Experimentally, it was found that the configuration at C-2′ profoundly affects the magnitude of the Cotton effect.[8,22] It was reported previously[24] that a cis-oriented hydroxyl group at C-2′ interacts with the base and that cis nucleosides gave a Cotton effect larger in magnitude than the trans anomers. It was found that[23] the amplitudes of the Cotton effect of α-D-rib-U and α-D-UMP are larger than their β anomers; however, the magnitudes of α-lyx nucleosides give smaller Cotton effects compared to their β anomers. Examination of molecular models suggests that the C-1′–C-2′ trans configuration allows the base to rotate more freely about the glycosidic bond. By inspection of the R_{OA} *vs.* ϕ_{CN} curve, it can be seen that a range of allowed values of ϕ_{CN} always results in decreasing the amplitude of a trans compound.

The main reason for beginning this study was to estimate the contribution of base–sugar interactions to the CD of polynucleotides. Table VIII shows the calculated B_{u2} rotational strengths for nucleosides with the glycosidic angle found in different double-stranded nucleic acids: A-form DNA,[25] B-form DNA,[26] and RNA-11.[27] One sees that in B-form DNA the calculated rotational strengths are very different from those of A-DNA, or anti mononucleosides. This means one cannot ignore base–sugar interactions in understanding the CD of double-stranded nucleic acids. The CD of the mononucleoside in solution may be very different from its contribution to the CD of the nucleic acid.

Acknowledgments. We wish to thank Dr. W. Curtis Johnson, Jr., for many helpful discussions, and Dr. A. M. Bobst for making some of the calculations. We would also like to express our gratitude to Dr. Joan Ingwall for kindly communicating to us her unpublished results.

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[24] T. L. V. Ulbricht, T. R. Emerson, and R. J. Swan, *Biochem. Biophys. Res. Commun.*, **22**, 505 (1966).

[25] W. Fuller, M. H. F. Wilkins, R. H. Wilson, and L. D. Hamilton, *J. Mol. Biol.*, **12**, 60 (1965).

[26] R. Langridge, D. A. Marvin, W. E. Seeds, H. R. Wilson, C. W. Hooper, M. H. F. Wilkins, and L. D. Hamilton, *ibid.*, **2**, 38 (1960).

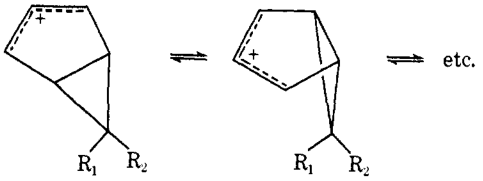
[27] S. Arnott, M. H. F. Wilkins, W. Fuller, and R. Langridge, *ibid.*, **27**, 535 (1967).

Communications to the Editor

A New Degenerate Cyclopropylcarbinyl Cation?

Sir:

The fivefold degeneracy of the bicyclo[3.1.0]hex-3-en-2-yl cation **1** is now firmly established.[1,2a] We wish



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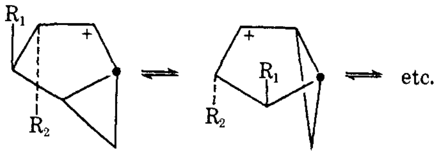
to describe here a remarkable experimental observation, and suggest that the results may be rationalized by a new degenerate carbonium ion rearrangement involving ions of the type **2**.[2a,b]



