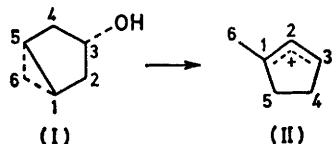


Cyclopropane Ring Opening of Bicyclo[3.1.0]hexan-3-ols in Fluorosulphuric Acid

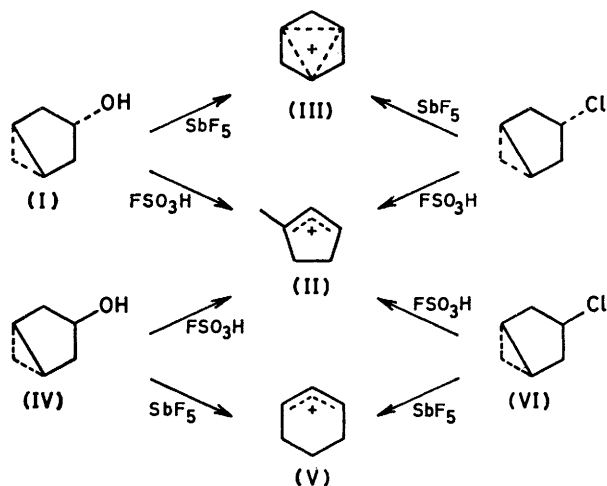
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Reactions of bicyclo[3.1.0]hexan-3-ols with fluorosulphuric acid give rise to cyclopentenium ions by a process involving initial opening of the cyclopropane ring. The process does not put deuterium onto any single carbon atom when carried out in deuteriated acid, and it is suggested that the first step of the reaction is opening of the cyclopropane ring to yield a mixture of isomeric olefins, which then protonate, and eliminate water from the carbocations formed to give the observed cyclopentenium ions. Reactions with antimony pentafluoride involve initial ionisation of the hydroxy-group and yield the trishomocyclopropenium ion or the substituted cyclopropenium ion, except for the 3-phenyl derivative, which behaves differently in that reaction involves ionisation of the hydroxy-group as the first step, but the product is still a cyclopentenium ion. Possible reasons for this behaviour are discussed.

THE reaction of *cis*-bicyclo[3.1.0]hexan-3-ol (I) with $\text{FSO}_3\text{H}-\text{SbF}_5-\text{SO}_2$ at -78° was observed by Olah¹ to yield the 1-methylcyclopentenyl cation (II). When the reaction was carried out with $\text{DF}-\text{SbF}_5-\text{SO}_2\text{ClF}$, there

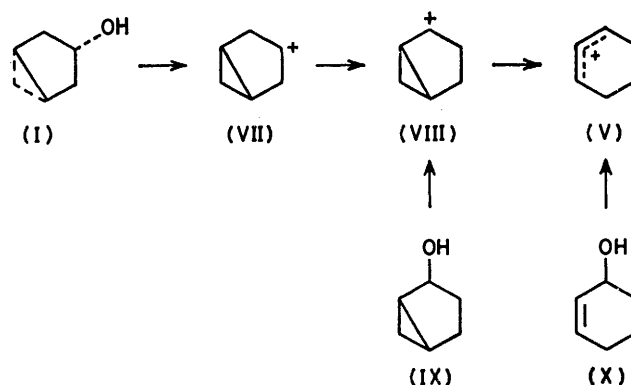


was no detectable deuterium incorporation into (II), suggesting that the reaction proceeded by ionisation at C-3 and migration of the charge to C-2, followed by opening of the cyclopropane ring. Subsequently, Masamune² showed that reaction of *cis*-bicyclo[3.1.0]hexan-3-yl chloride in $\text{SbF}_5-\text{SO}_2\text{ClF}$ at -78° gave the trishomocyclopropenium ion (III), and Olah³ demonstrated that the alcohol (I) reacted with $\text{SbF}_5-\text{SO}_2\text{ClF}$ at -78° to give the same ion. The *trans*-alcohol (IV), which behaved in a similar manner to the *cis*-alcohol with FSO_3H , reacted with SbF_5 to give the cyclohexenium ion (V), as did the *trans*-chloride (VI) with SbF_5 . Both *cis*- and *trans*-chlorides reacted with FSO_3H to give (II). The overall scheme is summarised in Scheme 1.



