ϕ_{s_0} and the quantum yield of the type II process due to the n,π^* singlet state in the presence of biacetyl (ϕ_s) against the biacetyl concentration, linear Stern–Volmer plots were obtained for both acetone and propylene in three individual runs with an average slope of 7.3 ± 0.5 l. mol^{-1} and an average intercept of 1.00 ± 0.04.

From the familiar expressions that $\phi_{s_0}/\phi_s = 1 + k_{q_s}[Q]\tau_s$ and $\phi_{t_0}/\phi_t = 1 + k_{q_t}[Q]\tau_t$, where ϕ_0 is the quantum yield of the type II process at zero quencher concentration, ϕ is the quantum yield of the type II process at various quencher concentrations, k_q is the quenching constant, τ is the mean lifetime of the excited state, k is the first-order rate constant for the type II process, and the subscripts s and t denote the respective terms for the singlet and the triplet states, the slopes of these plots obtained are $k_{q_s}\tau_s$ for the singlet excited state and $k_{q_t}\tau_t$ for the triplet state. The experimental slope for the Stern–Volmer plot of the triplet-state reaction of 2-hexanone has been reported to be 10;[7] therefore, $k_{q_s}\tau_s = 7.3$ and $k_{q_t}\tau_t = 10$.

ϕ_{s_0} and ϕ_{t_0} have been determined to be 0.097 and 0.15,[6] and are defined as $k_s\tau_s$ and $k_t\tau_t\phi_{isc}$, respectively, where ϕ_{isc} is the quantum yield of intersystem crossing from the singlet to the triplet state. We obtain

$$k_s = \frac{\phi_{s_0}}{\tau_s} = \frac{0.097k_{q_s}}{7.3} = \frac{k_{q_s}}{75}$$

and

$$k_t = \frac{\phi_{t_0}}{\tau_t\phi_{isc}} = \frac{0.15k_{q_t}}{10\phi_{isc}} = \frac{k_{q_t}}{67\phi_{isc}}$$

Since ϕ_{isc} is relatively high for aliphatic ketones[3] and the k_q's are likely to be similar for both excited states, our data indicate that the chemical reactivities of the n,π^* singlet and the n,π^* triplet states of 2-hexanone for the type II process are of the same order of magnitude. Assuming k_{q_s} and k_{q_t} are of the order of 10^{10} l. mol^{-1} sec^{-1}, k_s and k_t are then of the order of 10^8 sec^{-1}.

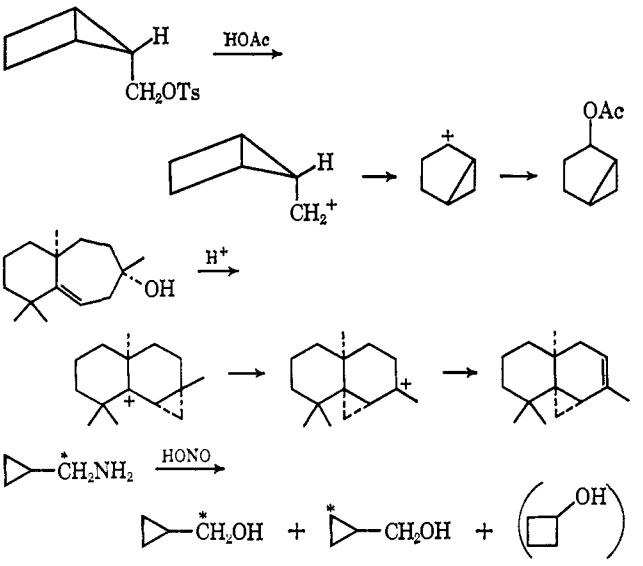
(17) The authors wish to thank the National Science Foundation for support of this work.
(18) National Science Foundation Trainee, 1966–1968.

N. C. Yang, Steven P. Elliott[17,18]
Department of Chemistry
University of Chicago, Chicago, Illinois 60637
Received April 15, 1968

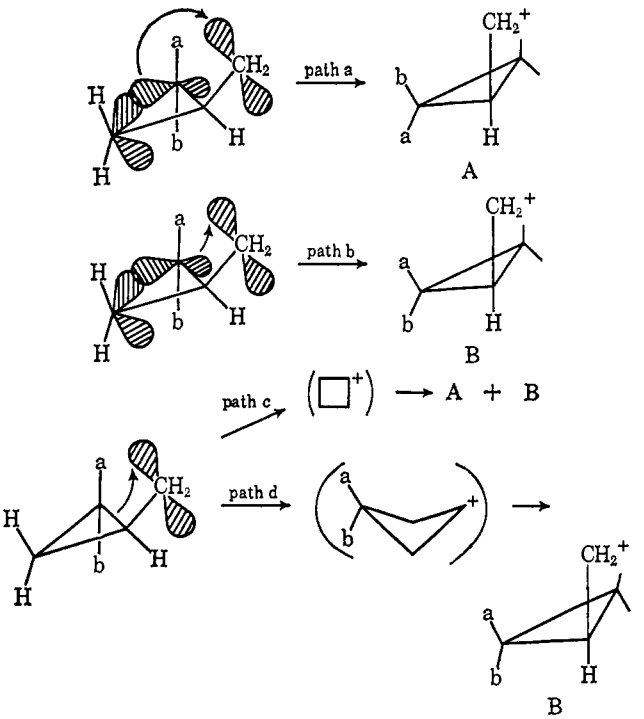
Stereochemistry of the Cyclopropylcarbinyl–Cyclopropylcarbinyl Rearrangement[1]

