Figure 1. Computer-drawn X-ray structure showing the absolute configuration of the p-bromophenacyl ester of tirandamycic acid.

(hydrazine hydrate and ethanolic acetic acid) to an allyl alcohol (4), which was not isolated but reduced further by lithium aluminum hydride to streptolol (5),[4] isolated as its monoacetate: $C_{20}H_{30}O_5$;[12] $[\alpha]^{29}D +112°$ (c 0.998, CHCl$_3$). The same monoacetate, $[\alpha]^{29}D +108°$ (c 1.12, CHCl$_3$), was obtained by acetylation of an authentic sample of streptolol, the lithium aluminum hydride reduction product of streptolic acid (6).[4] The two samples of streptolol acetate were identical in their nmr, ir, and mass spectral as well as tlc behavior in three solvent systems. Thus, the absolute stereochemistry of streptolic acid is the same as that of tirandamycic acid.
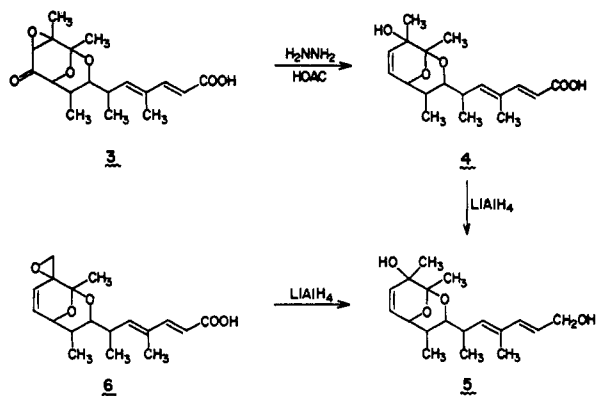

The stereochemistry of the β-methylaspartic acid portion of streptolydigin was earlier assigned as L-threo.[5] Similarly, the stereochemistry of the 2,3,6-trideoxyhexose was assigned as L-threo by independent methods in two laboratories.[13,14] It only remains to assign the anomeric configuration of the sugar. With L-threo stereochemistry the substituents at C-4 and C-5 of the trideoxyhexose portion of the antibiotic cannot both be equatorial and the sugar will adopt whatever conformation makes the bulky anomeric substituent at C-1 equatorial. This is conformation a if the anomeric configuration is α-L or conformation b if it is β-L. In conformation a the C-4 hydroxyl would be equatorial; in conformation b the C-4 hydroxyl would be axial. In fact, the half-band width of the C-4 proton of ydiginic acid[5] is 7 Hz, appropriate only for an

(12) High-resolution mass spectral data, obtained on a Varian MAT SM-1B mass spectrometer, were in agreement with the formula cited. The high-resolution mass spectrometer and data processing equipment employed in the present study were provided by National Institutes of Health Grants CA 11388 and GM 16864, from the National Cancer Institute and the National Institute of General Medical Sciences, respectively.

(13) C. L. Stevens, P. Blumbergs, and D. L. Wood, J. Amer. Chem. Soc., 86, 3592 (1964).

(14) A. C. Button, Ph.D. Thesis, University of Illinois, 1967.
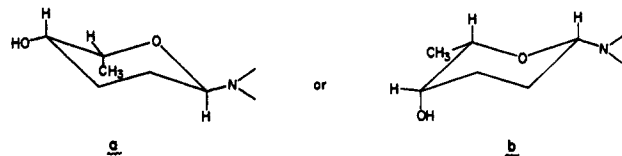
equatorial[15] proton, while the acetoxyl methyl singlet appears at δ 2.15, appropriate only for an axial acetoxyl.[16] Thus, conformation b is indicated, in which the C-1 configuration is S (β-L).

With this point settled the total absolute configuration of streptolydigin can be assigned as 2.

(15) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 2, Pergamon Press, New York, N. Y., 1966, p 700.

(16) F. W. Lichtenthaler, Chem. Ber., 96, 2047 (1963).

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Structure of $C_2H_5^+$ at Low Vibrational Energies

Sir:

The structure of simple carbocations has been a matter of extensive discussion in the recent literature.[1-5] In this communication we demonstrate that randomization of hydrogen atoms in ethyl ion is rapid relative to intermolecular hydride transfer and estimate an upper limit of the activation energy for hydrogen atom scrambling.