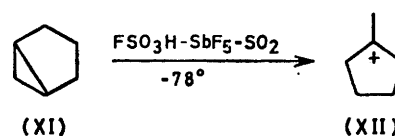
SCHEME 1

Formation of the trishomocyclopropenium ion has been discussed elsewhere.³ Formation of the cyclohexenium ion⁴ probably proceeds *via* the ion (VII). In support of this, we have shown that both *cis*-bicyclo[3.1.0]hexan-2-ol (IX) and cyclohexenol (X) give rise to the ion (V), and Olah³ has shown that a triphenyl derivative of (VII) is



stable at -140° before rearranging to a triphenyl derivative of (V) on warming to -80° .

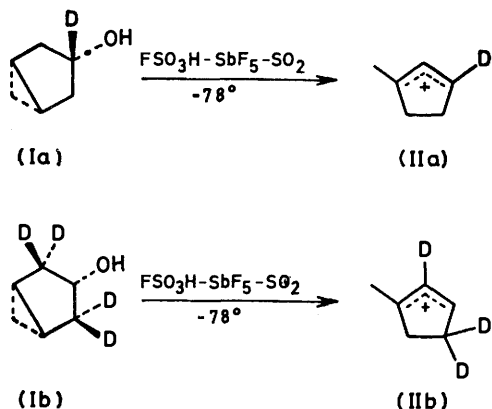
The detailed mechanism of formation of the 1-methylcyclopentenyl cation (II) from the bicyclo[3.1.0]hexan-3-yl alcohols and chlorides remains uncertain. We were able to confirm Olah's observation that deuterium incorporation from a deuteriated acid cannot be detected by ^1H or ^{13}C n.m.r. spectroscopy. As a further test, we reacted bicyclo[3.1.0]hexane (XI) with $\text{FSO}_3\text{H}-\text{SbF}_5-\text{SO}_2$ at -78° , and obtained the 1-methylcyclopentenyl cation (XII). Repetition of the experiment with



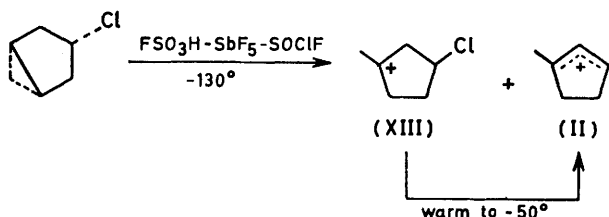
deuteriated acid again produced no detectable incorporation of deuterium. Clearly, formation of (XII) from (XI) must involve the uptake of one deuterium atom from the solvent, so that the deuterium must be scrambled over the ion (XII) so as to make it difficult to detect.

This implies that more than one route is involved in the opening of the cyclopropane ring.

We have investigated the opening of the cyclopropane ring of bicyclo[3.1.0]hexanes by use of deuterium labelling of the substrate. The first label was put on C-3 (Ia), and gave the labelled ion, (IIa). This indicates that the C-3 proton is not involved in the rearrangement leading to formation of (II). We therefore, labelled (I), at positions 2 and 4, to give the tetradeuterio-alcohol (Ib), which yielded the trideuterio-ion (IIb).

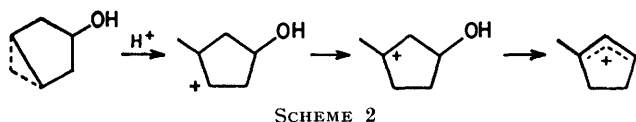


The labelling pattern of (IIb) is consistent with its formation from a 3-hydroxycyclopentyl cation, but we have not been able to observe this ion in superacid conditions. However, the reaction of *cis*-bicyclo[3.1.0]hexan-3-yl chloride in FSO_3H is known to yield the ion (II), as does the alcohol, so it is reasonable to suggest that the mechanisms may be similar, and Farcasiu⁵ has shown that the 3-chlorocyclopentyl cation is sufficiently stable to be observed.

