Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.86; H, 6.96; N, 6.45. Found: C, 71.98; H, 7.03; N, 6.40.

Similar manipulation of peak 4 (backside) gave β'-NO_2-S7 as a pale yellow solid, mp 65–66.5°; ir (CS_2, diagnostic peaks) 917, 901, and 839 cm^{-1}. See Discussion for pmr data.

Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.86; H, 6.96; N, 6.45. Found: C, 71.66; H, 6.80; N, 6.69.

In addition to pmr features noted in the Discussion, β- and β'-NO_2-S7 have nonaromatic pmr absorptions very similar to those described for α'-NO_2-S7.

Repeated preparative vpc (collection of peak 1) provided 5 mg of α-NO_2-S7 as a pale yellow oil: ir (CS_2, diagnostic peaks) 783, 748, and 732 cm^{-1}; nmr ($CDCl_3$) τ 2.63 (1 H, dd, β-H), ~2.78 and 2.89 (2 H, distorted dd and overlapped t, α'-H and β'-H, respectively), 7.02 (2 H, m, benzylic), 8.35 (6 H, broad m, $(CH_2)_3$), 9.20 and 9.42 (2 H each, broad s's, cyclopropyl H's); mass spectrum (70 eV) *m/e* 217 ($M\cdot^+$) and 189 (M − 28, 100%)[15] (compare α'-NO_2 isomer).

Independent Synthesis of β-NO_2-S7. 8-Nitro-1-methylenebenzosuberan. 8-Nitro-1-benzosuberone (8.6 g, 42 mmol) was subjected to reaction with triphenylphosphonium methylide (74 mmol) and work-up as reported for synthesis of 4-nitro-1-methyleneindan.[1b] The product (4.6 g, 54%) was a pale yellow oil: ir ($CHCl_3$, 1525, 1345, 910, 875, and 832 cm^{-1}; pmr ($CDCl_3$) τ 1.95 (1 H, d, 9-H), 2.03 (1 H, dd, 7-H), 2.79 (1 H, d, 6-H), 4.77 (1 H, d, syn vinyl), 4.92 (1 H, d, anti vinyl), 7.15 (2 H, m, benzylic), 7.60 (2 H, m, allylic), and 8.21 (4 H, m, other CH_2's).

β-NO_2-S7. Reaction of the above nitroalkene (2.74 g, 13.5 mmol) with iodomethylzinc iodide (135 mmol) and work-up as for synthesis of α'-NO_2-S5[13] afforded a mixture containing ~20% cyclopropanated material, which could not be separated on silver nitrate–silica gel chromatography. Enrichment *via* selective hexane extraction (−40°) and preparative vpc gave pure β-NO_2-S7, identical in all properties with the product isolated from nitration of S7 (see above).

Acknowledgment. Partial support of this work by the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

The Formation of Optically Active 1,2-Cyclononadiene from Two Different Cyclopropylidene Precursors[1]

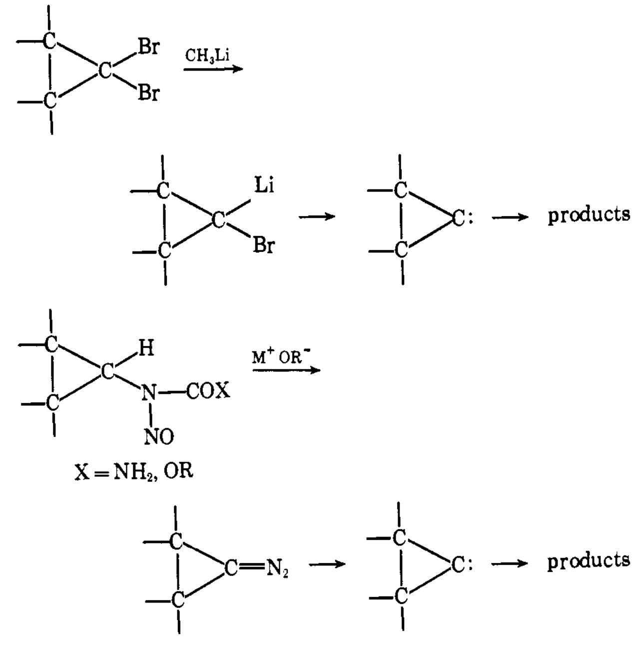
William R. Moore* and Robert D. Bach[2]

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. *Received June 18, 1971*

Abstract: Optically active 1,2-cyclononadiene (**7**) has been prepared by the opening of two different chiral cyclopropylidene precursors obtained by treatment of a *gem*-dibromocyclopropane with methyllithium and treatment of an *N*-nitrosourea (a diazocyclopropane precursor) with lithium ethoxide. At 0°, optically pure (1*R*,8*R*)-(−)-9,9-dibromo-*trans*-bicyclo[6.1.0]nonane (**2**) and (1*R*,8*R*)-(−)-*N*-nitroso-*N*-(9-*trans*-bicyclo[6.1.0]nonyl)urea (**6**) both give (*S*)-(−)-**7** having a high optical purity (slightly lower from **2**, which gives a higher optical purity at −78°). This result suggests that in the two cases, the transition states for ring opening are closely similar. The ring opening occurs by the equivalent of inward conrotation of the *trans*-methylene groups, a mode which reflects relief of strain. The possibility of the intervention of planar allene intermediates is considered. While such species are probably not important in this case, they may be in acyclic systems.