Sir:

The rearrangement of one cyclopropylcarbinyl ion to another occurs in the rearrangement of bicyclo[2.1.0]pentane-5-carbinyl derivatives to the bicyclo[3.1.0]hexyl-2 cation[2] in the rearrangement of widdrol to thujopsene[3] and in the label scrambling process of the cyclopropylcarbinyl ion itself.[4] Three



courses are possible for the reaction. First, the 2,3 bond may be involved, leading to rotation of the methylene group in the process. Second, the back side of the orbital forming the 2,3 bond may be involved, leading to no rotation of the methylene group. Finally, the rearrangement may proceed *via* a cyclobutyl cation as an intermediate or an activated complex. Here, different stereochemical results would be obtained if the ring is planar or if it is puckered. In the first case,

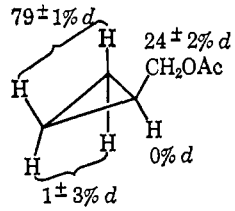


the relationship between location a and the carbinyl carbon is inverted, whereas in the second it is retained. In the third, a mixture of A and B should be obtained if the cyclobutane ring is planar, and B should be obtained if it is not.

The protolysis of bicyclobutanes occurs with retention of configuration leading to a cyclopropylcarbinyl ion.[5] When the reaction was carried out in acetic acid-

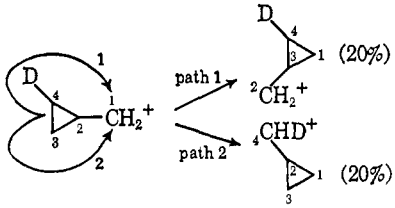
(1) This investigation was supported by Public Health Service Grant GM12800 from the National Institute of General Medical Service.
(2) K. B. Wiberg and A. J. Ashe, III, *Tetrahedron Letters*, 4245 (1965); *J. Am. Chem. Soc.*, **90**, 63 (1968).
(3) W. G. Dauben and L. E. Friedrich, *Tetrahedron Letters*, 1735 (1967).
(4) J. D. Roberts and R. H. Mazur, *J. Am. Chem. Soc.*, **73**, 3542 (1951).
(5) This has been observed by W. G. Dauben and W. T. Wipke, *Pure Appl. Chem.*, **9**, 539 (1964), and by us in the reactions of tricyclo[4.1.0.0^{2,7}]octane and bicyclobutane. This is also the mode of reaction of cyclopropanes (*cf.* C. H. DePuy, *Accounts Chem. Res.*, **1**, 33 (1968)).

d, the deuterium distribution in the cyclopropyl carbinyl acetate was determined *via* the nmr spectrum[6] to be as shown. Similar results were obtained with



the hydration of bicyclobutane. Here, the cyclopropylcarbinol contained 81 ± 3% *d* in the *cis*-β position, 17 ± 3% *d* in the carbinyl position, and 2 ± 3% *d* in the *trans*-β position. The precision of the analysis is not as good as for the acetate since the relatively broad α-ring proton had to be used as the internal standard. The results indicate that a negligible amount of deuterium appears in the *trans*-β position.

Since 20% of the deuterium appears in the carbinyl position, the cyclopropylcarbinyl–cyclopropylcarbinyl rearrangement must have occurred. However, because of the symmetry of the ion, the total amount of rearrangement must be twice as great since there are two equivalent ways (except for the deuterium) in which the rearrangement may occur. Despite the rearrangement *via* path 1 which retains the deuterium in the ring, no deuterium appears in the position *trans* to the carbinyl group. Rearrangement by process a shown above would have introduced 20% *d* into that position, and process c would have introduced 10% *d* into that position. Therefore, the rearrangement must have occurred *via* process b or d. It may be noted that such a process is also required in order to explain why *endo*-bicyclo[2.1.0]pentane-5-methyl tosylate, and not its *exo* isomer, is capable of rearranging to the northujyl cation.[2]



It is not possible to distinguish between processes b and d on the basis of the above data alone. Other experiments may serve to identify which is the correct process, and such experiments are in progress.

(6) A complete analysis of the nmr spectrum of cyclopropylcarbinol was made available to us by D. Barth. The deuterium distribution was determined by repeated integration of the nmr spectrum and use of the acetate methyl as an internal three-proton standard.