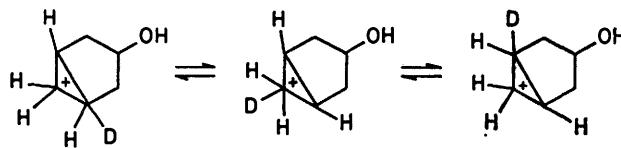


We, therefore, reacted *cis*-bicyclo[3.1.0]hexan-3-yl chloride with $\text{FSO}_3\text{H-SbF}_5\text{-SO}_2\text{ClF}$ at -130° in a bath of a liquid nitrogen-ethanol slush, and observed the spectrum of the resultant mixture. It was found to be a mixture of Farcasiu's ion (XIII) and the ion (II). On warming to -50° , only the ion (II) was observed.

This result clearly indicates how the ion (II) is formed, but reaction by the pathway of Scheme 2 would predict that, in deuteriated acid, the methyl group would be entirely CDH_2 , which is not observed.

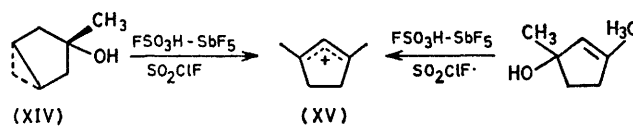


There are two obvious ways in which scrambling of the incorporated deuterium might take place. First, the protonated cyclopropane may have a sufficient lifetime for scrambling to take place before the ring is opened.

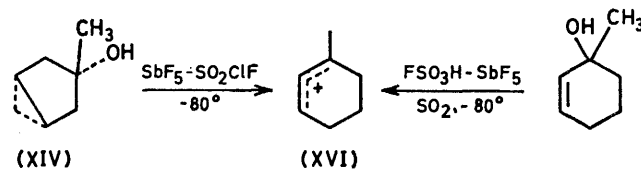


Secondly, the ring may be opened to yield a mixture of olefins, without deuterium incorporation. Subsequent reaction of the olefins with deuteriated acid would then incorporate deuterium onto different carbon atoms.

We sought to distinguish these possibilities by studying reactions of the 3-methyl-substituted bicyclohexanols, in the hope that the changed symmetry of the system would supply the necessary information. When 3-methyl-*cis*-bicyclo[3.1.0]hexan-3-ol (XIV) was reacted with $\text{FSO}_3\text{H-SbF}_5\text{-SO}_2\text{ClF}$ at -130° , the 1,3-dimethylcyclopentenium ion (XV) was observed. Its identity was confirmed by

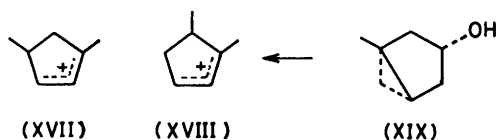


preparation from 1,3-dimethylcyclopent-2-enol, and by comparison with the proton spectrum of the ion described by Deno.⁶ The reaction also yielded a small amount (*ca.* 5%) of the methylcyclohexenyl cation (XVI) which was, however, the sole product when (XIV) was reacted with SbF_5 in SO_3ClF at -80° . The identity of this ion was confirmed by its formation from 1-methylcyclohex-2-enol. The behaviour of (XIV) is thus similar to that of (I).



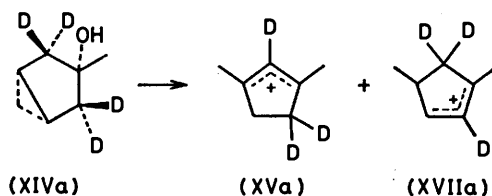
When (XIV) is reacted very slowly with $\text{FSO}_3\text{H-SbF}_5\text{-SO}_2\text{ClF}$ at -78° , it yields two main ions, one of which is (XV), plus a small amount of (XVI). On warming to -15° , the new ion rearranges to (XV). The new ion is not formed at lower temperatures (-130°) nor at higher temperatures (-50°) nor even if the reaction of (XIV) is carried out quickly at -78° (probably because this produces local heating). The ^{13}C spectrum of this new ion was consistent with either the 1,4-dimethylcyclopentenium ion (XVII) or the 1,5-dimethylcyclopentenium ion (XVIII). The ^1H n.m.r. spectrum was different from that of the 1,5-dimethylcyclopentenium ion reported by Sorensen,⁷ and the ^{13}C spectrum was different from that of the 1,5-dimethylcyclopentenium ion prepared by reacting 1-methyl-*cis*-bicyclo[3.1.0]hexan-3-ol (XIX) with $\text{FSO}_3\text{H-SbF}_5\text{-SO}_2$ at -78° .