Theoretical investigations of the ethyl cation have fluctuated between support of a classical ethyl ion structure favored by ab initio molecular orbital calculations and a nonclassical protonated ethylene structure favored by semiempirical calculations. In both cases the predicted structures are artificially favored. Hariharan, Lathan, and Pople have recently examined the structure of $C_2H_5^+$ by ab initio molecular orbital theory.[5] Their calculations used an extended basis set including polarization functions (d functions on carbon and p functions on hydrogen). These near Hartree–Fock results indicate the nonclassical form of ethyl ion to be more stable than the classical form by 0.9 kcal/mol. The inclusion of correlation energy, which was not explicitly considered by Hariharan, et al., may favor the nonclassical structure even more.

From the available experimental evidence it now seems established that ethyl ion produced by radiolysis,

(1) R. Sustman, J. W. Williams, M. J. S. Dewar, L. C. Allen, and P. von R. Schleyer, J. Amer. Chem. Soc., 91, 5350 (1969).

(2) J. W. Williams, V. Buss, L. C. Allen, P. von R. Schleyer, W. A. Lathan, W. J. Hehre, and J. A. Pople, J. Amer. Chem. Soc., 92, 2141 (1970).

(3) G. V. Pfeiffer and J. G. Jewett, J. Amer. Chem. Soc., 92, 2143 (1970).

(4) W. A. Lathan, W. J. Hehre, and J. A. Pople, J. Amer. Chem. Soc., 93, 808 (1971).

(5) P. C. Hariharan, W. A. Lathan, and J. A. Pople, Chem. Phys. Lett., 14, 385 (1972).

photolysis, and electron impact in the gas phase at ambient temperatures randomizes before it can undergo proton transfer or hydride abstraction.[6-8]
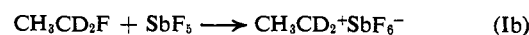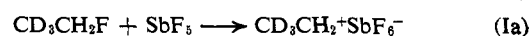
We have confirmed this randomization of hydrogen atoms in ethyl ion using high-pressure mass spectrometry[9] with CD_3CH_2I as the source of ethyl ion and as proton acceptor. The ratio of deuteron to proton transfer at a pressure of 0.1 Torr was found to be 1.29 ± 0.03 in excellent agreement with the ratio of 1.32 reported by Ausloos, Rebbert, Sieck, and Tiernan.[8] The production of ethyl ion by photon or electron impact relies upon fragmentation of parent ions initially formed with vibrational excitation. The thermal vibrational energy in the nascent ion is therefore augmented by the excess internal energy resulting from the well known kinetic shift. Therefore, the distinction between structures whose relative stabilities differ by no more than 4-5 kcal/mol may be obscured.

It is possible, however, to generate ions with very low vibrational energies in solution at low temperatures by chemical reaction in strong acids such as antimony pentafluoride or fluorosulfonic acid–antimony pentafluoride mixtures. Olah, et al., have produced a series of alkyl ions by addition of the corresponding alkyl fluorides to an antimony pentafluoride solution at reduced temperatures and have determined their structure using nmr spectroscopy.[10a] Olah, DeMember, Schlosberg, and Halpern recently investigated ethyl fluoride–antimony pentafluoride complexes at low temperature in SO_2 solution.[10b] When CD_3CH_2F was allowed to react with excess SbF_5–SO_2, FSO_3H–SbF_5–SO_2, or HF–SbF_5–SO_2 at −78°, the pmr spectra showed a statistical distribution of H and D in the $C_2H_2D_3$ moiety. When CH_3CH_2F was added to FSO_3D–SbF_5 or DF–SbF_5 at −78° in SO_2, there was no detectable incorporation of deuterium in the ethyl group. Olah, et al., concluded that the fast intramolecular exchange and slow intermolecular proton exchange were consistent only with an ethyl cation with randomized hydrogens. However, on the nmr time scale, one is unable to observe directly phenomena with lifetimes shorter than 10^{-5} sec.

With a normal frequency factor of $10^{13.2}$ sec^{-1} for 1,2-hydride shift[11] and requiring the rate constant to be 10^5 sec^{-1} or less, the minimum Arrhenius activation energy observable at −100° is about 7 kcal/mol. This is several times the currently best calculated energy difference between the classical structure and the bridged structure, which may be regarded as the transition state for hydride transfer. Hence, it is not unexpected that rapid intramolecular hydrogen scrambling is observed.

