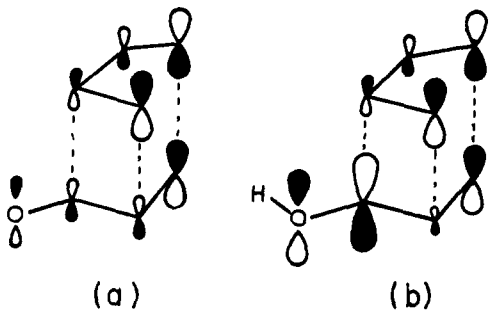

Figure 2. Diene HO–dienophile LU interactions in endo transitions states with (a) acrolein and (b) protonated acrolein.

in the catalyzed reactions resulting from the greatly increased secondary orbital interactions, as well as possible conformational changes in the complexed dienophile,[14] could reasonably be expected to cause such a large effect.

The model proposed here is similar to considerations of changes in dienophile electrophilicity made by others,[11] and suggests no change in mechanism from the normal concerted mechanism of the Diels–Alder reaction. However, this MO model does imply increased asynchroneity in bond-making processes, and if electrostatic effects (first-order interactions) are also considered, two-step mechanisms with cationic intermediates become probable in some cases. Several examples of the type are known,[15] and others have been suggested.[16] Nevertheless, the model proposed here shows that the phenomena generally observed on catalysis can be explained by the concerted mechanism, and allows predictions of the effect of Lewis acids on the rates, regioselectivity, and stereoselectivity of all concerted cycloadditions, including those of ketenes, 1,3 dipoles, and Diels–Alder reactions with "inverse electron demand."

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support of this research.

(15) H. W. Thompson and D. G. Mellilo, *J. Amer. Chem. Soc.*, **92**, 3218 (1970); J. Gasteiger and R. Huisgen, *ibid.*, **94**, 6541 (1972).

(16) M. F. Ansell and A. A. Charalambides, *J. Chem. Soc., Chem. Commun.*, 739 (1972).

(17) Camille and Henry Dreyfus Foundation Teacher-Scholar Grant Recipient, 1972–1977.

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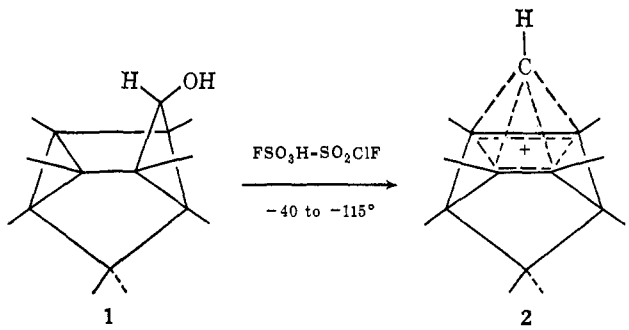
Received March 3, 1973

Degenerate Rearrangements of Bicyclo[3.2.1]octa-3,6-dien-2-yl Cations

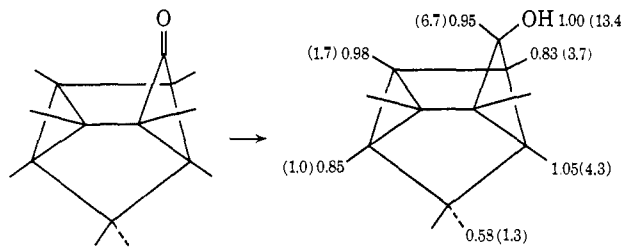
Sir:

We recently reported that the carbonium ion produced from **1** in FSO_3H–SO_2ClF over the temperature range −115 to −40° either has the symmetric structure **2** or is a mixture of ions which rapidly equilibrate with the same net effect on the ion's proton and ^{13}C nmr spectra.[1-3] We now find that replacement of the secondary hydrogen by a methyl group changes the structure of the carbonium ion produced; we also describe a novel and unexpected degenerate rearrangement of the ion which is formed.