The formation of allenes by way of cyclopropylidene intermediates is an extremely useful reaction which has made a wide variety of cyclic and acyclic allenes readily available.[3,4] Two generally useful methods for generating cyclopropylidenes are outlined in Scheme I. Since α eliminations are often considered to give "carbenoids," while loss of nitrogen from a diazoalkane is regarded as giving a more or less "free" carbene, it is possible that cyclopropylidenes generated in these different ways would exhibit quite different re-

Scheme I



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[1] Acknowledgment is made to the National Science Foundation for support of this research.

[2] National Institutes of Health Predoctoral Fellow, 1964–1967.

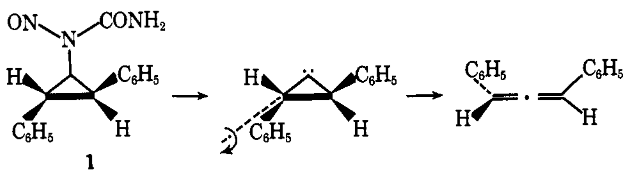
[3] (a) W. von E. Doering and P. M. Laflamme, *Tetrahedron*, **2**, 75 (1958); (b) W. R. Moore and H. R. Ward, *J. Org. Chem.*, **25**, 2073 (1960); (c) W. M. Jones, *J. Amer. Chem. Soc.*, **82**, 6200 (1960); (d) L. Skattebøl, *Tetrahedron Lett.*, 167 (1961); (e) W. R. Moore and H. R. Ward, *J. Org. Chem.*, **27**, 4179 (1962); (f) L. Skattebøl, *Acta Chem. Scand.*, **17**, 1683 (1963); (g) L. Skattebøl, *Org. Syn.*, **49**, 35 (1969), and references therein.

[4] (a) The addition of singlet carbon, generated in an arc, to olefins at *ca.* 77° K appears to give cyclopropylidenes which in turn yield allenes; P. S. Skell and R. R. Engel, *J. Amer. Chem. Soc.*, **89**, 2912 (1967), and references therein. (b) Recoil carbon atoms (from nuclear reactions) also add to ethylene to give allene as a major product; J. Nicholas, C. MacKay, and R. Wolfgang, *ibid.*, **88**, 1610 (1966), and references therein.

actions.[5] In this paper we examine a case which should be sensitive to such differences if they exist.

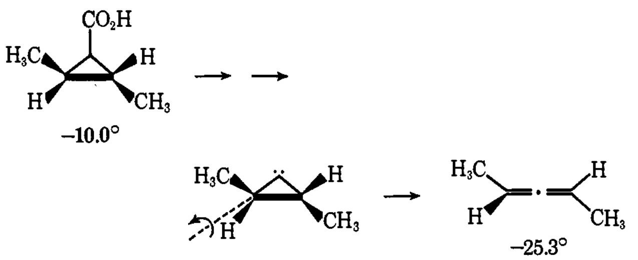
Jones, Wilson, and Tutwiler[6] found that the optically active *N*-nitrosourea **1** upon treatment with alkoxides gave optically active 1,3-diphenylallene. Subsequently, Jones and Wilson[7] determined the absolute configuration of **1** and this, taken with the assignment of the absolute configuration to 1,3-diphenylallene by Mason and Vane,[8] allowed the opening of the cyclopropylidene to be formulated as shown in Scheme II. The stereochemical control was attributed to a minimization of steric interference by rotating a hydrogen atom inward (away from the cyclopropylidene carbon), rather than a large phenyl group.