We have generated labeled ethyl ions by introducing the corresponding ethyl fluoride (CD_3CH_2F or CH_3CD_2F) to a solution of SbF_5 (0.2 M) in SO_2 at −78°

(reaction I). In the presence of a hydride (deuteride)

$$CD_3CH_2F + SbF_5 \longrightarrow CD_3CH_2^+SbF_6^- \quad \text{(Ia)}$$

$$CH_3CD_2F + SbF_5 \longrightarrow CH_3CD_2^+SbF_6^- \quad \text{(Ib)}$$

donor such as cyclohexane-d_0 (d_{12}) (0.1 M), ethyl ions undergo hydride (deuteride) transfer (reaction II) to

$$CD_3CH_2^+SbF_6^- + c\text{-}C_6H_{12} \longrightarrow C_2D_3H_3 + c\text{-}C_6H_{11}^+SbF_6^- \quad \text{(IIa)}$$

$$CH_3CD_2^+SbF_6^- + c\text{-}C_6D_{12} \longrightarrow C_2D_3H_3 + c\text{-}C_6D_{11}^+SbF_6^- \quad \text{(IIb)}$$

form ethane. This reaction is very fast, going to completion within seconds. The yield of ethane is approximately 90% with trace amounts of ethylene and butanes. Hydrogen atom scrambling in ethane produced in II is not important as shown by addition of CD_3CH_3 to a SbF_5–SO_2 solution at −78° and to a $c\text{-}C_6D_{12}$–SbF_5–SO_2 solution at room temperature. In both cases mass spectrometric and gas chromatographic analysis of the recovered, noncondensable vapors showed no decomposition of the ethanes and no change in the isotopic distribution of hydrogens. Experiments with ethyl-d_2 or -d_3 fluoride and perdeuteriocyclohexane at −78° yielded no ethanes containing more than three or four deuterium atoms, respectively, indicating that hydrogen exchange between ethyl ion and cyclohexane is not important at this temperature. Ethyl ions were also generated by addition of CD_3CH_2F to antimony pentafluoride and cyclohexane at 77°K with subsequent warming to room temperature with agitation. In this case, the yield of ethane decreases to approximately 50%.

From the isotopic distribution of the ethanes formed in reaction II it should be possible to ascertain the structure of the ethyl ion prior to addition of hydride ion. If the ground-state ion exists in a static classical structure, CD_3CH_3 would be the only ethane formed. On the other hand, if the ground-state ion exists only in a nonclassical structure, a deuteron will occupy the bridging position. Neglecting isotope effects, the incoming hydride will have an equal probability of going to either carbon. Therefore, the ratio of CD_2HCDH_2–CD_3CH_3 would be unity. However, if the hydrogen atoms are completely randomized as they have been found to be in the gas phase, the isotopically scrambled ions, $CDH_2CD_2^+$ and CD_2HCDH^+, are favored by a factor of 9 over $CD_3CH_2^+$ and the ratio of CD_2HCDH_2 to CD_3CH_3 would therefore be 9:1. Table I summarizes the partial mass spectra of CD_3CH_3, CD_2-$HCDH_2$, and mixtures of CD_2HCDH_2 and CD_3CH_3 prepared from authentic samples and those of ethanes obtained from reaction II. The spectra of the ethanes from reaction II are consistent with that of a 9:1 ratio of CD_2HCDH_2 to CD_3CH_3. The agreement of the

(6) P. Ausloos and S. Lias, J. Chem. Phys., 36, 3163 (1962).

(7) R. E. Rebbert and P. Ausloos, presented at the 155th Meeting of the American Chemical Society, San Francisco, Calif., April, 1968.

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(9) G. Sroka, C. Chang, and G. G. Meisels, J. Amer. Chem. Soc., 94, 1052 (1972).

(10) (a) G. A. Olah and P. von R. Schleyer, "Carbonium Ions," Wiley-Interscience, New York, N. Y., 1970, pp 715-783; (b) G. A. Olah, J. R. DeMember, R. H. Schlosberg, and Y. Halpern, J. Amer. Chem. Soc., 94, 156 (1972).

(11) (a) M. Saunders and E. L. Hagen, J. Amer. Chem. Soc., 90, 2436 (1968); (b) D. M. Brouwer and E. L. Mackor, Proc. Chem. Soc., London, 147 (1964).