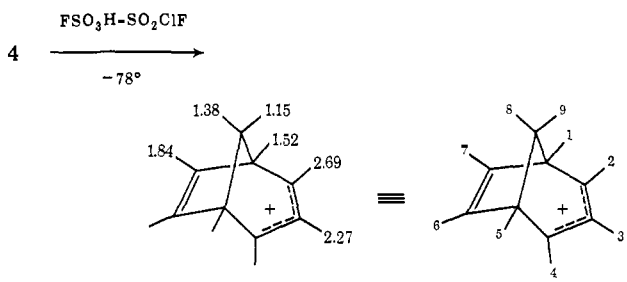
1 2

Treatment of **3**[4] (1.0 g in 10 ml of ether, 0°) with methyllithium gave a single crystalline tertiary alcohol **4**.[5-7] Unlike **1**, **4** did not give a sharp, well defined



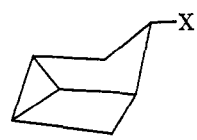
3 4

pmr spectrum over a wide temperature range in FSO_3H–SO_2ClF (1:4). But at −90° a well resolved spectrum was obtained, which we assign to the nonamethylbi-



5

(2) A similar ion is probably involved in the solvolysis of i: R. K.



i

Lustgarten, *ibid.*, **94**, 7602 (1972). Several systems which may be amenable to the formation of such ions have been described: R. M. Coates and K. Yano, *Tetrahedron Lett.*, 2289 (1972); S. Masamune, R. Vukov, M. J. Bennett, and J. T. Purdham, *J. Amer. Chem. Soc.*, **94**, 8239 (1972).

(3) These ions are bis homo derivatives of the $(CH)_5^+$ ions discussed by W.-D. Stohrer and R. Hoffmann, *ibid.*, **94**, 1661 (1972), and studied experimentally by S. Masamune and coworkers, *ibid.*, **94**, 8955, 8956 (1972).

(4) H. Hart and G. M. Love, *ibid.*, **93**, 6266 (1971).

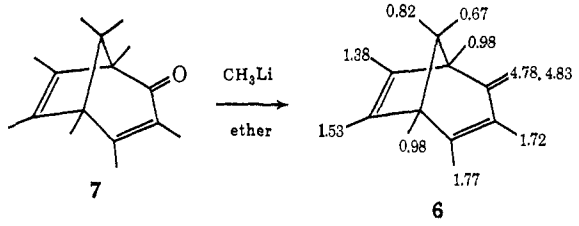
(5) The structures show proton chemical shifts in ppm from TMS and in parentheses the relative slopes of the downfield shifts caused by adding Eu(fod)$_3$. The solvent for neutral substances was carbon tetrachloride. The internal reference for the carbonium ion spectra was $(CH_3)_4N^+BF_4^-$, δ 3.13.

(6) Analytical data and mass spectra were consistent with the structure.

(7) Nearly quantitatively yield, sublimes, ir 3450 cm^{-1}; the stereochemistry follows from the Eu-shift data.

(1) H. Hart and M. Kuzuya, *J. Amer. Chem. Soc.*, **94**, 8958 (1972).

cyclo[3.2.1]octa-3,6-dien-2-yl cation (**5**).[8] Solutions of the ion, when quenched at −78° with CH_3OH–$NaOCH_3$, gave a single hydrocarbon **6** in nearly quantitative yield. The structure of **6** is based on its spectra[9] and its independent synthesis from **7**.[4,10] Solutions of



7 6

6 in FSO_3H–SO_2ClF at low temperatures gave the same spectra as did **4**.

The unusual changes in the pmr spectrum of **5** as the temperature is raised from −125 to −50° are shown in Figure 1. Above −90°, the peak at δ 1.52 remains sharp showing that the bridgehead methyls (1,5) do not equilibrate with the remaining methyls.[11] At −80° the signals (δ 1.38, 1.15) due to methyls 8 and 9 have coalesced, and those (δ 2.27, 1.84) of methyls 3, 6, and 7 are considerably broadened. These coalesce at about −74°, and at −64° their combined signal has also coalesced with that (δ 2.69) due to methyls 2 and 4. These changes are reversible, but if the temperature is maintained at −60° or above for an extended time, a unique irreversible change occurs which will be discussed in a separate communication. The pseudo-first-order rate constant for the equilibration process as determined from the line shapes of the signals for methyls 8 and 9[12,13] was 15.1 ± 0.1 sec^{-1} at −88°, $\Delta E^{\ddagger}$ 7.4 kcal/mol, $A = 1.2 \times 10^{10}$ sec^{-1}.