Scheme II



Inasmuch as optical purities were not known, it was not possible to determine the degree of stereospecificity.[9] In generalizing this method of asymmetric synthesis, Jones and coworkers[10] reported the conversion of several optically active *trans*-2,3-dialkylcyclopropylidene precursors to optically active allenes. In one case, the stereochemical course of the reaction was investigated.[11] The absolute configuration of (−)-*trans*-2,3-dimethylcyclopropanecarboxylic acid was determined by decarboxylating it to (+)-*trans*-2,3-dimethylcyclopropane, a compound which had previously been shown to have the 1*S*,2*S* configuration.[12] Combining this result with Brewster's assignment[13] of the *R* configuration to (−)-1,3-dimethylallene allowed Jones and Walbrick[11] to conclude that *trans*-2,3-dimethylcyclopropylidene opened in the same sense as had been observed in the diphenyl case (Scheme III). These results also give an indication of the degree of stereospecificity in the ring opening. Optically pure (−)-trans-2,3-dimethylcyclopropanecarboxylic acid should have a rotation of *ca.* $[\alpha]_D$ −50.5°[14] and thus should lead to allene having a rotation of *ca.* $[\alpha]_D$ − 128°, corresponding to a molecular rotation of $[\Phi]_D$ −87° (CCl_4). Brewster's method[13a] leads to a predicted molecular rotation of $[\Phi]_D$ −119° (CCl_4) for the optically pure allene. These estimates suggest that ring opening involved a fairly high degree of stereospecificity but that some loss of optical integrity probably occurred.

Scheme III

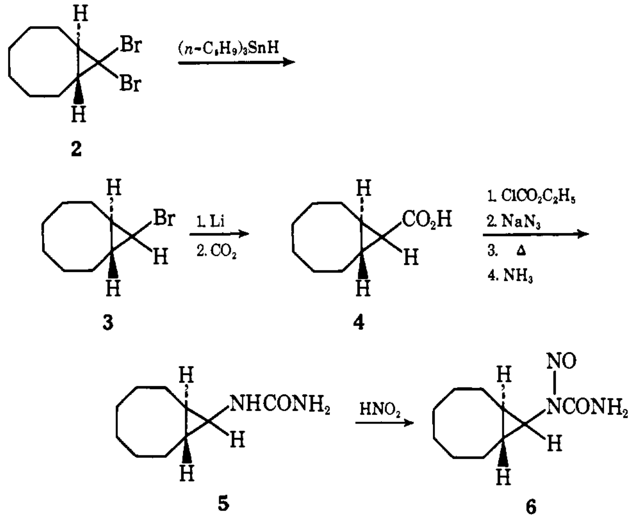


Recently we reported the synthesis of optically active 1,2-cyclononadiene from the dibromocarbene adduct of optically active *trans*-cyclooctene.[15] Since the degree of stereospecificity was high,[16] it appeared to be an excellent system for comparing the two methods of generating cyclopropylidenes.

Results

The desired diazocyclopropane precursor was synthesized from the dibromocarbene adduct of *trans*-cyclooctene (**2**) by the method outlined in Scheme IV.

Scheme IV



Racemic materials were employed in pilot experiments before optically active (−)-**2** was used. Since the reactions employed in Scheme IV cannot effect either racemization or isomerization to the cis series, the nitrosourea **6** must have an optical purity as high as that of the starting dibromide **2**, which, as we have discussed previously,[15] must be very close to 100%.

Treatment of (−)-**6** with lithium ethoxide at 0° gave 1,2-cyclononadiene (**7**) with a rotation of $[\alpha]^{25}_D$ −159°

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[5] Many cases have been cited for (apparent) differences in behavior of formally identical carbenoids and carbenes. References to the original literature can be found in the following reviews: (a) G. Kobrich, *Angew. Chem., Int. Ed. Engl.*, **6**, 41 (1967); (b) W. Kirmse, "Carbene, Carbenoide und Carbenanaloge," Verlag Chemie, Weinheim, Bergstr., 1969.

[6] W. M. Jones, J. W. Wilson, Jr., and F. B. Tutwiler, *J. Amer. Chem. Soc.*, **85**, 3309 (1963).

[7] W. M. Jones and J. W. Wilson, Jr., *Tetrahedron Lett.*, 1587 (1965).

[8] S. F. Mason and G. W. Vane, *ibid.*, 1593 (1965).

[9] The 1,3-diphenylallene clearly was not optically pure since recrystallization raised the rotation by a factor of more than two. It is stated that the *trans*-2,3-diphenylcyclopropanecarboxylic acid probably was optically pure (ref 10, footnote 16). If so, substantial loss of optical integrity occurred.

[10] J. M. Walbrick, J. W. Wilson, Jr., and W. M. Jones, *J. Amer. Chem. Soc.*, **90**, 2895 (1968).

[11] W. M. Jones and J. M. Walbrick, *Tetrahedron Lett.*, 5229 (1968).

[12] W. von E. Doering and W. Kirmse, *Tetrahedron*, **11**, 272 (1960).

[13] (a) J. H. Brewster, *Top. Stereochem.*, **2**, 33 (1967). (b) G. Lowe (*Chem. Commun.*, 411 (1965)) anticipated Brewster's assignment and provided a general rule for assigning absolute configurations to allenes based on rotations at 589 nm. (c) Caserio and her coworkers applied Lowe's rule to 1,3-dimethylallene and also provided an independent confirmation of the assignment of configuration based on asymmetric reductions with an optically active organoborane reagent: W. L. Waters and M. C. Caserio, *Tetrahedron Lett.*, 5233 (1968); W. L. Waters, W. S. Linn, and M. C. Caserio, *J. Amer. Chem. Soc.*, **90**, 6741 (1968).