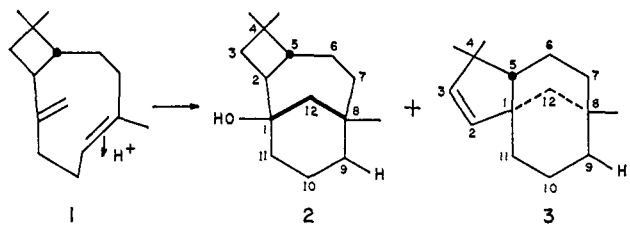
Kenneth B. Wiberg, Gunter Szeimies
Department of Chemistry
Yale University, New Haven, Connecticut
Received April 23, 1968

Stereochemistry of Proton Addition in Ring Closure of a 1,5-Diene[1]

Sir:

In contrast to extensive studies of ring-fusion geometry[2] in acid cyclizations of 1,4-dienes the proton addition step has received little stereochemical scrutiny.[3] We now describe a study of a diene that closes to two products from two different precursor conformations (or sets of conformations) and show unambiguously that these conformations are adopted prior to proton attachment, that the C–H and C–C bonds are formed by *trans* addition to each conformation, and that no conformational flipping intervenes after the C–H bond is made even though a tertiary cationic center could develop formally.[4] These conclusions require no assumptions about the precise nature of the conformations, their relative stabilities, the energy barriers separating them, the direction of attack by the H^+, or the stabilities of intermediates or products.

Our substrate was caryophyllene (**1**) which is known to undergo cyclization on acid treatment to give (among other products) caryolan-1-ol (**2**) and clov-2-ene (**3**).[5,6] The flexibility in the nine-membered ring likens it to an acyclic diene and permits attainment of both configurations for the C-12 bridging carbon in the products. Molecular models reveal that **2** and **3** can arise only from two distinctly different conformations of **1** or of a tertiary cation derived from **1**. In particular, closure to **2** in which the C-12 bridge is β oriented can occur only from a form in which the olefinic methyl projects "up" (*i.e.*, *syn* to the angular hydrogen next to the *gem*-dimethyl unit); closure to **3**, with its α-oriented bridge, must occur from a form with the methyl group projecting "down" (*i.e.*, *anti* to the reference hydrogen).[7,8] These two conformations of the *endo* unit are formally interconverted by conformational flipping (A ⇄ B).[9] Alternatively the H^+ could add



(2) (a) G. Stork and A. W. Burgstahler, *J. Amer. Chem. Soc.*, 77, 5068 (1955); (b) A. Eschenmoser, L. Ruzicka, O. Jeger, and D. Arigoni, *Helv. Chim. Acta*, 40, 2191 (1957); (c) extensive studies by W. S. Johnson, *et al.*, reviewed in *Accounts Chem. Res.*, **1**, 1 (1968).

(3) (a) W. S. Johnson, *Pure Appl. Chem.*, 7, 317 (1963); (b) H. E. Ulery and J. H. Richards, *J. Amer. Chem. Soc.*, **86**, 3113 (1964); (c) I. G. Mursakulov, A. V. Semenovsky, W. A. Smit, and V. F. Kucherov, *Tetrahedron*, **23**, 1621 (1967); (d) for possible implications in terpene biogenesis see D. H. R. Barton and G. P. Moss, *Chem. Commun.*, 261 (1966); E. E. van Tamelen, *Accounts Chem. Res.*, **1**, 111 (1968); E. Caspi, J. M. Zander, J. B. Greig, F. B. Mallory, R. L. Conner, and J. R. Landrey, *J. Amer. Chem. Soc.*, 90, 3563 (1968).

(4) Contrast a report (ref 3c) of stereochemical loss after proton addition in the cyclization of geranylacetone and the suggestion that the nonstereospecificity is due to creation of a tertiary cation.

(5) A. Aebi, D. H. R. Barton, and A. S. Lindsey, *J. Chem. Soc.*, 3124 (1953); A. Aebi, D. H. R. Barton, A. W. Burgstahler, and A. S. Lindsey, *ibid.*, 4659 (1954); A. Nickon, *Perfumery Essent. Oil Records*, **45**, 149 (1954).

(6) Caryophyllene is partially transformed to isocaryophyllene (*cis* endocyclic double bond) during this treatment. In separate experiments, however, we established that isocaryophyllene is not converted to caryolanol or to clovene under the same conditions.

(7) No precise shapes are implied, but at the instant of ring closure two grossly different conformations must exist ("methyl up" and "methyl down") to account for the products.

(8) Although the exocyclic double bond must also be able to position itself to form both β- and α-oriented bridges, the geometric aspects of the *exo* unit as well as the changes that occur after the bridge is formed are not pertinent to the stereochemical considerations in this paper.

(9) For interconversion barriers in *trans*-cyclononene and related systems see A. C. Cope, K. Banholzer, H. Keller, B. A. Pauson, J. J. Whang, and H. J. S. Winkler, *J. Amer. Chem. Soc.*, 87, 3644 (1965);

(1) Supported by the National Institutes of Health (Grant GM 06304) and an Esso Education Foundation Fellowship to F. Y. E.