Reaction of tetradeuterio-(XIV) with $\text{FSO}_3\text{H-SbF}_5\text{-SO}_2\text{ClF}$ slowly at -78° gave deuteriated (XV) and (XVII). Since the ion (XV) has a plane of symmetry the

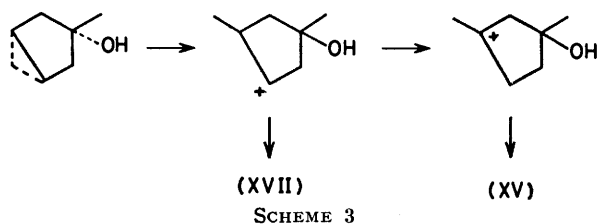


presence of deuterium is revealed by a reduction in the intensity of the peak due to C-4 and C-5. Evidence that deuterium is present, and at least mainly on one atom comes from consideration of the peak due to C-1 and C-3. This is a single peak in the unlabelled ion (XV), but in the labelled ion (XVa) it is separated into two, one peak being 6.7 Hz downfield from the resonance in the undeuteriated ion and the other 5.0 Hz upfield. Saunders⁸ has found similar shifts in the 1-deuteriocyclohexenyl cation.

The formation of (XV) and (XVII) from (XIV) could



be explained in terms of a process such as that in Scheme 3. This simple scheme, however, does not explain the experimental observations to date. As applied to reaction of (I), it predicts that a deuterium atom would be incorporated in the methyl group of the ion, which is not observed. As applied to the reaction of (XIV), it predicts that at low temperatures, the initially formed secondary ion will yield (XVII) as the main observed ion,

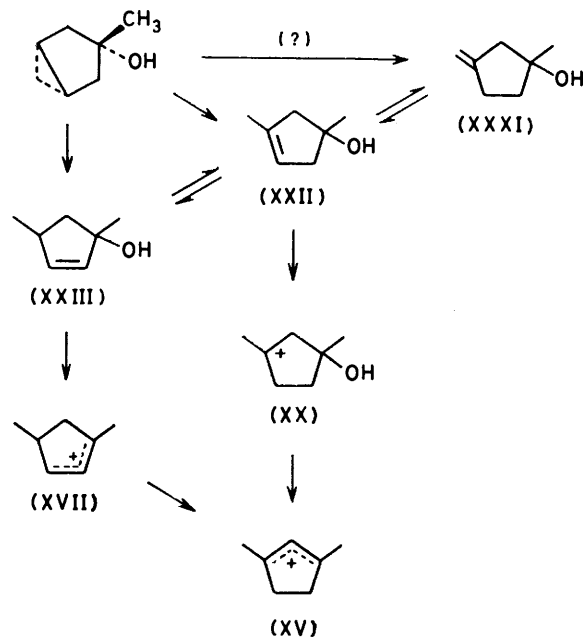


and that as the temperature is raised, then tertiary ion formation will compete more successfully with formation of (XVII), and lead to increasing amounts of (XV) in the observed mixture. In fact, (XV) is the sole product at high and low temperatures, and (XVII) is observed only in the intermediate temperature range.

We suggest that the first step of the reaction consists not of opening the cyclopropane ring to give a carbocation, but rather opening to give an olefin, as in Scheme 4.