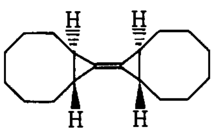
[14] This estimate is based on the rotations reported by Jones and Walbrick.[11] Acid with $[\alpha]_D$ −10.4° gave dimethylcyclopropane with $[\alpha]_D$ +9.63° and acid with $[\alpha]_D$ +6.15° gave cyclopropane with $[\alpha]_D$ −5.5°. The *trans*-2,3-dimethylcyclopropane obtained by Doering and Kirmse,[12] which should have been optically pure, had $[\alpha]_D$ −46.0°.

[15] A. C. Cope, W. R. Moore, R. D. Bach, and H. J. S. Winkler, *J. Amer. Chem. Soc.*, **92**, 1243 (1970).

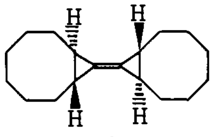
[16] W. R. Moore, R. D. Bach, and T. M. Ozretich, *ibid.*, **91**, 5918 (1969).

(c 1.16, CH_2Cl_2). Because treatment of (−)-**2** with methyllithium at 0° gives 1,2-cyclononadiene with a rotation of $[\alpha]D$ −150° (CH_2Cl_2),[15] it is evident that both the methyllithium-induced α elimination of **2** and the lithium ethoxide induced decomposition of **6** lead to opening of the three-membered ring in the same stereochemical sense. The slightly higher rotation found for the allene obtained from **6** indicated that the α elimination from the dibromide was not completely stereospecific at 0°, so we examined the reaction at a lower temperature to see if higher selectivity would result. In fact, at −78°, from (−)-**2** we obtained 1,2-cyclononadiene with a rotation of $[\alpha]^{25}D$ −166° (CH_2Cl_2). This result provides unequivocal experimental proof that at 0° neither method for generating the allene is completely stereospecific. However, based on our estimate of the rotation of optically pure allene,[16] viz. $[\alpha]^{25}D$ 170–175° (CH_2Cl_2), it is quite clear that these reactions do exhibit a very high degree of stereospecificity.

In connection with other studies in progress on the coupling of α-halocyclopropyllithium reagents, we examined the possibility of forming a biscyclopropylidene derivative from **2**. Previous results[17] showed that employing methyllithium which contained at least 1 equiv of lithium iodide leads to formation of an α-iodocyclopropyllithium intermediate at −78° which upon warming affords a substantial amount of the coupling product. When racemic **2** was subjected to these conditions, the crystalline "dimer" **8** was isolated in 16% yield. Glc analysis indicated that this was a 1:1 mixture of the expected stereoisomers **8a** and **8b**. Formation of **8** has some significance in interpreting the results of opening of the related cyclopropylidene to optically active allene. While the dibromide **2** clearly must retain some of the substantial strain of *trans*-cyclooctene, this strain does not cause ring opening to be so accelerated that other reactions typical of α-halocyclopropyllithium intermediates are precluded.



8a



8b

Discussion

The fact that the two methods for generating optically active 1,2-cyclononadiene give very nearly the same stereochemical results[18a] certainly suggests that in the product-forming stages, these reactions are similar.[18b] This case does not stand as an isolated result. We have found in studying several other systems that when these two methods are used for generating cyclopropylidenes which can react in different ways, such as competitive modes of intramolecular C–H insertion as well as opening to allenes, the similarities in the nature and relative amounts of the products formed are much more impressive (to us) than are the differences.[22]

The two types of reaction clearly involve different intermediates in the steps preceding the product-forming stage, namely an α-halocyclopropyllithium and a diazocyclopropane. Both types of intermediate clearly have the potential of generating a carbene which would serve as the immediate precursor of the products. But the timing of the loss of the leaving group (lithium halide or nitrogen) raises a subtle question, not easily answered. Our results cannot establish whether or not in either case a carbene actually is formed as a discrete intermediate which enters into the product-determining step. In any event, in neither case is a "free" carbene likely since the reaction conditions involve a variety of polar species capable of interacting with a carbene. The fact remains that the two reaction paths lead to essentially the same end result. In view of this parallel behavior, it appears reasonable to us to conclude that the *product-forming transition states* for these two reactions must be very similar. As a working model, we suggest that both types of reaction can be interpreted in terms of the generation of short-lived cyclopropylidenes, influenced by the nature of the immediate environment in which they are generated,[23] which give rise to closely related product-forming transition states. The latter may reflect environmental differences peculiar to the reaction conditions, but still must be sufficiently similar that both reaction routes give rise to nearly the same product spectrum. For the present case, our discussion will employ this model in considering those structural features which appear to be important in determining the stereochemical outcome.