One way to account for the observed exchange is *via* a 1,2-vinyl shift (Scheme I). This may occur in either of two equivalent ways (A and B), each of which ensures that methyls 1 and 5 remain unique and 8 and 9 exchange. Both paths also equilibrate methyls 2, 3, 4, 6, and 7. However, in path A methyl 2 remains at the terminus of the allyl cation; the same is true of methyl 4 in path B. Consequently the signal due to these methyls would be expected to equilibrate with that of methyls **6** and **7** at a slightly slower rate than does the signal for methyl **3**, as observed. The overall result is the circumambulation of the bridgehead carbons and the one-carbon bridge around the 2,3,4,6,7 framework.

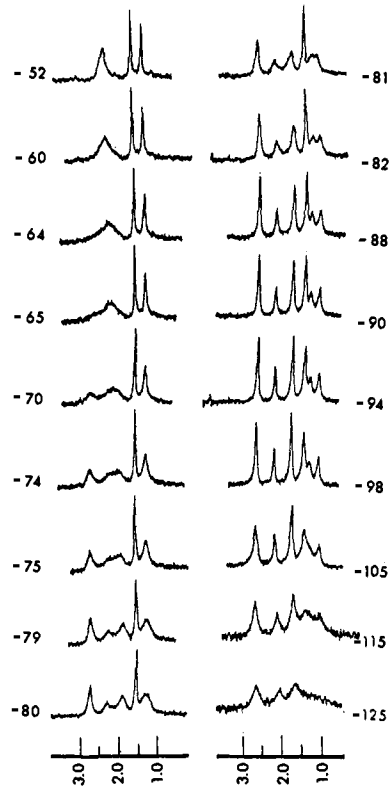
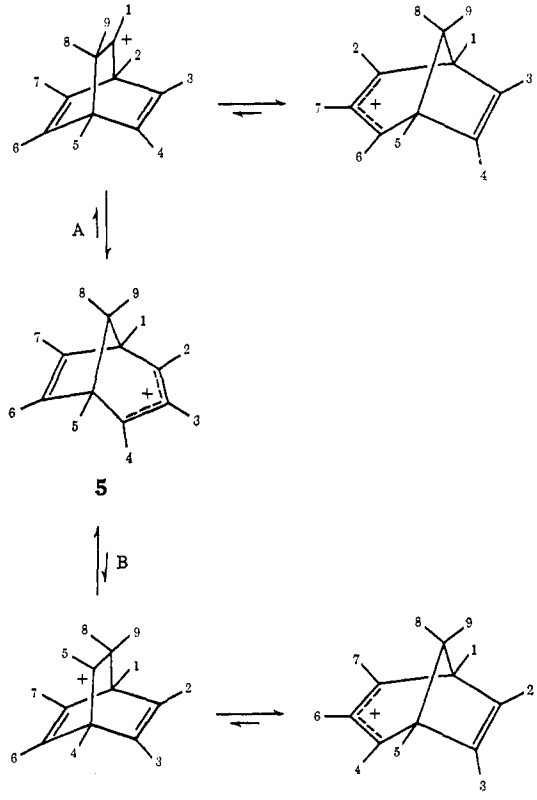


Figure 1. The temperature-dependent nmr spectrum of **5** in FSO_3H–SO_2ClF (1:4), reduced 1000 times. In the −90° spectrum, peaks from low to high field are assigned as follows: peak 1 (methyls 2 + 4), 2 (3), 3 (6 + 7), 4 (1 + 5), 5 and 6 (8 and 9). The variable temperature probe was calibrated before use.

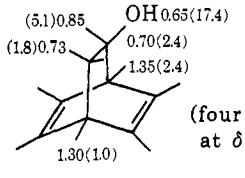
Scheme I



(8) The nmr chemical shifts are consistent with this structure; for comparison with similar 1,2,3-trimethylallyl cations see N. C. Deno in "Carbonium Ions," Vol. 2, G. A. Olah and P. von R. Schleyer, Ed., Wiley-Interscience, New York, N. Y., 1970, p 796.

(9) Ir 1592, 1612 cm^{-1}; $\lambda_{max}^{95\%\ EtOH}$ 247 nm (ε 13,800); *m/e* 230 (M^+).