At very low temperatures, formation of (XXII) would be predicted by the Saytzeff rule, and this would lead to (XX) and thence (XV). As the temperature was raised, formation of (XXIII), and hence (XVII), would in-

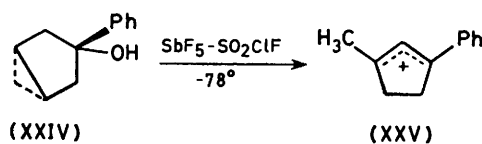
crease. However, the higher temperatures would also favour isomerisation of (XXIII) to (XXII), so that further rises in temperature would lead only to formation of (XV) as observed. A similar scheme for formation of (II) from (I) would lead to deuterium being distributed over three carbon atoms, and would hence be difficult to



detect. In fact, formation of (XV) *via* (XXIII) and (XVII) does not require deuterium incorporation, and a similar route could be written for the formation of (II) from (I).

A reaction of this type is somewhat unexpected, and unprecedented at the temperatures involved. A detailed mechanism for the acid catalysed opening of the cyclopropane ring to an alkene has not been written, but if deuterium is not incorporated, then the initially formed intermediate must be on edge or face protonated cyclopropane. If such an intermediate does lead to opening of the cyclopropane ring, then stabilisation of a positive charge on C-3, by, for example, a phenyl group, should also lead to formation of a cyclopentenium ion rather than a cyclohexenium ion.

We therefore reacted 3-phenyl-*cis*-bicyclo[3.1.0]-hexanol (XXIV) with $\text{SbF}_5\text{-SO}_2\text{ClF}$ at -78° , and obtained only the 3-methylphenylcyclopentenium ion (XXV). Reaction of the 3-methyl alcohol (XIV) and



the unsubstituted *trans*-alcohol (IV) with $\text{SbF}_5\text{-SO}_2\text{ClF}$ yielded cyclohexenium ions by migration of the charge at C-3 to C-2, followed by interaction with the cyclopropane

ring. Phenyl substitution probably prevents this migration, so that interaction of the positive centre at C-3 with the cyclopropane ring can be observed. We cannot exclude the possibility of dication formation, but we have no evidence to support this suggestion either.

The 3-methyl-1-phenylcyclopentenium ion (XXV) was also the sole product of reacting (XXIV) with $\text{FSO}_3\text{H-SbF}_5\text{-SO}_2\text{ClF}$ at -120° . At temperatures below -90° the ^{13}C n.m.r. spectrum of (XXV) clearly showed the two *ortho*-carbon atoms of the phenyl ring as separate peaks, and the two *meta*-carbon atoms as separate peaks showing that rotation of the phenyl ring is slow. On warming the solution to temperatures above -90° , the peaks broadened, and the *meta*-carbon peaks coalesced at -70° , and the *ortho*-carbon peaks at -55° , giving an average value of the free energy of activation for rotation of the phenyl ring of $10.5 \text{ kcal mol}^{-1}$.

Our data are thus consistent with the initial step for the formation of (II) from (I) being opening of the cyclopropane ring to an olefin without incorporation of a proton from the solvent, followed by ionisation of the hydroxy-group. However, the plane of symmetry possessed by all the systems studied restricts observation, and it is not possible to give a detailed mechanism.

EXPERIMENTAL

Materials.—The purity of all materials described in this section was checked by g.l.c., using a 5 ft packed capillary column of Carbowax 20M on Celite.

cis-Bicyclo[3.1.0]hexan-3-ol.—Cyclopentadiene, purified by the method of Moffett,⁹ was hydroborated to cyclopent-2-enol.¹⁰ Reaction by the Simmons-Smith procedure,¹¹ using di-iodomethane with a Zn-Cu couple prepared by the method of Schank and Schechter¹² gave the required product.

Bicyclo[3.1.0]hexan-3-one.—This was prepared by oxidation of the alcohol by the chromic acid method.¹³

It was purified by chromatography on a Florisil column using 7 : 3 pentane-ether as the eluant, and finally purified by sublimation to give a crystalline *solid*, m.p. $37-38^\circ$ (Found: C, 75.05; H, 10.85. $\text{C}_7\text{H}_{12}\text{O}$ requires C, 74.95; H, 10.8%), ν_{max} . 3 300, 2 900, 1 450, 1 370, 1 280, 1 245, 1 130, 1 115, 1 050, 1 023, 912, 890, and 750 cm^{-1} .