The stereochemistry of the opening of the three-membered ring takes on particular significance because the degree of stereospecificity is high. Fortunately, it is possible to assign configurations to the species in question. Cope and Mehta provided unequivocal chemical evidence that (+)-*trans*-cyclooctene has the S configuration.[24] Since the addition of dibromocarbene to *trans*-cyclooctene must occur with retention of configuration, the absolute configuration of each intermediate shown in Scheme IV is known. Recently, we have established that (+)-1,2-cyclononadiene has the R configuration.[25] This result establishes that cyclopropylidene **9** has undergone predominant ring open-

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(17) W. R. Moore and M. G. McGrath, in preparation.

(18) (a) While we believe that the difference in rotations (9°, *ca.* 6%) is real (the uncertainty in rotations is estimated to be *ca.* ±2°), we feel that it is too small to warrant any detailed mechanistic interpretation. (b) A referee has criticized our interpretation of this result, stating that "... opening of the cyclic system is controlled by steric requirements of the ring and at least according to models, should open stereospecifically regardless of precursor." We agree that the opening is sterically controlled; this is the basis of much of our discussion in which we point out that there clearly are *opposing* steric effects. But on what basis, barring omniscience, can one predict with *certainty* which effect will be dominant? This is not a trivial question (consider ref 19); we felt compelled to establish the absolute configuration of 1,2-cyclononadiene before we could answer it.

(19) In weighing the relative importance of steric effects and strain, it would not be unreasonable to expect that (−)-**2** would open in the sense that Jones found for **1**.[20] In referring to our results[15] Krow[21] has made this assumption and thus has incorrectly assigned the R configuration to (−)-**7**.

(20) This possibility has been discussed: R. D. Bach, Ph.D. Dissertation, Massachusetts Institute of Technology, 1967.

(21) G. Krow, *Top. Stereochem.*, **5**, 38 (1970).

(22) W. R. Moore, D. B. Ledlie, and S. D. Clark, manuscript in preparation.

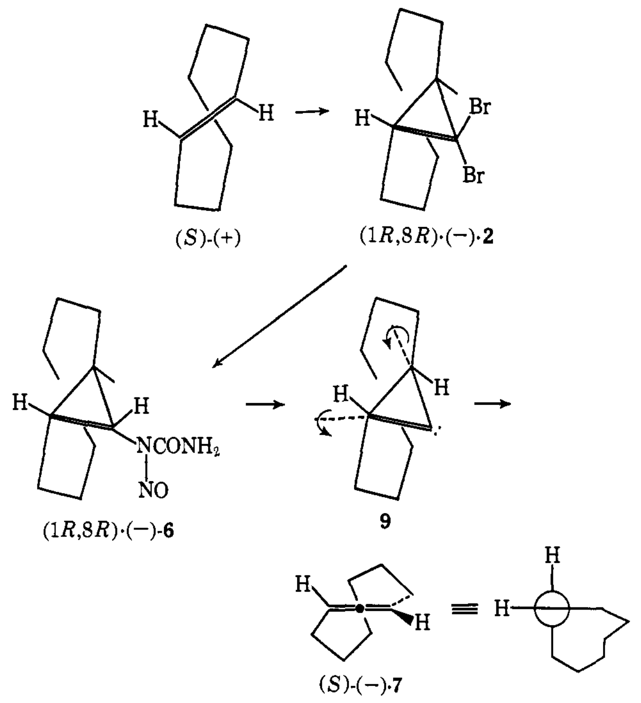
(23) For example, it seems probable that a cyclopropylidene would be subject to polarization by proximate species. In the case of a cyclopropylidene generated from an α-bromocyclopropyllithium intermediate, the lithium bromide which is eliminated as either a molecular species or part of a growing aggregate would exert a significant polarizing effect. We will elaborate this view in the future.

(24) A. C. Cope and S. A. Mehta, *J. Amer. Chem. Soc.*, **86**, 5626 (1964).