(10) **6** was also obtained from the tertiary alcohol ii and acid; ii



(four allylic methyl groups at δ 1.62, 1.68)

ii

(mp 164°, sublimes) was obtained from the corresponding ketone.[4]

(11) This result rigorously excludes the 1,2-bridge shift, which would equilibrate methyls 1–7, as the process being observed. Labeling experiments show that such shifts do occur, but at a rate too slow to observe by nmr. Details will be presented in a full paper.

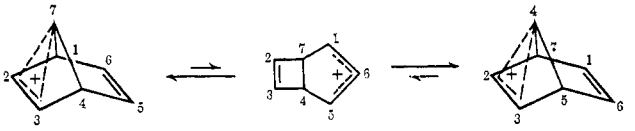
(12) The nmr pattern was compared at five temperatures (from −57 to −88°) with theoretical curves for cyclohexane-d_{11}: F. A. Bovey, "Nuclear Magnetic Resonance Spectroscopy," Academic Press, New York, N. Y., 1969, p 188.

(13) At temperatures below −98° certain peaks, in particular that due to methyls 1 and 5, begin to broaden and overlap. This may be a consequence of the increased lifetime of the intermediate ions (**8–10**) and an averaging of their spectrum with that of **5**.

Scheme I is a formalism for rationalizing the nmr results; the intermediate ion **8** may, however, better be represented by structure **9** or **10**.[14]

9 10

We call attention to the complementary relationship between our results and those observed several years ago on the 7-norbornadienyl cation (**11**).[15] There a



11 12 11′

stepwise circumambulatory motion of five carbons (1, 6, 5, 4, 7) with respect to the two "bound" vinyl carbons (2, 3) was rationalized *via* the [3.2.0] allylic ion **12**. Ion **12** was not observed at −78° in the nmr spectrum, the only detectable ion being **11**. When the ring system is expanded by one carbon atom, as we report here, the converse obtains; only the allylic ion (*i.e.*, **5**) can be observed by nmr; the intermediate ion (**8–10**) goes undetected. This inversion in the relative stabilities of the ions is reasonable since the cationic site is now "off-center" with respect to the stabilizing double bond (see **10**).

The mechanism by which **5** is formed from **4** is being investigated.

Acknowledgment. We are indebted to the National Science Foundation and the National Institutes of Health for financial support and to Professors Max T. Rogers and D. G. Farnum for stimulating discussions.

(14) H. Hogeveen and C. J. Gaasbeek, *Recl. Trav. Chim. Pays-Bas*, 88, 367 (1969).

(15) R. K. Lustgarten, M. Brookhart, and S. Winstein, *J. Amer. Chem. Soc.*, 89, 6350 (1967).

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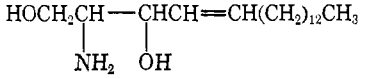
Received February 1, 1973

A Stereoselective Synthesis of D-*erythro*-Sphingosine

Sir:

We would like to report a short, highly stereoselective synthesis of D-*erythro*-sphingosine (**1**) (1,3-dihydroxy-

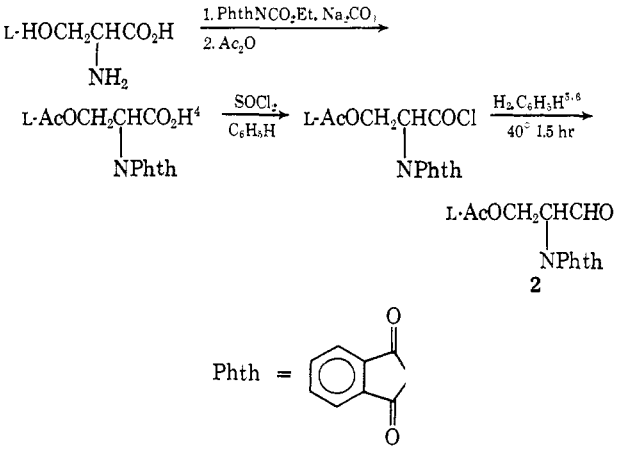


1

2-aminooctadec-2-*trans*-ene), the most widely occurring of the sphingolipid bases.[1] The attractive features of this novel synthesis, not shared in combination by those previously reported,[2] are its brevity, the direct formation of a chiral product with predominantly the correct stereochemistry, and its potential for ready adaptation to the synthesis of other homologs, ceramides, cerebrosides, and more complex sphingolipids.