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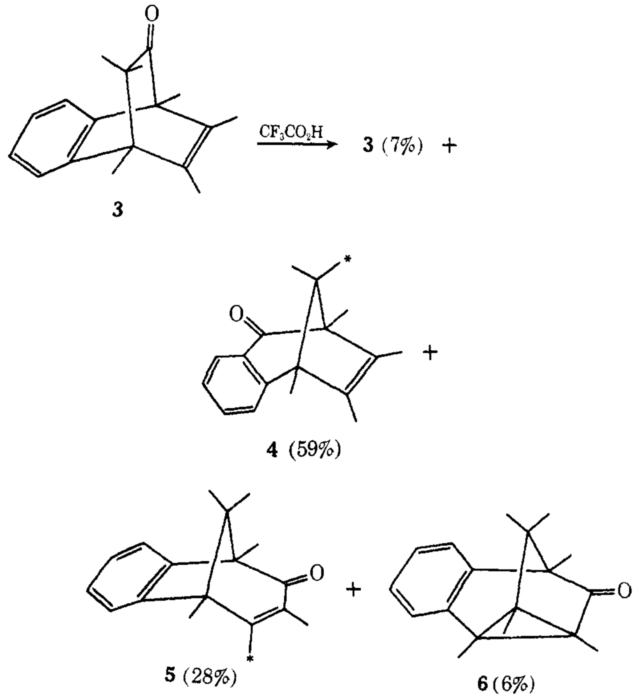
We recently described[3] the acid-catalyzed isomerization of the β,γ-unsaturated ketone **3** to a mixture of the isomeric ketones **3**–**6**. The same equilibrium mixture



was obtained from each of the four ketones. As part of a mechanistic study of this rearrangement, ketone **4** was treated with a large excess of CF_3CO_2D at 60°, at which temperature proton–deuteron exchange in the

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[1] D. W. Swatton and H. Hart, *J. Amer. Chem. Soc.*, **89**, 5075 (1967); R. F. Childs and S. Winstein, *ibid.*, **90**, 7146 (1968); H. Hart, T. R. Rodgers, and J. Griffiths, *ibid.*, **91**, 754 (1969); V. A. Koptyug, L. I. Kuzubora, I. S. Isaev, and V. I. Mamatyuk, *Chem. Commun.*, 389 (1969).

[2] (a) For a review of degenerate carbonium ions, see R. E. Leone and P. v. R. Schleyer, *Angew. Chem., Int. Ed. Engl.*, **9**, 860 (1970). For pertinent references on cyclopropylcarbinyl-cyclopropylcarbinyl rearrangements, see Z. Majerski and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **93**, 665 (1971). (b) The black dot is used only as a marker, to indicate the fixed positions of the cyclopentane ring carbons relative to the positions of the substituents.

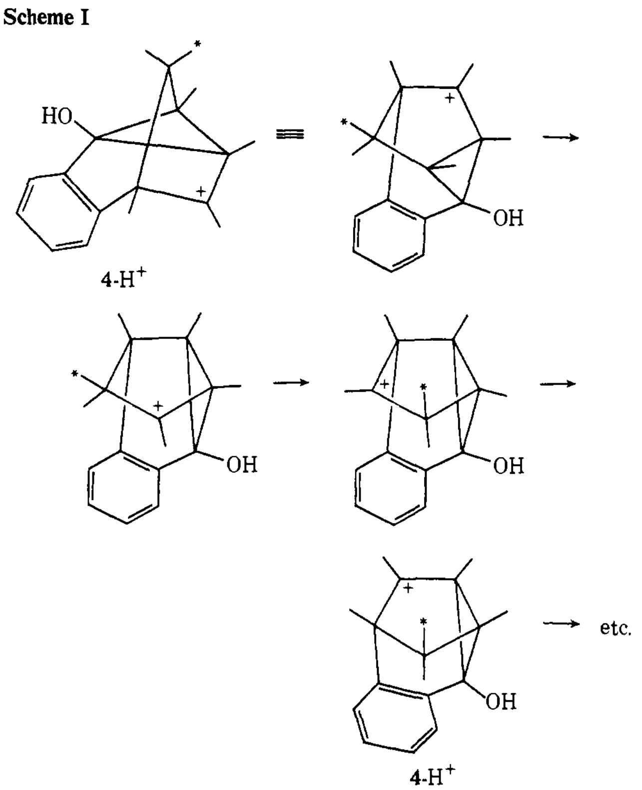
[3] H. Hart and G. M. Love, *Tetrahedron Lett.*, 2267 (1971).

methyl groups was much faster than rearrangement to the other three ketones.[4] *Five of the six methyl groups underwent deuterium exchange; the sharp singlet at* τ *8.97, assigned unambiguously*[5] *to the 8-anti methyl group (asterisk), remained unscathed.* When the counterexperiment was performed, using labeled **4** and ordinary trifluoroacetic acid, *signals corresponding to the protons in all five exchangeable methyls appeared simultaneously.*

In marked contrast to **4**, ketone **5** treated in the same manner with CF_3CO_2D underwent deuterium exchange only at the asterisked allylic methyl, presumably *via* acid-catalyzed enolization.