Table I. Partial Mass Spectra of CD_2HCDH_2, CD_3CH_3, and CH_2DCHD_2–CD_3CH_3 Mixtures and of Ethanes Obtained in SO_2 and Cyclohexane[a]

m/e	CD_2HCDH_2	CD_3CH_3	CD_2HCDH_2:CD_3CH_3 1:1	CD_2HCDH_2:CD_3CH_3 9:1	Ethane formed in SO_2	Ethane formed in Cyclohexane
33	100	100	100	100	100[b]	100[c] 100[c]
32	71	51	62	69	67	71	69
31	183	72	128	173	170	175	166
30	270	340	303	277	282	279	280

[a] All spectra have been corrected for abundance of ^{13}C. [b] CH_3-CD_2F and $c\text{-}C_6D_{12}$. [c] CD_3CH_2F and $c\text{-}C_6H_{12}$.

spectra of the ethanes from reaction of $C_2D_3H_2^+$ with cyclohexane-d_0 and $C_2H_3D_2^+$ with cyclohexane-d_{12} is taken to indicate that secondary deuterium isotope effects are not important. It is of interest to note that the data of Ausloos, et al.,[3] also show that secondary deuterium isotope effects are unimportant in the hydride abstraction reaction of ethyl ion in the gas phase. We conclude therefore that hydrogen atoms in ethyl ion are completely randomized prior to hydride transfer even at low vibrational energies and lifetimes very much shorter than those observable by nmr spectroscopy.

Although the ground-state structure of the ethyl ion cannot be ascertained from these data, it is possible to estimate the activation energy for intramolecular hydride transfer. From the observed randomization of hydrogens in ethyl ion, it follows that the rate of the intramolecular hydride shift must be rapid with respect to the rate of intermolecular hydride transfer. Intermolecular hydride transfer may be assumed to occur on the first collision of ethyl ion and cyclohexane as it does in the gas phase.[12] For the ethanes formed in SO_2 solution the rate of intermolecular hydride transfer is limited by the rate of diffusion which is approximately 4×10^9 l./(mol sec).[13] At a cyclohexane concentration of 0.1 M, the pseudounimolecular rate constant is 4×10^8 sec^{-1}. For the hydrogen atoms to become completely randomized prior to hydride transfer, the unimolecular rate constant for 1,2-hydride shift in ethyl ion must be at least an order of magnitude greater than the rate of hydride transfer. With a normal frequency factor of $10^{13.2}$ sec^{-1} for 1,2-hydride shift and requiring the unimolecular rate constant for randomization to be greater than 4×10^9 sec^{-1}, one calculates the maximum permissible Arrhenius activation energy to 3.5 kcal/mol. However, ethyl ions formed in neat cyclohexane undergo hydride transfer at a rate determined by the collision frequency in the liquid, which corresponds to a pseudounimolecular rate constant of 6×10^{10} sec^{-1}[13] and an upper bound on the Arrhenius activation energy of 1.9 kcal/mol. Although this estimate does not identify the ground-state structure for the ethyl ion, it does indicate that the two structures must be very close in terms of stability as suggested by Hariharan, Lathan, and Pople.[5]

(12) J. H. Futrell and T. O. Tiernan in "Fundamental Processes in Radiation Chemistry," P. Ausloos, Ed., Wiley-Interscience, New York, N. Y., 1968, pp 171–280.

(13) M. V. Smoluchowski, Z. Phys. Chem., 92, 129 (1918).

J. H. Vorachek, G. G. Meisels,* R. A. Geanangel, R. H. Emmel

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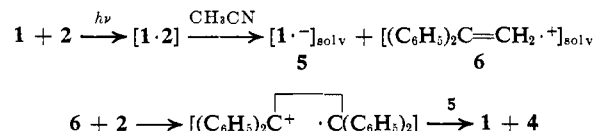## Radical Ions in Photochemistry. I. The 1,1-Diphenylethylene Cation Radical[1]

Sir:

As part of our effort to define the scope and limitations of the photocycloaddition of carbonyl compounds

to olefins, our attention was attracted by the recent finding that aromatic esters, substituted with electron-withdrawing groups, for example methyl p-cyanobenzoate (1), can undergo this reaction.[2] The mechanism first proposed[2a] involved reaction of the n,π^* triplet of 1 in the usual sense.[3] The same authors[2b] later considered an exciplex mechanism with the electron-deficient ester acting as the acceptor.[4]