(25) W. R. Moore, H. W. Anderson, S. D. Clark, and T. M. Ozretich, *ibid.*, **93**, 4932 (1971).

ing with the stereochemical consequences shown in Scheme V, a result which corresponds to either conrotatory or monorotatory opening (they are indistinguishable here) with the methylene groups moving inward. It is important to note that the sense of the rotation is *opposite*[19] to that observed by Jones and coworkers[6,7,10,11] for *trans*-2,3-diphenylcyclopropylidene and *trans*-2,3-dimethylcyclopropylidene. As these authors suggested, a preference for one mode of conrotatory (or monorotatory) opening must have a steric origin. A group which rotates inward—away from the cyclopropylidene carbon atom—must experience nonbonded repulsions. Hence a hydrogen atom, by virtue of its small size, will be more readily accommodated than any other group. Steric control of this sort is graphically illustrated in the strikingly different behavior of tri- and tetrasubstituted cyclopropylidenes. The former open to allenes, but the latter, due to retardation of ring opening, survive long enough to undergo virtually complete intramolecular C–H insertion, yielding bicyclobutane derivatives.[26]

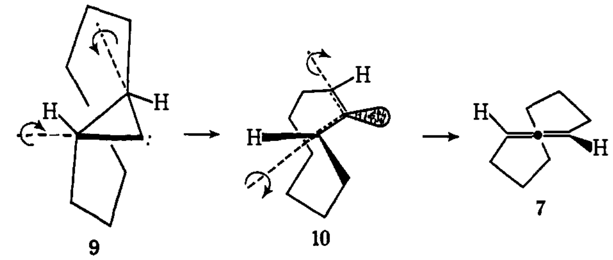
Scheme V



In the case of cyclopropylidene **9**, however, this sort of steric effect clearly must be overwhelmed by another effect which directs the opening in the opposite sense. The *trans*-bicyclo[6.1.0]nonane system is strained in the same sense as in *trans*-cyclooctene, but to a lesser extent. Rotation of the 1,8-hydrogen atoms inward should tend to *increase* the torsional strain, whereas rotation in the opposite sense (Scheme V) must *decrease* this strain. Clearly the relief of strain must be more than sufficient to override the steric repulsions encountered on rotating the methylene groups inward. The fact that cyclopropylidene **9** undergoes opening to 1,2-cyclononadiene rather than intramolecular C–H insertion establishes that the rate of allene formation must be comparable to that of simpler cyclopropylidenes.

While we have described the formation of 1,2-cyclononadiene in terms of a one-step least-motion opening of cyclopropylidene **9**, we must note that the stereochemical outcome does not preclude two-step mechanisms involving formation of an intermediate planar bent allene, a species which would serve as a precursor for the orthogonal allene. A planar bent allene would be equivalent to an allyl radical sans the central hydrogen atom (or the corresponding allyl cation sans the central proton). In one case, we have presented evidence for just such an intermediate, *viz.*, 1,2-cyclohexadiene.[27] At first thought, it may seem that intervention of a planar allene would guarantee formation of a racemic product. Indeed, in a case in which an *acyclic* allene is being formed from a chiral cyclopropylidene, such planar intermediates would be nondissymmetric and accordingly would lead to a racemic product. In contrast, in the present cyclic system, whether such potential planar intermediates would be dissymmetric or not would depend upon the orientation of the methylene chain. Dissymmetric conformations clearly are not only possible but are also probable. Provided the chirality of the methylene chain, *i.e.*, the sense in which it is twisted, were maintained throughout the transformation from cyclopropylidene to planar allene to orthogonal allene, the sequence would amount to a stereospecific pathway.[28] This possibility is illustrated in Scheme VI for disrotatory opening.[29] It is apparent that this two-step process would lead to opening of the three-membered ring in the stereochemical sense which we have observed. Since the formation of a transoid system, **10**, which must be somewhat strained should tend to inhibit this mode of opening, this process probably is not the main pathway. In acyclic systems, the formation of optically active allenes can only be accounted for by the sterically favored mode of opening proposed by Jones (Scheme III). However, if racemic allene is formed, it may not be the result of opening in the reverse (sterically hindered) sense but may well be due to the intervention of planar intermediates.

Scheme VI



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(26) (a) W. R. Moore, K. G. Taylor, P. Müller, S. S. Hall, and Z. L. F. Gaibel, *Tetrahedron Lett.*, 2365 (1970); (b) W. R. Moore and J. B. Hill, *ibid.*, 4343, 4553 (1970).

(27) (a) W. R. Moore and W. R. Moser, *J. Amer. Chem. Soc.*, **92**, 5469 (1970); (b) W. R. Moore and W. R. Moser, *J. Org. Chem.*, **35**, 908 (1970).

(28) While the barrier to interconversion of species of different chirality would be expected to be low, there would be no reason to assume that it would be lower than the barrier to conversion to a normal (orthogonal) allene.

(29) (a) Conrotatory opening to a planar allene intermediate seems unlikely, if not precluded, because the system would have to pass through essentially the same geometry which would lead to the stable orthogonal allene. (b) It should be noted that disrotatory opening, **9** → **10**, presumably would be catalyzed by metal ions such as lithium if the ion were coordinated with the filled in-plane orbital on the central carbon atom. Loss of the metal ion would occur in the conversion **10** → **7**. The opening would then be analogous to the opening of a cyclopropyl cation to an allyl cation and might validly be considered to be a noncarbene process. Future studies should shed some light on this possibility.

