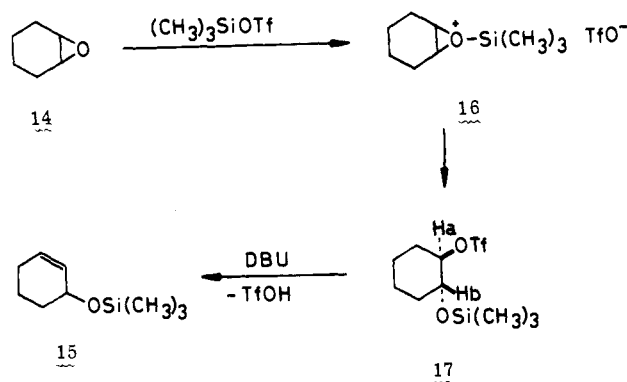


Scheme I



methylsilyl ether was obtained in a reasonable yield. The trimethylsilyl group was readily removed by treating with dilute hydrochloric acid or KF in methanol. Several examples of this transformation are given in Table I. The reaction of cyclic substrates possessing ordinary ring size (entries 1–3) proceeded at room temperature to give the desired allyl trimethylsilyl ethers. The reaction of epoxycyclooctane (**2**), however, led to the transannular cyclization product **3** (entry 4). Tetra-, tri-, and 2,2-disubstituted oxiranes reacted with **1** at dry ice temperature (entries 6–14).⁶ Notably the reaction of 1,2-epoxy-1-methylcyclohexane (**4**) afforded specifically product **5** possessing an exocyclic methylene group (entry 7). Since hydroxy group reacts with **1** spontaneously, giving a trimethylsilyl ether, alcoholic oxiranes could be subjected to the reaction with 2 equiv of **1** directly without any protection (entries 10, 13, and 14). Reaction of the bifunctional compounds **6** and **8** with 1 equiv of **1** led chemoselectively to the corresponding allyl trimethylsilyl ethers **7** and **9**, respectively, leaving the keto or ester group intact.⁷ *trans*-2,3-Epoxycitronellol (**10**) was converted stereoselectively to the olefin **11** having *E* configuration (entry 13). The *cis* analogue **12** led to a mixture of the isomeric olefins **11** and **13** with the former predominating (4:1 ratio) (entry 14). Thus this simple isomerization method, complementary to the existing techniques, would provide a useful tool in the synthesis of complex organic molecules.

Unlike epoxycycloalkanes, ordinary 2,3-dialkylated oxiranes were inert to the standard reaction conditions. Monoalkylated substrates did not react either. Under forcing conditions, these oxiranes underwent ring opening to produce alkenyl silyl ethers as the major or exclusive product.⁸

A representative procedure for the oxirane to allyl silyl ether conversion follows. A solution of **1** (2.26 g, 10.2 mmol) in benzene (20 mL) was placed under argon atmosphere and to this was added a mixture of 1,2-epoxycyclohexane (**14**, 1.06 g, 10.7 mmol) and DBU (2 mL) in benzene (5 mL) at 22 °C. The mixture was stirred at this temperature for 20 h and poured onto a column of silica gel (15 g) which had been treated with ammonia. The column was eluted with hexane-ether mixture (2:1, 300 mL). The elute was concentrated in vacuo (200 mmHg) at room temperature and distilled. Redistillation of the fraction boiling at 50–60 °C (50 mmHg) gave pure 3-trimethylsilyloxycyclohexene (**15**, 1.51 g, 87% yield).

Apparently the efficiency of this isomerization reaction is ascribed to the eminent affinity of silicon for oxygen and high electronegativity of trifluoromethanesulfonyl group.⁹ Convincing evidence was obtained for operation of the addition-elimination mechanism as outlined in Scheme I. When a mixture of **1**, **14**, and triethylamine (1:1:1 ratio) in hexane was allowed to stand at 19 °C, a single, labile adduct **17** was obtained. The *trans* stereochemistry was substantiated by the ¹H NMR spectrum (CCl_4 solution) exhibiting characteristic H_a and H_b signals at δ 4.47 (ddd) and 3.57 (ddd), respectively,

