C^{13}-H}$ coupling constants (Table II).

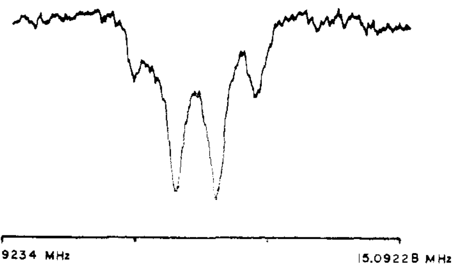

Figure 3. C^{13} INDOR spectrum of $CH_3C^{13}O_2H_2^+SbF_6^-$ (HF solution) observed at 60.0097652 MHz.

The proton spectrum of protonated benzoic acid at −70° has a single OH absorption with a 3.5-Hz $J_{C^{13}O-H}$ coupling. The magnitude of this coupling suggests that the single absorption is a result of rapid rotation about the C–O bonds causing averaging of the two coupling constants. Protonated benzoic acid would be expected to have less double bond character associated with the C–O bonds than the other protonated acids studied due to resonance interaction with the phenyl ring.

The carbon-13 resonance spectra of methyl- and phenylcarboxonium and -oxocarbonium ions were also obtained in hydrogen fluoride solution of the isolated oxocarbonium ion complexes prepared from the acyl fluoride and antimony pentafluoride[5] in the presence, however, of enough moisture to cause partial hydrolysis.

$$\mathrm{RCOF + SbF_5 \longrightarrow RC\overset{+}{O}\,SbF_6^- \longrightarrow RCO_2H_2^+\,SbF_6^-}$$

Owing to the fact that the ionic complexes showed only limited solubility in HF (5–7% solution only could be obtained), it was again necessary to prepare the complexes with the highest C^{13} isotopic concentration (53%) available. In the case of the methylcarboxonium and -oxocarbonium ions, the resonances were observed indirectly in 5-mm sample tubes by the INDOR method of Baker.[17] The greater sensitivity of this method is apparent from the fact that the quartets observed for the two ions were well resolved, while in the direct spectrum only broad peaks were observed. The INDOR spectrum of the methylcarboxonium ion is shown in Figure 3. The chemical shifts obtained by this method agree well with those obtained for the ions in FSO_3H-SbF_5 solution (Table I).

Experimental Section

Formic, acetic, and benzoic acids with 56% C^{13} enrichment of the carboxyl carbon atom were obtained from Merck Sharp and Dohme of Canada, Ltd. Carbon-13-enriched sodium propionate was prepared from ethylmagnesium bromide and carbon dioxide from 53% enriched barium carbonate following the procedure for sodium acetate-1-C^{14}.[18]

The carboxylic acid with C^{13} enrichment of the carboxyl carbon atom was dissolved at −80° in fluorosulfonic acid–antimony pentafluoride (1:1 *M*) using SO_2 as a diluent. A Varian Associates Model HA-60-IL spectrometer operating at 15.1 MHz with a Varian Associates Model V4331A probe adapted to accept a 17-mm dewar flask was used in conjunction with a V-4540 temperature controller. The solution was contained in a 13-mm nonspinning sample tube. A 56% C^{13}-enriched sample of methyl iodide contained in a concentrically mounted, sealed, 5-mm sample tube was used as a reference.[19] The spectra were calibrated by using an audiooscillator to generate side bands of the observed signals.

The method used for obtaining INDOR spectra has been described previously.[5,17] Proton spectra were recorded on a Varian Associates A-56-60-A nmr spectrometer.

Acknowledgments. Support of this work by a grant from the National Institutes of Health is gratefully acknowledged. Dr. E. B. Baker, Chemical Physics Laboratory, The Dow Chemical Company, Midland, Mich., is thanked for the INDOR spectrum.

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(17) E. B. Baker, *J. Chem. Phys.*, **37**, 911 (1962).

(18) A. Murray and D. L. Williams, "Organic Syntheses with Isotopes," Part I, Interscience Publishers, Inc., New York, N. Y., 1958, p 34.