We will discuss evidence which bears on this possibility in subsequent papers.

Experimental Section[30]

9,9-Dibromo-*trans*-bicyclo[6.1.0]nonane (2) was prepared in both racemic and optically active form as described previously.[15]

9-Bromo-*trans*-bicyclo[6.1.0]nonane (3). Tri-*n*-butyltin hydride (14.5 g, 0.050 mol) was added (1 hr) dropwise with stirring to 14.1 g (0.050 mol) of racemic **2** while maintaining the temperature below 40° with a cooling bath. After an additional 2-hr period at 25°, the mixture was distilled (20-cm Vigreux column) to give 9.7 g (95%) of **3**: bp 52–56° (0.25–0.40 mm); mass spectrum, *m/e* 202 and 204 (M^+). *Anal.* Calcd for $C_9H_{15}Br$: C, 53.21; H, 7.45; Br, 39.34. Found: C, 53.99; H, 7.67; Br, 38.52.[31]

The reaction was repeated on 15.2 g (0.054 mol) of optically active **2**, $[\alpha]^{25}\mathrm{D}$ −43.8° (*c* 4.4, CH_2Cl_2), yielding 10.0 g (92%) of optically active **3**, $[\alpha]^{25}\mathrm{D}$ −47.4° (*c* 6.4, CH_2Cl_2).

9-Carboxy-*trans*-bicyclo[6.1.0]nonane (4). A well-stirred dispersion of 2.0 g of lithium in 150 ml of ether under helium was cooled to 0° and 9.85 g (0.049 mol) of optically active **3** was added dropwise. After a 6-hr period at 0°, the lithium reagent was added (by cannula) to a well-stirred slurry of ether–Dry Ice. The mixture was warmed to 0°, hydrolyzed, and extracted with dilute aqueous sodium hydroxide. Acidification (HCl) of the alkaline extract followed by extraction with ether and evaporation of the solvent (25° (1 mm)) gave 7.1 g (87%) of crude solid **9**. After several recrystallizations from pentane, 3.0 g (37%) of crystalline **4** was obtained: mp 85–86°; $[\alpha]^{26}\mathrm{D}$ −30.3° (*c* 2.2, CH_2Cl_2); ir ($CHCl_3$) 3500–2200, 1680, 1455, 945, 910 cm^{-1}. *Anal.* Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.38; H, 9.48.

In a preliminary experiment, racemic **4** was prepared in 54% yield, mp 109–110°.

***N*-(9-*trans*-Bicyclo[6.1.0]nonyl)urea (5).**[32] A well-stirred solution of 1.0 g (6.0 mmol) of optically active **4** and 0.70 g (7.0 mmol) of triethylamine in 20 ml of acetone was cooled to 0° and 0.76 g (7.0 mmol) of ethyl chloroformate was added slowly (1 hr). After an additional 1.5 hr at 0°, 0.91 g (14 mmol) of sodium azide in 10 ml of ice water was added dropwise. The white suspension was stirred for 1 hr at 0° and then it was poured onto 100 ml of cracked ice and the acyl azide was extracted with toluene (three 25-ml portions). The toluene solution was dried ($MgSO_4$) and then it was refluxed for 4 hr. The solution was cooled to 25° and ammonia was passed in for 1.5 hr. Filtration gave 0.90 g of the urea. Recrystallization from absolute ethanol afforded 0.68 g (63%) of **5** as white platelets: mp 189–190°; $[\alpha]^{25}\mathrm{D}$ −121.0° (*c* 1.6, absolute ethanol); ir (KBr) 3460, 3260, 3155 (broad), 2980, 2920, 2850, 1660, 1604, 1450 cm^{-1}; mass spectrum, *m/e* 182 (M^+).

In a preliminary experiment, racemic **5** was obtained in 74% yield after recrystallization from ethanol, mp 196.5–197.5°. *Anal.* Calcd for $C_{10}H_{18}N_2O$: C, 65.89; H, 9.95; N, 15.37. Found: C, 65.83; H, 9.97; N, 15.12.

The infrared spectrum of the racemic compound taken in KBr is significantly different from that of the optically active compound in the fingerprint region. The compound is not sufficiently soluble in chloroform to give a strong solution spectrum for comparison.

***N*-Nitroso-*N*-(9-*trans*-bicyclo[6.1.0]nonyl)urea (6).** A well-stirred solution of 0.70 g (3.8 mmol) of optically active **5** in 3.5 ml of glacial acetic acid and 1.8 ml of acetic anhydride was cooled to 0° and a solution of 0.26 g (3.8 mmol) of sodium nitrite in 3.5 ml of water was added dropwise. After 15 min, ice water was added causing the separation of a yellow oil which soon solidified. The yellow solid was collected, washed, and dried under reduced pressure (1 mm) for 20 hr to give 0.50 g (62%) of **6**: mp 88.5–89° dec; $[\alpha]^{25}\mathrm{D}$ −90.3° (*c* 1.4, CH_2Cl_2); ir ($CHCl_3$) 3525, 3410, 2995, 1740, 1680, 1580, 1510 cm^{-1}.

