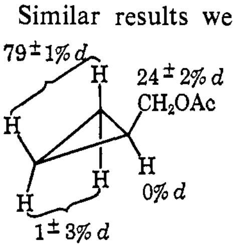
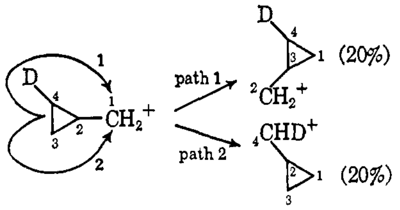
d, the deuterium distribution in the cyclopropyl carbinyl acetate was determined *via* the nmr spectrum[6] to be as shown. Similar results were obtained with



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.

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[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.

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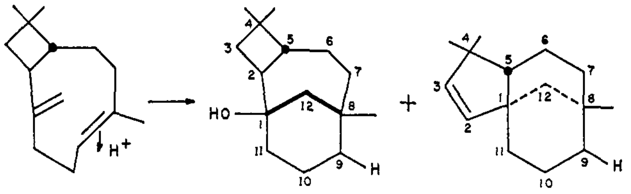
Stereochemistry of Proton Addition in Ring Closure of a 1,5-Diene[1]

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



1 2 3

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

[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.

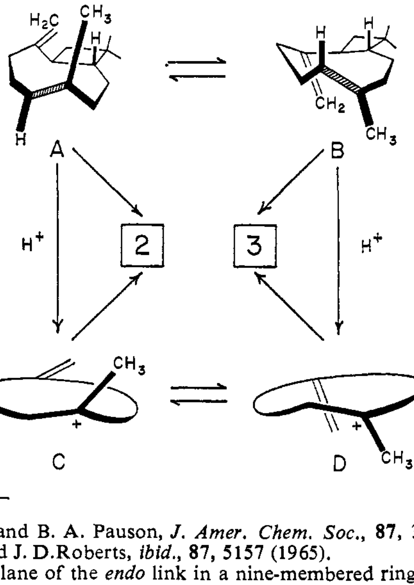
[9] For interconversion barriers in *trans*-cyclononene and related systems see A. C. Cope, K. Banholzer, H. Keller, B. A. Pauson, J. J. Whang, and H. J. S. Winkler, *J. Amer. Chem. Soc.*, **87**, 3644 (1965);

to the *endo* double bond and the resulting cation could adopt the "methyl up" and "methyl down" forms by conformational flipping ($C \rightleftarrows D$). The C-12 to C-8 bond can be created only from the inside face[10] of the *endo* link, but the H^+ could attack from either the inside face or the outside face of the *endo* double bond. Therefore, net *cis* or *trans* addition is possible, and six stereochemically distinct paths are recognizable. For D^+ initiation, these paths are summarized in Table I along with the predicted D configurations.

Table I

		Deuterium configuration	
Path	Description	Caryo-lanol	Clo-vene
1	*trans* addition to A and to B with no intervening flipping	β	α
2	*cis* addition to A and to B with no intervening flipping	α	β
3	D^+ attack from "outside" on A only followed by interconversion of C and D	β	β
4	D^+ attack from "inside" on A only followed by interconversion of C and D	α	α
5	D^+ attack from "outside" on B only followed by interconversion of D and C	α	α
6	D^+ attack from "inside" on B only followed by interconversion of D and C	β	β

Cyclization of caryophyllene with D_2SO_4 in anhydrous ether at 0° for 12 min, followed by alkaline hydrolytic work-up, gave caryolan-1-ol (17% d_0, 81% d_1, 1.5% d_2, 0.5% d_3) and clov-2-ene, which was oxidized to clovenic anhydride (15.5% d_0, 82.5% d_1, 2% d_2). Recovered caryophyllene had 97% d_0, 3% d_1. The deuterium configurations in the tricyclic products were determined by infrared spectral comparisons with authentic samples of caryolan-1-ol-9α-*d* and -9β-*d* and the corresponding clovenic-α-*d* and -β-*d* anhydrides, which were synthesized by stereospecific routes.[11] Infrared examination of artificial mixtures established that as little as 3% of the caryolanol-α-*d* could be detected in the β-*d* epimer, and as little as 4% of clovenic-β-*d* anhydride could be detected in the α-*d* epimer. The natural abundance compounds do not show bands in the relevant fingerprint regions and so do not interfere in the spectroscopic assays. Examination of the products from cyclization showed that the deuterium had the β configuration in caryolanol (>97%) and the α configuration in clovenic anhydride (>96%). These results are compatible only with path 1.[12] Importantly, if D^+ attack and ring closure are synchronous (they need not be!), antiplanar addition requires the six-membered ring to develop *via* a boatlike transition state rather than *via* the (presumably) more stable chairlike form.[13]