with vicinal coupling constant of 10 Hz.¹⁰ This product upon treatment with DBU in benzene afforded the allyl silyl ether **15**. As would be expected, the electrophilically induced nucleophilic ring opening is made more rapid by increased alkyl substitution. When an unsymmetrically trisubstituted oxirane is used, the ring opening occurs preferentially at the more substituted carbon.¹¹ Thus the sense of the regioselectivity of this process is opposite that observed in the cleavage of oxiranes with sodium phenylselenide⁴ in which the displacement takes place at the less substituted carbon. In the second olefin-forming step (**17** → **15**), proton abstraction occurs away from the trimethylsiloxy group. The observed selectivity, particularly with the stereoisomeric oxiranes, **10** and **12**, suggests the operation of an E2 mechanism with anti stereochemistry rather than intramolecular syn elimination.

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- (8) Reaction of *trans*-2,3-dihexyloxirane, **1**, and pyridine in benzene at 70 °C for 10 h produced trimethylsilyl ethers of 8-tetradecen-7-ol (17%) and 6- and 7-tetradecen-7-ols (65%). 2-Octyloxirane upon treatment with **1** and 2,6-lutidine (benzene, 80 °C, 14 h) and then DBU (25 °C, 8 h) gave (*Z*)-1-decen-1-ol trimethylsilyl ether in 80% yield.
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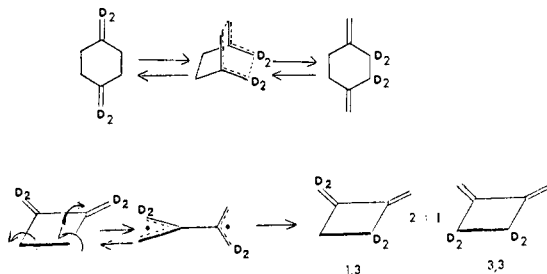
Received December 28, 1978

2,2'-Bisallylmethane: Thermal Degenerate Rearrangement of 1,3-Dimethylenecyclopentane. Partly Stereospecific Generation of a Biradical

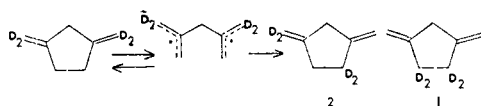
Sir:

Upon thermolysis 1,5-diene systems undergo a [3,3]-sigmatropic shift (Cope rearrangement)¹ unless steric constraints prevent the termini of the diene from strongly interacting. Under these circumstances [1,3] shifts intervene,² the stereochemistry of which has been interpreted as resulting from the operation of both Woodward-Hoffmann orbital symmetry conservation and Berson-Salem adjacent orbital control.³ In an effort to delineate the crossover point between concerted [3,3] shifts and other processes, the pyrolyses of 1,4-dimethylenecycloalkanes have been investigated. 1,4-Dimethylenecyclohexane (DMCH) undergoes a [3,3] shift via a

"boat"-like transition state which may resemble [2.2.2]propellane,⁴ but 1,2-dimethylenecyclobutane (DMCB) cleaves to a 2,2'-bisallyl biradical which recloses to DMCB resulting in formal [1,3]- and [3,3]-shift products in a 2:1 ratio, kinetically.⁵ Significantly, the latter reaction, though apparently nonconcerted, proceeds with substantial (95%) stereospecificity via a conrotatory C₃-C₄ bond rupture with simultaneous C₁C₂ rotation in a fashion that is as meshed-bevel gears at the intersection of the rotation axes. The behavior of the interfacial material, 1,3-dimethylenecyclopentane (DMCP) is therefore of concern, and we here report that it behaves as DMCB⁵ does.