The synthesis involves the simple conversion of the commercially available L-serine whose chiral center corresponds to that of sphingosine (**1**)[3] to the L-aldehyde **2**[7] by N-phthaloylation, O-acetylation, acid chloride formation, and catalytic hydrogenation as indicated in Scheme I.

Scheme I



Addition (*ca.* 15 min) of 6.6 g of the chiral aldehyde **2**[7] in 30 ml of benzene–ether (2:1) to 0.024 mol of *trans*-pentadecenyldiisobutylalane in hexane (40 ml)[8] at 5–10° and allowing an additional hour for warming to room temperature furnished directly D-*erythro*-*O*-acetyl-*N*-phthaloylsphingosine (**3**)[9] (1.5 g) obtained as an oil, $[\alpha]_D$ +3.3° (*c* 0.37, EtOH),[10] along with the unnatural threo isomer **4** (0.4 g), mp 55–63°.[11] The

(1) For recent reviews, see: (a) K. A. Karlsson, *Lipids*, **5**, 878 (1970); (b) J. Kiss, *Advan. Carbohyd. Chem. Biochem.*, **24**, 381 (1969); (c) P. Morell and P. Braun, *J. Lipid Res.*, **13**, 293 (1972).

(2) The various chemical approaches to the synthesis of the sphingolipid bases reported to date have been recently reviewed: D. Schapiro, "Chemistry of Sphingolipids," Hermann, Paris, 1969.

(3) R. M. Burton, M. A. Sodd, and R. O. Brady, *J. Biol. Chem.*, **233**, 1053 (1958).

(4) J. C. Sheehan, M. Goodman, and G. P. Hess, *J. Amer. Chem. Soc.*, 78, 1367 (1956).

(5) The conditions used are a modification of those described by W. Foye and W. E. Lange, *J. Amer. Pharm. Ass. Sci. Ed.*, **45**, 742 (1956).

(6) The optical rotation of triacetyl-D-*erythro*-sphingosine prepared from **1** obtained below ($[\alpha]_D$ −10.6° (*c* 0.3, $CHCl_3$)) is in essential agreement with the literature value (*Beilstein III*, **4**, 855) indicating that the hydrogenation of the acid chloride to produce **2** proceeded without racemization. By contrast, H. Seki, *et al.* (*Chem. Pharm. Bull.*, **20**, 361 (1972)), report that extensive racemization occurred during the catalytic hydrogenation of alkoxyformic anhydrides of *N*-acetylamino acids.

(7) Obtained as a colorless oil. A comparison of intensity ratios of the aldehydic proton and the phthaloyl and $-CH_2CH-$ protons indicated the crude product to contain *ca.* 50% of the desired aldehyde.

(8) H. Newman, *Tetrahedron Lett.*, 4571 (1971).

(9) The apparent change in configuration of C-2 from L in the serine derivatives to D in sphingosine and its derivatives is actually the result of a change in reference origin. In the former series, as with all amino acids, the molecule is, according to convention, oriented in two dimensions with its carboxyl group up. This puts the amino group having the L optical configuration on the left. In the latter series, the terminal OH is oriented upward. This now places the same amino function on the right, therefore, the D optical configuration.

(10) Satisfactory analytical data were obtained for this compound.

(11) After further thick-layer chromatographic purification (2-mm silica gel; C_6H_6–EtOAc, 9:1) of the product isolated from the partition chromatogram. Since Re tlc of this product still showed slight contamination with a slightly faster running impurity, its optical rotation was not measured. Unequivocal characterization of **4** was accomplished by converting it exclusively to the known *N*-acetyl-D-*threo*-sphinganine (E. F. Jenny and C. A. Grob, *Helv. Chim. Acta*, **36**, 1454 (1953)) by catalytic hydrogenation, followed by blocking group removal as described in the main discussion and then N-acetylation (by the method of R. C. Gaver and C. C. Sweeley, *J. Amer. Chem. Soc.*, 88, 3643 (1966)).