These observations suggest that the double bond in the 2-carbon bridge is essential to the extensive exchange observed in **4**, and that the aryl ring in that position blocks the analogous rearrangement in **5**. We suggest that **4** protonates on the carbonyl oxygen to give the cyclopropylcarbinyl ion **4**-H$^+$.[7] The rearrangements which rationalize the deuterium exchange results are shown in Scheme I. The carbon atoms which constituted the three-carbon bridge in the starting ketone "revolve" with respect to the five-membered ring. In this way the positive charge may be located on any carbon atom in the five-membered ring. Exchange presumably occurs through equilibration with the corresponding alkene.[8]

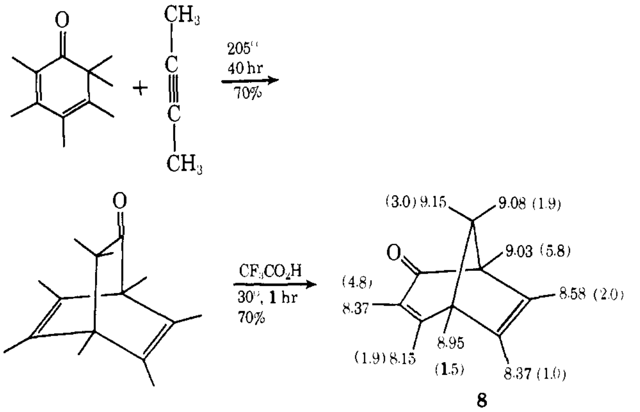
Scheme I



An essential feature of the mechanism is that the methyl migration be stereospecific, so that a positive charge never develops adjacent to the asterisked methyl. That is, the asterisked methyl revolves around the opposite face of the five-membered ring from the three-carbon bridge.

The multistep rearrangement is depicted in Scheme I as stepwise, though it may be partially concerted. All the intermediates are cyclopropylcarbinyl cations except one, the immediate product of methyl migration. Accordingly this step may provide the highest energy barrier in the entire process. It will be important to assess the effect of structural changes (in **2**) on the reaction.

To test the proposed exchange mechanism we synthesized the octamethyldienone **8** in the manner shown.[9,10] When **8** was treated with excess CF_3CO_2D at 30° (the reaction was followed by nmr) *five of the*



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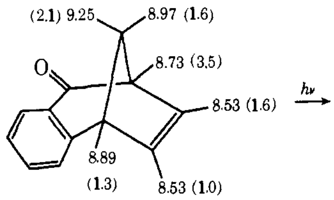
(4) The reaction was followed by nmr. Using a 200:1 molar ratio of CF_3CO_2D–**4**, equilibrium with regard to exchange was reached in about 24 hr; at this time, only a trace of **5** was detectable by nmr or vpc.

(5) It is essential to the argument that the nmr signals of the methyl protons in **4** be unambiguously assigned. This was done as follows.



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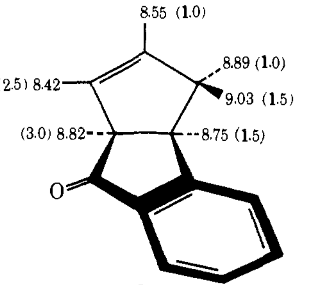