(19) The relaxation time of methyl iodide in our experience was sufficiently short to permit facile homogeneity adjustment of the magnetic field. Dr. G. E. Maciel first observed the advantageous relaxation properties of methyl iodide (~2 sec). The shift of methyl iodide with respect to carbon disulfide was taken as 216.6 ppm: H. Spisecke and W. G. Schneider, *J. Chem. Phys.*, **35**, 722 (1961).

D-Nor Steroids. II. Carbonium Ion Reactions Yielding C-Homo-D-bisnor Steroids[1,2]

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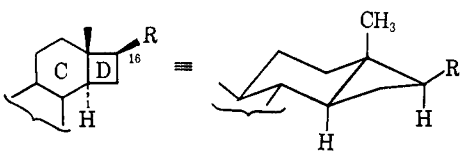
Abstract: Syntheses of the pseudo-equatorially substituted D-nor steroids **7** and **19** are described. Both the deamination of the 16β-amine **7** and attempted *p*-toluenesulfonate formation from the 16β-alcohol **19** result in the production of rearranged products with a C-homo-D-bisnor steroidal skeleton. These results correlate well with previous observations on the tendency of *endo*-5-substituted bicyclo[2.1.1]hexanes (in which the C_5 substituent also occupies a pseudo-equatorial position) to undergo particularly facile rearrangement involving participation of a cyclobutyl carbon–carbon bond.

Within the last half dozen years, many research groups, including one at Cornell, have described syntheses of D-nor steroids.[2,4] One of our original motivations for developing a route to this class of compounds was the opportunity they would provide to explore carbonium ion reactions of a cyclobutane ring held in a specific conformation by virtue of its *trans* fusion to a cyclohexane ring (*i.e.*, the adjacent C ring). Formula **1** shows the conformational situation of a



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16β-substituted D-nor steroid; the 16β substituent occupies a pseudo-equatorial position in this configuration. The corresponding 16α compounds should have pseudo-axial conformations. We have planned to examine carbonium ion reactions such as deaminations and solvolyses in both the 16β and 16α series, and we now wish to report results obtained with the more readily accessible pseudo-equatorially (16β) substituted D-nor-1,3,5(10)-estratrienes.

Synthesis and Deamination of 3-Methoxy-16β-amino-D-nor-1,3,5(10)-estratriene

3-Methoxy-D-nor-1,3,5(10)-estratriene-16β-carboxylic acid (**2**) was prepared from estrone methyl ether[5] es-

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(1) Partial support of this research by the National Institutes of Health (GM-10090) and by Hoffmann-LaRoche, Inc., is acknowledged with pleasure.

(2) For part I, see J. Meinwald, G. G. Curtis, and P. G. Gassman, *J. Am. Chem. Soc.*, **84**, 116 (1962). For some synthetic work complementary to that described in this manuscript, see R. Rausser, *et al.*, *Steroids*, in press.

(3) On leave (1965–1966) from the Laboratoire de Chimie Organique II, Faculté des Sciences, Université de Caen, Caen, France.

(4) (a) J. L. Mateos and O. Chao, *Bol. Inst. Quim. Univ. Nal. Auton. Mex.*, **13**, 3 (1961); (b) M. P. Cava and E. Moroz, *J. Am. Chem. Soc.*, **84**, 115 (1962); (c) G. Müller, C. Huynh, and J. Mathieu, *Bull. Soc. Chim. France*, 296 (1962); (d) A. Hassner, A. W. Coulter, and W. S. Seese, *Tetrahedron Letters*, 759 (1962); (e) H. Reimann, H. Schneider, O. Z. Sarre, C. Federbush, C. Towne, W. Charney, and E. P. Oliveto, *Chem. Ind.* (London), 334 (1963); (f) J. L. Mateos and R. Pozas, *Steroids*, **2**, 527 (1962); (g) J. L. Mateos, O. Chao, and H. Flores R, *Tetrahedron*, **19**, 1051 (1963); (h) A. Horeau and H. B. Kagan, *ibid.*, **20**, 2431 (1964); (i) E. Ghera, *Tetrahedron Letters*, 4181 (1965); (j) G. Quinkert, C. Cimbollek, and G. Buhr, *ibid.*, 4573 (1966); (k) E. Ghera, *ibid.*, 17 (1967).