Racemic **6**, prepared as above, was obtained in 60% yield, mp 112–112.5° dec. Satisfactory elemental analyses could not be obtained on either the racemic or optically active compound.

Optically Active 1,2-Cyclononadiene from 6. A well-stirred suspension of 0.50 g (2.4 mmol) of optically active **6** in 20 ml of pentane was cooled to 0° and 0.25 g of lithium ethoxide was added. The suspension changed from yellow to white within 10 min. After 30 min the mixture was filtered and concentrated by evaporation. Short-path distillation (<0.5 mm, trap at −78°) gave 0.063 g of volatile material. Pure, 1,2-cyclononadiene was obtained by glc employing an all-glass system with a 240 × 1 cm column of 10% 1,2,3-triscyanoethoxypropane on Chromosorb W operating at 61° (inlet at 80°). The allene had a rotation of $[\alpha]^{25}\mathrm{D}$ −159° (*c* 1.6, CH_2Cl_2) and an infrared spectrum (neat) indentical with that of an authentic sample of the racemic allene.

Optically Active 1,2-Cyclononadiene from 2. A well-stirred solution of 1.15 g (4.1 mmol) of **2**, $[\alpha]^{25}\mathrm{D}$ −43.8° (*c* 2.2, CH_2Cl_2), in 75 ml of ether was cooled in a Dry Ice–acetone bath and 12 ml of 1.6 *M* methyllithium (prepared from methyl chloride) in ether was added dropwise (30 min). Water was added, the aqueous layer was shaken with ether, and the combined extracts were dried ($MgSO_4$). Evaporation of the ether and short-path distillation gave 0.25 g of volatile material. 1,2-Cyclononadiene was purified by glc as described above. The pure sample had a rotation of $[\alpha]^{25}\mathrm{D}$ −166° (*c* 1.4, CH_2Cl_2) and an infrared spectrum identical with that of an authentic sample of the racemic allene.[33]

Bis(9-*trans*-bicyclo[6.1.0]nonylidene) (8). A well-stirred solution of 3.6 g (12.7 mmol) of racemic **2** in 100 ml of ether was cooled to −78° (Dry Ice–acetone bath) and 50 ml of 0.5 *M* methyllithium in ether (the reagent, which had been prepared from methyl iodide, was greater than 0.5 *M* in lithium iodide) was added dropwise. The mixture was stirred at −78° for 1 hr and then was allowed to warm slowly to room temperature. Water was added and the ether layer was separated, washed with water, and dried ($MgSO_4$). Evaporation of the volatile materials (80° (1 mm)) gave an oil which solidified on standing. Two recrystallizations from methanol–ethanol gave 0.25 g (16%) of **8**: mp 81–83°; ir 2950, 2920, 2845, 1447, 1350, 1110, 955 cm^{-1}; nmr ($CDCl_3$) δ 0.9–2.5 only; mass spectrum, *m/e* 244 (M^+). The Raman spectrum did not show any C=C absorption in the anticipated region; three weak bands were observed at 2465, 2425, and 2380 in addition to many bands below 1500 cm^{-1}. *Anal.* Calcd for $C_{18}H_{28}$: C, 88.45; H, 11.55. Found: C, 88.44; H, 11.65.

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[30] Physical constants were determined with the following instruments: Perkin-Elmer Model 337 infrared spectrometer, Hitachi-Perkin-Elmer Model RMU-6D mass spectrometer, Varian A-60 nuclear magnetic resonance spectrometer, Zeiss photoelectric polarimeter (the rotations at 546.1 and 577.8 nm were used to calculate the value at the sodium D line), Hoover Thomas capillary melting point apparatus. The glc separations employed either an F and M Model 720 or a homemade (all glass) instrument. Elemental analyses were performed by Dr. S. M. Nagy and associates. All reactions were carried out under nitrogen unless otherwise indicated.

[31] Glc analysis indicated that the monobromide contained 2–3% of a more volatile material, presumably a hydrocarbon formed by reduction of **3** or decomposition (loss of HBr). This material was still present after a subsequent distillation through a Teflon spinning band column.

[32] This synthesis is based on the method of J. Weinstock, *J. Org. Chem.*, **26**, 3511 (1961).

[33] Subsequent preparations have given allene having essentially the same rotation; W. R. Moore and T. M. Ozretich, unpublished observations, and ref 16.