7

The methyl protons appear as five singlets, those at τ 8.53 being accidentally degenerate in carbon tetrachloride. This degeneracy was readily broken with the europium shift reagent Eu(DPM)$_3$; the two peaks became homoallylically coupled quartets, $J = 1$ Hz. The numbers in parentheses are the normalized slopes (the lowest slope arbitrarily chosen as 1.0) of the straight lines obtained when the chemical shifts of the various methyl protons were plotted as a function of added shift reagent.[6] The only possible ambiguity is in the τ 8.97 and 8.89 assignments; since one of these signals remained in the CF_3CO_2D exchange experiment, further confirmation of the assignment was sought. Irradiation of **4** gave the expected 1,3-acyl shift ketone **7**. Once again assignments were made using the chemical-shift differences (allylic methyls at low field and homoallylically coupled) as well as slopes obtained with the europium shift reagent. When an exchanged sample of **4** containing only the sharp methyl singlet at τ 8.97 was irradiated, the only methyl signal in the nmr spectrum of the photolysis product **7** was a sharp singlet at τ 8.89. Since the photoisomerization necessarily involves a 1,3 suprafacial shift, the assignments are confirmed.

(6) P. V. Demarco, T. K. Elzey, R. B. Lewis, and E. Wenkert, *J. Amer. Chem. Soc.*, **92**, 5734, 5737 (1970); H. Hart and G. M. Love, *Tetrahedron Lett.*, 625 (1971).

(7) Classical structures are written for all ions, to clarify the presentation.

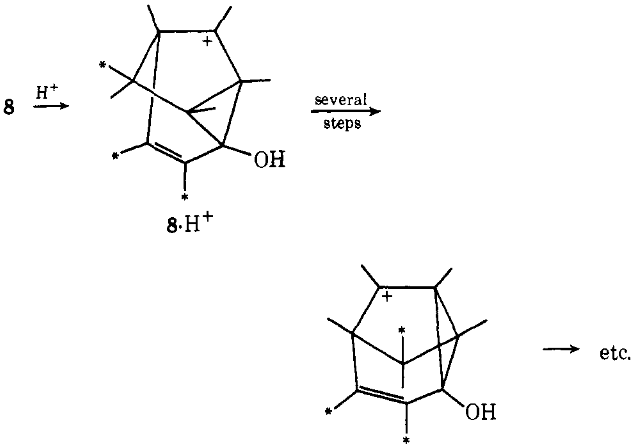
(8) Some base (*i.e.*, water) is readily tolerated. The exchange proceeds as fast at 60° in CF_3CO_2D containing 10% D_2O as in pure CF_3CO_2D; there is some rate diminution with 20% D_2O, and 40% D_2O essentially stops the reaction.

(9) We are indebted to Mr. E. Perry for working out conditions for the first step.

(10) Nmr assignments of **8** are based on chemical shifts, exchange with NaOMe–MeOD, and europium shift reagent slopes, as well as on photochemical results to be published separately.

eight methyl groups underwent deuterium exchange. The singlet at τ 9.08 and two homoallylically coupled quartets at 8.15 and 8.37 remained. When exchanged **8** was treated with NaOMe–MeOD the signal at τ 8.15 disappeared and that at 8.37 sharpened to a singlet, confirming the conclusion that the two methyls on the three-carbon bridge had not exchanged under acidic conditions.

These observations are consistent with the proposed exchange mechanism; the asterisked methyls do *not* exchange.



The postulated degenerate carbonium ion **2**, while it rationalizes the experimental observations presented, may not constitute a unique explanation for the results. The mechanism's correctness and generality are being put to further experimental tests.

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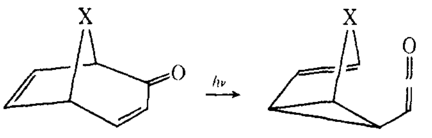
A Novel Intramolecular Ketene Cycloaddition. Functionalized Tetracyclo[3.3.0.0^{2,8}.0^{3,6}]octanes

Sir:

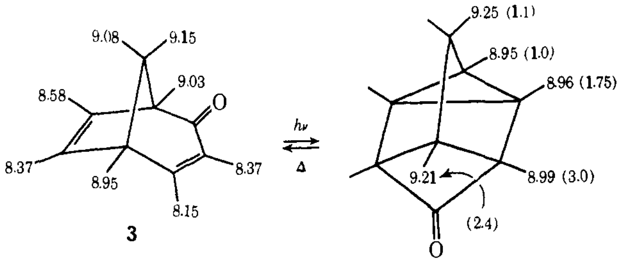
Compounds of the type **1** have been shown to photoisomerize to ketenes **2** (in published examples, X has been an electron pair,[1] or a CH_2, CH=CH,[2] o-C_6H_4,[2,3] or EtO_2CNNCO_2Et[2] group). The ketenes were detected in all cases by low-temperature infrared spectroscopy, and in all but the first example by trapping with a nucleophile. In the absence of a nucleophile, ketenes **2** recyclize to **1** or dimerize.[2]



1 2

We wish to report that ketene **2** (X = CH_2), when completely substituted with methyl groups, reacts differently from its unsubstituted analog. It neither reacts with nucleophiles nor recyclizes to **1**, but undergoes a facile and synthetically useful intramolecular $2_\pi + 2_\pi$ cycloaddition.

Irradiation of **3**[4] (1% solution in methanol, Pyrex) gave a single photoproduct, $\nu_{C=O}$ 1760 cm^{-1} (cyclobutanone), no nmr allylic methyl signals, in 100% chemical yield. We assign the product the tetracyclic structure **4** (1,2,3,4,5,6,7,7,8-octamethyltetracyclo[3.3.0.0^{2,8}.0^{3,6}]octan-4-one). The nmr spectrum consisted of five sharp singlets, three of which (τ 9.25, 8.99, and 8.96) were twice the area of the other two (all assigned as shown in the formula). Europium shift reagent caused downfield shifts of all the signals[5] but caused no broadening of the signals assigned to degenerate methyl pairs. These data favor structure **4** over the other plausible but asymmetric cyclobutanone structure **5**.



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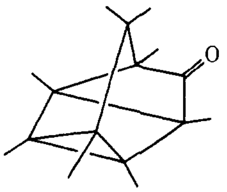

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Photoproduct **4** isomerizes thermally to **3** in carbon tetrachloride at 100° with a half-life of 50 min. Advantage was taken of this thermal rearrangement to unequivocally demonstrate the symmetric structure of **4**. Ketone **3**, when treated with NaOMe–MeOD, gave the trideuterio compound **6** (which lacked the low-field methyl signal at τ 8.15; the asterisked methyl is CD_3). Irradiation of **6** gave **7** (peak at τ 8.96 in **4** reduced 50% in area). When **7** was heated, the expected 1:1 mixture of **6** and **8** was obtained (1.5 protons at τ 8.15, 4.5 protons at τ 8.37), clearly demonstrating the symmetry of the photoproduct **4**.

A similar rearrangement of **4** to **3** appears to occur on electron impact.[6] Although the mass spectra of **4** and **3** were virtually identical at 70 eV (base peak at m/e 217 due to M − CH_3, and the peak at m/e 204 due to M − CO was relatively minor), when the ionizing voltage was lowered to 20 eV the peak due to

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(1) O. L. Chapman and J. D. Lassila, *J. Amer. Chem. Soc.*, **90**, 2449 (1968). In this example a methoxyl group was present at C_1 or C_7.

(2) O. L. Chapman, M. Kane, J. D. Lassila, R. L. Loeschen, and H. E. Wright, *ibid.*, **91**, 6856 (1969).

(3) A. S. Kende, Z. Goldschmidt and P. T. Izzo, *ibid.*, **91**, 6858 (1969).

(4) Synthesized as described in the accompanying communication; H. Hart and G. Love, *ibid.*, **93**, 6264 (1971). The numbers in the formula are the nmr chemical shifts of the methyl signals, in τ (CCl_4 solvent).

(5) The numbers in parentheses are the relative slopes of these signals with added Eu(DPM)$_3$, the lowest slope arbitrarily taken as 1.0. These slopes, as well as experiments with three differently labeled samples of **3** (CD_3 in place of certain CH_3 groups), permit the unequivocal nmr assignment shown.

(6) The inlet temperature was kept as low as possible, approximately 70°, to avoid the thermal isomerization.