Reaction of 2,5-dihydrofuran with acetic–toluenesulfonic mixed anhydride[11] in acetonitrile at reflux for 16 hr produced the acetoxy tosylate[6a] **5** (90%) which was treated with sodiomalonic ester in tetrahydrofuran (THF)–hexamethylphosphoric triamide at 25° for 2 hr to afford 63% of the acetoxy malonic ester derivative **6**.[6] Deacetylation (K$_2$CO$_3$ in ethanol at 75° for 2 hr) gave **7** which was converted *via* **8**[6a] (dihydropyran–toluenesulfonic acid in ether) to monoester **9**[6] (sodium cyanide in dimethyl sulfoxide at 160° for 4 hr,[12] 64% from **6**). From **9**, the acid **10**[6] was prepared by saponification (>95% yield), and the alcohol **11**[6] was formed by reduction (70% yield) with lithium aluminum hydride. The iodide **12**[6a] was obtained from the alcohol **11** by sequential reaction with toluenesulfonyl chloride–pyridine (0°, 12 hr) and displacement of tosylate by iodide (sodium iodide–acetone, 25°, 0.5 hr, and 50°, 1 hr) (92% overall yield). Finally, reaction of the iodide **12** with the sodium salt of the acid **10** (from NaH) in dimethylformamide provided in 64% yield the bistetrahydropyranyl[6] derivative of the ester diol **4**, and the free diol **4** was obtained by cleavage of the tetrahydropyranyl groups at 25° in methanol–THF containing a small amount of toluenesulfonic acid.

The efficacy of the synthesis of **2** by the allylic dihalide–nickel carbonyl cyclization process depends in part on the unreactivity of σ- and π-allylnickel intermediates toward the ester function. Our previous experience with this method of cyclization leads to the expectation that the efficient synthesis of macrolides of larger ring size than **2** is possible and, further, that a variety of functional groups on the substrate dihalide can be tolerated. Further, it seems probable that the method should be applicable to macrocyclic lactams. We hope to provide additional information on these points in due course.

Acknowledgment. This research was supported by the National Science Foundation and the National Institutes of Health.

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(12) A. P. Krapcho, G. A. Glynn, and B. J. Grenon, *Tetrahedron Lett.*, 215 (1967).

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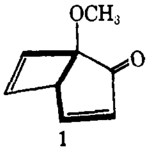
The Thermal Rearrangement of 1,4,4-Trimethylbicyclo[3.2.0]hepta-2,6-diene to 2,2,6-Trimethylbicyclo[3.2.0]hepta-3,6-diene

Sir:

Two distinct mechanistic interpretations of the apparent antara,antara Cope rearrangements of bicyclo[3.2.0]hepta-2,6-dienes and bicyclo[4.2.0]octa-2,7-dienes have been advanced.



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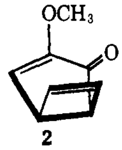
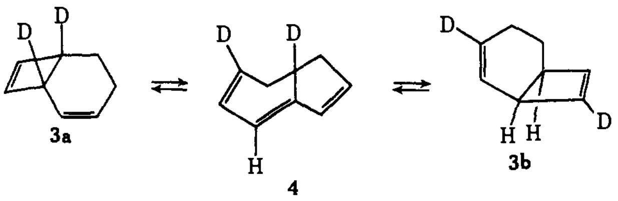


2

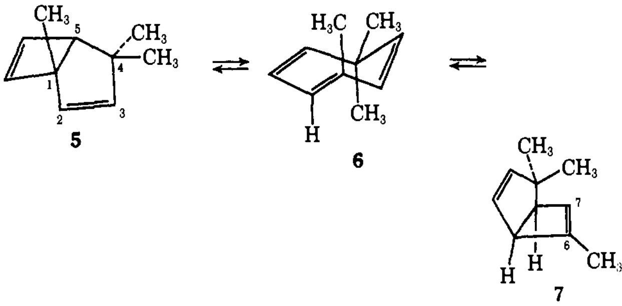
According to the first,[1] isomerizations like **1** → **2** are concerted $_{\pi}2_a + {}_{\sigma}2_s + {}_{\pi}2_a$ intramolecular cycloreactions permitted to occur in a fashion conserving orbital symmetry.[2]



According to the second,[3] isomerizations like the degenerate bicyclo[4.2.0]octa-2,7-diene equilibration (**3a** ⇌ **3b**) involve an intermediate cis,trans,cis cyclic triene, **4**, formed and collapsing through conrotatory electrocyclic valence isomerizations of the cyclobutene ⇌ butadiene variety.