A. C. Cope and B. A. Pauson, *J. Amer. Chem. Soc.*, **87**, 3644 (1965); G. Binsch and J. D.Roberts, *ibid.*, **87**, 5157 (1965).

[10] The plane of the *endo* link in a nine-membered ring is probably roughly perpendicular to the rest of the ring, hence the arbitrary terms "inside" and "outside" to represent the two faces of the olefinic plane.

[11] Described in the Ph.D. dissertation of F. Y. Edamura, Johns Hopkins University 1965. The synthetic schemes were made available to the editor and to the referees and will be described elsewhere.

[12] Any combination of two or more competing paths is also excluded.

[13] The chemical and spectroscopic (ir and nmr) properties of several substituted caryolane and clovane derivatives (including X-ray studies of 1-halocaryolanes) are consistent with chairlike geometry for the six-membered ring containing carbons 9, 10, and 11.[5,11]

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The Stereochemistry of the Silicon–Cobalt Bond and Some Implications for Homogeneous Transition Metal Catalysis[1]

Sir:

Recent discovery of methods for the preparation of compounds containing the transition metal–silicon bond,[2,3] together with the novel properties of these substances,[4] has stimulated lively interest in this area of chemistry during the past 3 years. The elegant studies of Chalk and Harrod[2b] concerning the silylcobalt carbonyls has appreciably increased the understanding of the mechanisms of homogeneous transition metal catalysis in organosilicon chemistry. Studies carried out in our laboratories[5-8] showed that transition metal catalyzed reactions of the silicon–hydrogen bond were highly stereospecific and suggested the possible involvement of intermediates possessing transition metal–silicon bonds. These observations led us to the conclusion that stereochemical studies could make a significant contribution toward elucidating

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[1] Support of this work by a grant from the National Science Foundation is gratefully acknowledged.

[2] (a) A. J. Chalk and J. F. Harrod, *J. Am. Chem. Soc.*, **87**, 16 (1965); (b) A. J. Chalk and J. F. Harrod, *ibid.*, **89**, 1640 (1967).

[3] (a) B. J. Aylett and J. M. Campbell, *Chem. Commun.*, 217 (1965); (b) B. J. Aylett and J. M. Campbell, *ibid.*, 159 (1967); (c) W. Jetz, *et al.*, *Inorg. Chem.*, **5**, 2217 (1966); (d) W. Jetz and W. Graham, *J. Am. Chem. Soc.*, **89**, 2773 (1967); (e) J. D. Cotton, *et al.*, *Chem. Commun.*, 965 (1967); (f) J. Chatt, *et al.*, *ibid.*, 700 (1966); (g) J. Chatt, *et al.*, *ibid.*, 869 (1967); (h) F. Glockling and K. A. Hooton, *ibid.*, 219 (1966); (i) F. Glockling and K. Hooton, *J. Chem. Soc.*, *A*, 1067 (1967).

[4] (a) A. P. Hagen and A. G. MacDiarmid, *Inorg. Chem.*, **6**, 686 (1967); (b) Y. L. Baay and A. G. MacDiarmid, *Inorg. Nucl. Chem. Letters*, **3**, 159 (1967); (c) A. P. Hagen and A. G. MacDiarmid, *Inorg. Chem.*, **6**, 1941 (1967).

[5] L. H. Sommer, J. E. Lyons, H. Fujimoto, and K. W. Michael, *J. Am. Chem. Soc.*, **89**, 5483 (1967).

[6] L. H. Sommer, K. W. Michael, and H. Fujimoto, *ibid.*, **89**, 1519 (1967).

[7] L. H. Sommer and J. E. Lyons, *ibid.*, **89**, 1521 (1967).

[8] L. H. Sommer and J. D. Citron, *J. Org. Chem.*, **32**, 2470 (1967).