3-Phenyl-*cis*-bicyclo[3.1.0]hexan-3-ol.—Reaction of phenyl-lithium with bicyclo[3.1.0]hexan-3-one gave the required compound in 96% yield. Recrystallisation from pentane gave a *solid*, m.p. $66-67^\circ$ (Found: C, 82.6, H, 8.2. $\text{C}_{12}\text{H}_{14}\text{O}$ requires C, 82.7, H, 8.1%), ν_{max} . 3 360, 2 900, 1 440, 1 370, 1 248, 1 050, 1 035, 970, 940, 840, 812, 740, and 695 cm^{-1} .

cis-Bicyclo[3.1.0]hexan-3-yl Chloride.—This was prepared by reaction of the *cis*-alcohol with thionyl chloride, as described by Freeman.¹⁴

trans-Bicyclo[3.1.0]hexan-3-yl Chloride.—This was prepared by reaction of the *cis*-alcohol with *N*-chlorosuccinimide in dry tetrahydrofuran to which triphenylphosphine had been added.¹⁵ After stirring for 4 h at room temperature, the mixture was evaporated to dryness, and the product extracted with pentane to give a yellow oil (61% yield) which was distilled at 40° at water-pump pressure.

1,3-Dimethylcyclopent-2-enol.—3-Methylcyclopent-2-enone, prepared by the method of Robinson,¹⁶ was reacted with methylmagnesium iodide.⁶

endo-2-Bicyclo[3.1.0]hexanol.—Addition of HCl to cyclopentadiene⁹ gave 3-chlorocyclopentene, which was hydrolysed¹⁷ to cyclopent-2-enol. A Simmons-Smith reaction, as described by Friedrich,¹⁸ gave the required alcohol.

1-Methyl-*cis*-bicyclo[3.1.0]hexan-3-ol.—Methylcyclopentadiene, prepared by depolymerisation of the dimer,¹⁹ was hydroborated²⁰ to 1-methylcyclopent-2-enol, which gave the required product *via* a Simmons-Smith reaction.²⁰

Bicyclo[3.1.0]hexane.—A Simmons-Smith^{11,12} reaction of cyclopentene gave the alkane in good yield.

^1H and ^{13}C n.m.r. spectra of all the bicyclo[3.1.0]hexanes described above have been analysed and reported elsewhere.²¹

^{13}C N.m.r. chemical shifts of cyclopentyl and cyclohexyl carbocations (p.p.m. relative to Me_4Si)

Ion	Ring carbon atoms						Methyl on C number			
	1	2	3	4	5	6	1	3	4	5
Methylcyclopentenyl (II)	263.9	149.1	225.1	47.4	51.4		28.7			
1,3-Dimethylcyclopentenyl (XV)	248.5	147.6	248.5	48.7	48.7		26.5	26.5		
1,4-Dimethylcyclopentenyl (XVII)	264.9	147.6	228.7	54.4	58.2		29.1		15.3	
1,5-Dimethylcyclopentenyl (XVIII)	267.3	148.2	224.0	54.4	57.6		27.9			16.3
3-Chloro-1-methylcyclopentenyl (XIII)	334.9	70.3	58.3	37.5	61.5		39.5			
3-Phenyl-1-methylcyclopentenyl* (XXV)	234.5	144.1	222.7	40.5	45.5		25.1			
Cyclohexenyl (V)	224.4	141.9	224.4	37.1	17.5	37.1				
1-Methylcyclohexenyl (XVI)	248.9	140.8	207.5	33.3	19.4	41.4	35.3			

* Phenyl on C-3 has the resonances *ipso*-carbon 132.9, *ortho*-carbon 136.6, 135.2, *meta*-carbon 131.9, 131.4, *para*-carbon 139.7.

trans-Bicyclo[3.1.0]hexan-3-ol.—We were unable to obtain good yields using the Meerwein-Pondorff method,¹⁰ so obtained this alcohol by lithium aluminium hydride reduction of the ketone, followed by chromatography on a Florisil column, using 4 : 1 pentane-ether as the eluant.