An argument in support of the second view,[3] based on the failure of bicyclo[3.3.0]octa-2,6-diene to achieve this equilibration even at much higher temperatures,[4] has been countered by the observation that, in bicyclo[3.2.0] systems, a methoxy group at C-1 and the carbonyl group at C-2 are essential.[1] These functions are able to stabilize the concerted antara,antara transition state electronically or geometrically, and hence the lack of reactivity in a bicyclo[3.3.0]hydrocarbon is not surprising.[1]

We now report that 1,4,4-trimethylbicyclo[3.2.0]hepta-2,6-diene (**5**), a hydrocarbon lacking the oxygen functionality previously considered essential,[1] but possessing the cyclobutene moiety absent in bicyclo[3.3.0]octa-2,6-diene and necessary for production of the postulated cis,trans,cis cyclic triene intermediate **6**, undergoes the apparent antara,antara Cope rearrangement quite readily.



Hydrocarbon **5** was synthesized through treating the tosylhydrazone derivative (mp 118–121°; *m/e* = 318.140) of 1,4,4-trimethylbicyclo[3.2.0]hept-6-en-2-one, a photoisomer of eucarvone,[5,6] with methyllithium in ether.[7,8] The diene **5** was purified by glpc on an SE-30 column; *m/e* 134.109; nmr (CDCl$_3$) 3 H singlets at δ 1.03, 1.08, and 1.29, and 1 H absorptions at 2.58 (broad), 5.27 (dd, $J \cong 6$ and 1 Hz), 5.59 (d, $J \cong 6$ Hz), 6.02 (d, $J = 3$ Hz) and 6.48 (d, $J = 3$ Hz, C(7)–H).

Pyrolysis of **5** in the gas phase at 200° gave the known 3,7,7-trimethylcycloheptatriene[9] and diene **7**, having

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(1) T. Miyashi, M. Nitta, and T. Mukai, *Tetrahedron Lett.*, 3433 (1967); *J. Amer. Chem. Soc.*, **93**, 3441 (1971).

(2) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

(3) J. E. Baldwin and M. S. Kaplan, *Chem. Commun.*, 1560 (1970); *J. Amer. Chem. Soc.*, **93**, 3969 (1971).

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(5) G. Büchi and E. M. Burgess, *J. Amer. Chem. Soc.*, **82**, 433 (1960).

(6) H. Hart and T. Takino, *ibid.*, **93**, 720 (1971).

(7) R. H. Shapiro and M. J. Heath, *ibid.*, **89**, 5734 (1967).

(8) G. Kaufman, F. Cook, H. Shechter, J. Bayless, and L. Friedman, *ibid.*, **89**, 5736 (1967).

(9) J. A. Berson and R. M. Willcott, III, *ibid.*, **88**, 2494 (1966).

3 H nmr singlets at δ 0.99, 1.04, and 1.70 (broad), and signals at 2.8 (m, 1 H, C-1(H)), 3.5 (m, 1 H, C-5(H)), and 5.3–5.8 (m, 3 H, vinyl protons), in a 4:1 ratio. An alternative formulation for the bicyclic product, 2,2,7-trimethylbicyclo[3.2.0]hepta-3,6-diene, is excluded since a C(6)–H resonance well below the other olefinic absorptions is absent.

For the isomerization **5** → **7** at 200°, $k \leqq 2 \times 10^{-5}$ sec^{-1}; it is thus about 100 times slower than the conversion **1** → **2**,[1] but at least 10^{11}-fold faster than the degenerate and unobserved bicyclo[3.3.0]octa-2,6-diene rearrangement.[3,4] That a cis,trans,cis tropone might be more accessible, relative to its bicyclic precursor, than a cis,trans,cis tropilidene seems resonable, considering the larger bond angle and lower bending force constant for the C–CO–C unit.

Whatever the final resolution of this mechanistic controversy may be, the propensity shown by bicyclo[4.2.0]- and bicyclo[3.2.0]dienes **3** and **5** for this type of rearrangement, and the absence of rearrangement in bicyclo[3.3.0]octa-2,6-diene at 450° for 85 min,[4] does not deserve to be discounted as a pertinent fact through postulating that heteroatom functionality is essential. It is not.

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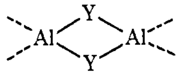
The SNi-Si Mechanism. Reductive Displacement of Good Leaving Groups with Retention of Configuration by Diisobutylaluminum Hydride. Stereochemical and Mechanistic Crossover with the Etherate Complex of Diisobutylaluminum Hydride

Sir:

A large number of dimeric aluminum compounds contain bridge 4 rings (I).[1] It is interesting to consider this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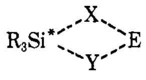
II

structural feature of formally trivalent aluminum compounds (R_3Al, etc.), together with the SNi-Si mechanism (II) in which the attacking reagent is EY.[2] Structure II may be an intermediate or transition state in which E is the electrophilic part and Y the nucleophilic part of the attacking reagent.