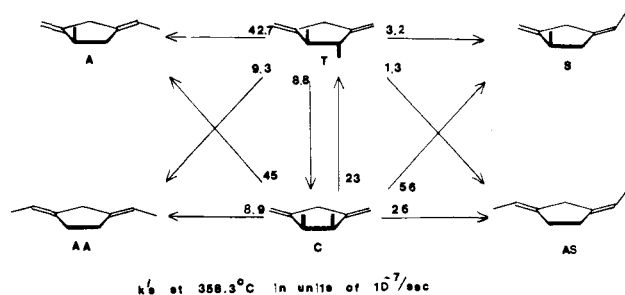


In a well-condition vessel at 370.5 °C, 1,3-bis(dideuteriomethylene)cyclopentane (DMCP-*d*₄,⁶ ~5 Torr with 100 Torr of N₂) undergoes random methylene group scrambling as evidenced by NMR and ozonolysis. After 24 at 370.5 °C, three samples of DMCP-*d*₄ were individually oxidized and had a *d*₂:*d*₄ ratio of 1.99 ± 0.09 in the succinic anhydride after one-third conversion to the equilibrium mixture. Assuming a first-order reaction, a crude rate constant suggests an activation free energy of 53 kcal/mol which is about the bond dissociation energy estimated for the C₄-C₅ bond considering an allyl radical resonance energy of 12.5 kcal/mol and a reactant strain energy of 5 kcal/mol. Thus, DMCP apparently cleaves to a 2,2'-bisallylmethane which recloses in a random manner.



In an effort to determine a rotational preference in ring opening, *trans*- and *cis*-4,5-dimethyl-1,3-dimethylenecyclopentanes (T and C)⁶ were pyrolyzed at 358.3 °C. T gives mostly *anti*-1-ethylidene-3-methylene-4-methylcyclopentane (A)⁷ and small amounts of *anti,anti*-1,3-diethylidencyclopentane (AA)⁸, as well as C. On the other hand, C gives A, and its syn isomer (S)⁷ in nearly equal quantities along with *anti, syn*-1,3-diethylidencyclopentane (AS)⁸ and some T. In order to quantitate the conversions, the first-order rate constants below for the interconversions were found to provide calculated concentrations from numerical integration of the differential rate expressions of the scheme that matched the experimental data as a function of time.⁹

These results indicate (a) that the reaction is first order; (b) that, if a single biradical is involved in the isomerization of T and a single one in the isomerization of C, each formed by the



same rotational modes, then conrotatory opening of the system occurs to generate bisallylmethane biradicals which reclose faster than they undergo rotation around the methallyl radicals; and (c) that a third rotation twisting the two developing allylic system occurs since the global rate constants for reaction of T and of C are similar; an in-plane conrotatory opening of C should have been substantially retarded by steric effects.

The stereospecificity in the ring opening may be attributed simply to steric effects forcing bond rotations so as to generate the most stable conformation of the transition state leading to the diradical.

A companion paper describes partial stereospecificity in the closure of the 2,2'-bisallylmethane biradical.

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- (6) DMCP, T, and C were prepared from the dicarboxylic acid resulting from ozonolysis of the appropriate norbornene derivative.
- (7) The ¹H NMR values of A and S are virtually indistinguishable thus preventing rigorous assignment of stereochemistry. However, if a single intermediate is involved in the rearrangement of T and a single intermediate in the pyrolysis of C, as the *d*₂:*d*₄ ratio from DMCP-*d*₄ suggests, the stereochemical assignments necessarily follow from the observation of AA as the [3,3]-shift product from T, and AS as the 3,3-shift product from C.⁸
- (8) ¹H NMR: AA, δ 1.54 (d, *J* = 7 Hz, 6 H), 2.30 (s, 4 H), 2.86 (s, 2 H), 5.20 (d, *J* = 7 Hz, 2 H); AS, δ 1.56 (apparent t, *J* = 6 Hz, 6 H), 2.27 (br s, 4 H), 2.84 (s, 2 H), 5.22 (m 2 H).
- (9) The experimental and calculated mole fractions at five different reaction times over the first half-life for reaction of T and C agreed within 1–4% of one another with the rate constants cited. A table with all of the data was made available to the editor and referees.

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2,2'-Bisallylmethane: Thermal Degenerate Rearrangement of 1,3-Dimethylenecyclopentane. Partly Stereospecific Closure of a Biradical

Sir:

The 2,2'-bisallylmethane diradical (2,2'-BAM) appears to be generated as an intermediate upon thermolysis of 1,3-dimethylenecyclopentane (DMCP).¹ This conclusion derives from the finding that formal [1,3]- and [3,3]-shift products are formed in a 2:1 ratio, respectively.¹ However, pyrolysis of *cis*- and of *trans*-4,5-dimethyl-DMCP leads to stereoisomeric products from each in a manner that indicates partial stereospecificity in the formation of the biradical.¹ This communication reports stereospecificity in the closure of the biradical to the [1,3]-shift product with partial inversion of configuration of the migrating carbon. In addition, different rate- and product-determining deuterium isotope effects further substantiate the intervention of an intermediate.