2,2,4,4-Tetradeuteriobicyclo[3.1.0]hexan-3-one.—The exchange with deuterium oxide as described by Winstein¹⁰ was used, but reaction was continued for 24 h to obtain >95% incorporation of deuterium.

3-Methyl-*cis*-bicyclo[3.1.0]hexan-3-ol.—Reaction of methylmagnesium iodide with bicyclo[3.1.0]hexan-3-one followed by conventional work-up gave the product in 88%

Preparation of Carbocations.—Solutions of the carbocations were made up by adding slowly a solution of the substrate, in SO_2 or SO_2ClF , to a stirred solution of fluorosulphuric acid, antimony pentafluoride, or a mixture of the two, in the same solvent at dry ice-alcohol bath temperatures. In a few cases, solutions in SO_2ClF were made up in a liquid nitrogen-ethanol slush at -135° . Solutions of the ion were transferred to a 12 mm tube, sealed with plastic film, and the spectra recorded on a Varian XL-100-15 spectrometer. Details of the spectra are given in the Table.

REFERENCES

- ¹ G. A. Olah, G. Liang, and Y. K. Mo, *J. Am. Chem. Soc.*, 1972, **94**, 3544.
- ² S. Masamune, M. Sakai, A. V. Kemp-Jones, and T. Nakashimo, *Can. J. Chem.*, 1974, **52**, 855.
- ³ G. A. Olah, G. K. S. Prakash, T. N. Rawdah, D. Whittaker, and J. C. Rees, *J. Am. Chem. Soc.*, 1979, **101**, 3935.
- ⁴ G. A. Olah, G. K. S. Prakash, and T. N. Rawdah, *J. Org. Chem.*, 1980, **45**, 965.
- ⁵ D. Farcasiu, *J. Am. Chem. Soc.*, 1978, **100**, 1015.
- ⁶ N. E. Deno, H. G. Richey, jun., N. Friedman, J. D. Hodge, J. J. Houser, and C. U. Pittman, jun., *J. Am. Chem. Soc.*, 1963, **85**, 2991.
- ⁷ R. Bladec and T. S. Sorensen, *Can. J. Chem.*, 1972, **50**, 2806.
- ⁸ M. Saunders and M. R. Kates, *J. Am. Chem. Soc.*, 1977, **99**, 8071.
- ⁹ R. B. Moffett, *Org. Synth.*, 1952, **32**, 41.
- ¹⁰ S. Winstein, E. C. Friedrich, R. Baker, and Y. I. Lin, *Tetrahedron*, 1966, Suppl. 8, Part II, 621.
- ¹¹ S. Winstein and J. Sonnenberg, *J. Am. Chem. Soc.*, 1961, **83**, 3235.
- ¹² R. S. Shank and H. Shechter, *J. Org. Chem.*, 1959, **24**, 1825.
- ¹³ W. G. Dauben and G. H. Berezin, *J. Am. Chem. Soc.*, 1967, **89**, 3449.
- ¹⁴ P. K. Freeman, F. A. Raymond, and M. F. Grostic, *J. Org. Chem.*, 1967, **32**, 27.
- ¹⁵ A. K. Bose and B. Lal, *Tetrahedron Lett.*, 1973, 3937.
- ¹⁶ R. M. Acheson and R. Robinson, *J. Chem. Soc.*, 1952, 1127.
- ¹⁷ K. Alder and F. H. Flock, *Chem. Ber.*, 1956, **89**, 1732.
- ¹⁸ E. C. Friedrich and M. A. Saleh, *J. Am. Chem. Soc.*, 1973, **95**, 2617.
- ¹⁹ S. M. Csicsery, *J. Org. Chem.*, 1960, **25**, 518.
- ²⁰ Y. I. Lin, Ph.D. Thesis, U.C.L.A., 1967.
- ²¹ J. C. Rees and D. Whittaker, *Org. Magn. Reson.*, in the press.