Comparison of I and II leads immediately to the interesting prediction that the use of organoaluminum reagents (R_2AlY), in which E in EY is a formally trivalent aluminum center, should greatly favor reactions at asymmetric silicon proceeding with retention of configuration.[3] Indeed, we have proposed that many *retention* reactions at asymmetric silicon proceed by mechanism SNi-Si, and we wish to report below stereochemical results which validate the above prediction and thereby provide strong additional evidence for the importance of the SNi-Si mechanism.[4]

We have found that a variety of functional groups on silicon can be reduced to give a silicon–hydrogen bond with i-Bu_2AlH. Reductions have been carried out using optically active R_3Si^*X, in which R_3Si^* is α-naphthylphenylmethylsilyl.[2a] Table I gives the stereochemical results for reduction of seven optically active silanes with i-Bu_2AlH in hexane solvent. In this solvent i-Bu_2AlH is trimeric and association involves hydrogen bridges.[5]

$$R_3Si^*X + i\text{-}Bu_2AlH \longrightarrow R_3Si^*H + Bu_2AlX$$

Table I. Reductions of R_3Si^*X with i-Bu_2AlH in n-Hexane

Reaction no.	Si*X	Product	Predominant stereochemistry,[a] %
1	(+)-Si*OCH_3	(+)-SiH	Retention, 100
2	(−)-Si*O(−)Men[b]	(+)-SiH	Retention, 100
3	(+)-Si*OPh	(+)-SiH	Retention, 99
4	(+)-Si*F	(+)-SiH	Retention, 98
5	(−)-SiSCH_3	(+)-SiH	Retention, 77
6	(−)-SiSC_6H_4-p-CH_3	(+)-SiH	Retention, 92
7	(−)-Si*Cl	(+)-SiH	Retention, 100

[a] *For a definition of, and reasons for, the term "predominant* stereochemistry," see L. H. Sommer, J. D. Citron, and G. A. Parker, *J. Amer. Chem. Soc.*, 91, 4729 (1969). [b] Men is menthyl.

Retention of configuration for reactions 1–3 in Table I engenders no surprise since reductions of the designated compounds with lithium aluminum hydride, containing formally tetravalent aluminum, also proceed with *retention* of configuration.

However, reduction of the compounds designated in reactions 4–7 in Table I with lithium aluminum hydride proceeds with *inversion* of configuration.[2a] Thus, the change from $LiAlH_4$ to i-Bu_2AlH produces a dramatic change in stereochemistry favoring *retention* of configuration as predicted on the basis of an SNi-Si mechanism model. The most striking result of all in Table I is the entirely new finding of a reaction of acyclic R_3Si^*Cl proceeding with pure *retention* of configuration.

Previously,[6] based on reactions of acyclic R_3Si^*X with strong nucleophiles, we formulated the "SN2-Si stereochemistry rule" of inversion of configuration for good leaving groups X, whose conjugate acids have pK_a less than ~6, providing the entering group Y is more basic than the leaving group X.

The above rule does not always apply to F as a leaving group for special reasons already given.[6] Paralleling one of those reasons (the high capacity of F for coordination with an electrophilic center), the present work shows that the rule may also not apply to special

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[1] For an excellent review, see G. E. Coates and K. Wade, "Organometallic Compounds," 3rd ed, Vol. 1, Methuen, London, 1967, pp 295–343.

[2] (a) For references up to 1965, see: L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill, New York, N. Y., 1965, Chapters 3, 4, 6, 10, and 11; (b) for a later reference which also cites numerous pertinent references, see: L. H. Sommer and H. Fujimoto, *J. Amer. Chem. Soc.*, **91**, 7040 (1969).

[3] This prediction receives further support from the fact that the covalent radii of aluminum and silicon are closely similar, being 1.25 and 1.17 Å, respectively.

[4] Overall geometry for SNi-Si is postulated (see ref 2) to be either a tetragonal pyramid at Si with X and Y basal and cis, or a trigonal bipyramid with X and Y equatorial and apical, respectively. In the latter case, pseudorotation of II to a second intermediate II, in which X is apical and the 4-ring structure is still intact, is possible.[2b]

[5] Reference 1, pp 340–341.

[6] L. H. Sommer, G. A. Parker, N. C. Lloyd, C. L. Frye, and K. W. Michael, *J. Amer. Chem. Soc.*, **89**, 857 (1967).