When we irradiated solutions of 1 and 1,1-diphenylethylene (2) in benzene-d_6 and in acetonitrile-d_3 under comparable conditions,[5] the rate of formation of 2-methoxy-2-(p-cyanophenyl)-3,3-diphenyloxetane (3) decreased slightly with increasing solvent polarity whereas 2 was consumed about ten times faster in the nitrile solution.[6] A new product was isolated in 70% yield (column chromatography on silica gel) from a preparative run in acetonitrile and identified as 1,1,4-triphenyl-1,2,3,4-tetrahydronaphthalene (4) by ^{1}H and ^{13}C nmr, mass spectrum, and elemental analysis. A confirmation of this structure was accomplished by synthesis *via* a different route.[7]

Exciplexes are known to be sensitive to solvent polarity: in polar solvents they dissociate into the radical ions.[8,9] This encourages us to propose a mechanism for the formation of 4 in which electron transfer to 1 from 2 occurs as a key step. The polar solvent, acetonitrile, then allows the radical ions to dissociate which enables electrophilic attack by the cation radical 6 on the ground-state olefin 2. Ring closure, back-electron transfer from the anion radical 5, and aromatization conclude the mechanistic sequence. Formation of the oxetane 3 can then be envisioned as a reaction of the exciplex which competes with dissociation.

$$1 + 2 \xrightarrow{h\nu} [1 \cdot 2] \xrightarrow{CH_3CN} [1 \cdot^-]_{solv} + [(C_6H_5)_2C{=}CH_2 \cdot^+]_{solv}$$
$$5 \qquad\qquad 6$$

$$6 + 2 \longrightarrow [(C_6H_5)_2C^+ \quad \cdot C(C_6H_5)_2] \xrightarrow{5} 1 + 4$$

This mechanism is supported by the fact that we observe a transient absorption upon flash photolysis of an acetonitrile solution, 0.1 M in both 1 and 2, which is similar to the reported absorption of the 1,1-diphenylethylene cation radical 6.[10] This transient cannot be the exciplex[11] because of its lifetime ($\tau_{1/2} \approx 0.5$ msec). Continuous irradiation with a 1-kW xenon–mercury

(2) (a) Y. Shigemitsu, H. Nakai, and Y. Odaira, *Tetrahedron*, 25, 3039 (1969); (b) Y. Shigemitsu, Y. Katsuhara, and Y. Odaira, *Tetrahedron Lett.*, 2887 (1971).

(3) (a) D. R. Arnold, *Advan. Photochem.*, 6, 301 (1968); (b) P. J. Wagner and G. S. Hammond, *ibid.*, 5, 21 (1968).

(4) Aromatic esters such as 1 are known to have a π,π^* configuration in the lowest triplet: D. R. Arnold, J. R. Bolton, and J. A. Pedersen, *J. Amer. Chem. Soc.*, 94, 2872 (1972).

(5) All irradiations were carried out on argon purged solutions in sealed Pyrex tubes using a 450-W medium-pressure mercury vapor lamp (Hanovia L679A) unless otherwise stated. The rate of reaction was followed by nmr.

(6) In the absence of 1 solutions of 2 in either solvent remained unchanged even upon prolonged irradiation.

(7) 1,1,4,4-Tetraphenyl-1-butene, prepared according to G. Wittig, *Ber.*, 64, 442 (1931), was cyclized to 4 by refluxing with $AlCl_3$ in CCl_4.

(8) A. Weller, "Nobel Symposium 5, Fast Reactions and Primary Processes in Chemical Kinetics," S. Claesson, Ed., Almqvist and Wiksell, Stockholm, 1967, p 413, and references cited therein.

(9) T. Okada, H. Oohari, and N. Mataga, *Bull. Chem. Soc. Jap.*, 43, 2750 (1970).

(10) W. H. Hamill, "Radical Ions," E. T. Kaiser and L. Kevan, Ed., Wiley, New York, N. Y., 1968, p 404.

(11) In some cases the exciplex has absorption which coincides with that of the radical ions: R. Potashnik and M. Ottolenghi, *Chem. Phys. Lett.*, 6, 525 (1970).