energy curve for a substituent in a ring system will be a sum of all of the interactions customarily considered in force-field calculations. If the curve is considered as a function of some variable and, of course, artificial bond distance between the ring and the substituent, it is not unreasonable that the curve for one ring system may cross that of another ring system. The ordering of steric sizes will depend on the actual bond length and therefore the order of conformational energies of substituents may become reversed. In the endo position of bicyclo[2.2.1]heptane, the van der Waals interactions will be more serious at short distances than in the axial position of cyclohexane. Furthermore, bond bending, bond stretching, and torsional changes may be more easily accomplished in cyclohexane than the strained, relatively constrained bicyclo[2.2.1]heptane. The carbon–oxygen bond distance is approximately 0.1 Å shorter than the carbon–carbon bond distance, and as a consequence the shape of the potential energy curves for hydroxyl and methyl could indeed cross. In a similar manner, the carbon–nitrogen bond of nitro compounds is expected to be shorter than the carbon–carbon bond of carbomethoxy compounds, and the potential energy curves may again cross.

From these observations, it can be concluded that using conformational energies derived from cyclohexane in other ring systems is unwise in even a qualitative sense and may lead to seriously incorrect interpretations of data. Force-field calculations and experimental determinations of representative substituents such as a methyl group in a variety of bicyclic ring systems are in progress.

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Elimination Reactions of Cyclooctylammonium Salts in Liquid Ammonia

Sir:

On the basis of deuterium labeling and comparative rate studies, Sicher and coworkers[1] have suggested that the Hofmann elimination reaction with medium-ring compounds afforded cis-olefins by an anti mechanism and trans-olefins by a syn mechanism (syn–anti dichotomy). Using specifically labeled cis- and trans-N,N,N-trimethylcyclooctylammonium-2-d_1 hydroxides, Coke and Mourning[2] found that indeed trans-cyclooctene is formed by a 100% syn elimination with syn k_H/k_D = 1.94. The cis-olefin, however, was apparently formed by a 51% syn and 49% anti mechanism with an anti k_H/k_D = 2.64 (calculated). In an investigation of the modified Hofmann elimination, Wittig and Polster[3] found that reaction of trimethylcyclooctylammonium bromide with phenyllithium in diethyl ether gave an olefin mixture containing 80% cis-cyclooctene, but that

with potassium amide in liquid ammonia the trans-olefin predominated (85%). The striking difference in product composition and the high proportion of a cis-olefin suggested the intervention of an α', β (ylide) mechanism. Despite the extensive investigation of the Hofmann elimination reaction with alicyclic derivatives,[4] a definitive study of these reactions in liquid ammonia has not appeared. We wish to report several examples of reactions of trialkylcyclooctylammonium salts in liquid ammonia using potassium amide as the base that proceed by a syn α', β mechanism.[5a]

The elimination reaction of N,N,N-dimethylbenzyl-cis-cyclooctylammonium-2-d_1 chloride (1) in liquid ammonia ($-33°$) using KNH_2 as the base afforded a mixture of olefins that was 95.4% cis-cyclooctene and 4.6% trans-cyclooctene. Since elimination with the trans 2-d_1 salt 2 proceeded without loss of deuterium, the formation of cis-olefin must proceed by a 100% syn pathway. The dimethylbenzylamine recovered from 1 contained ca. 66% of the deuterium lost by syn elimination (syn k_H/k_D = 1.47). However, approximately 12% of the deuterium initially present in 1 could not be accounted for in the products isolated from the reaction because of exchange.[5b] On the basis of these data a minimum of 64% of the cis-olefin must arise by an α', β elimination. Incorporation of ca. 1.0% deuterium in the dimethylbenzylamine derived from 2 suggests that the trans-cyclooctene is also formed by an intramolecular ylide pathway.

Similarly, the data in Table I show that the trans-olefin from 3 and the cis-olefin from 4 are both formed by a syn elimination without loss of deuterium (within experimental error). The observation of both cis- and trans-olefins being derived completely by a syn mechanism is unique, and we can therefore directly measure the isotope effect for the formation of both olefins. In the formation of trans-cyclooctene from 4 loss of hydrogen results in trans-cyclooctene-d_1 (85.5%) and loss of deuterium results in trans-cyclooocente-d_0 (14.5%) and a syn k_H/k_D = 5.89 can be calculated from these data. The difference in isotope effects for the formation of trans-cyclooctene and cis-cyclooctene (syn k_H/k_D = 2.07) is significant since it has been assumed that[2] the isotope effects for the formation of these olefins should be approximately the same for a syn E2 elimination.[6]
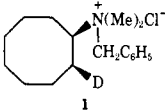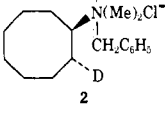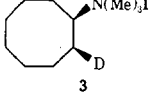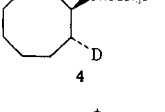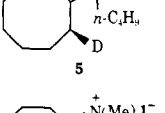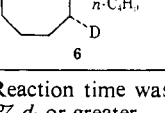
In order to examine the possibility of an α', β mechanism for the formation of both cis- and trans-cyclooctene, we prepared the N,N,N-dimethyl-n-butyl-2-d_1 iodides 5 and 6. As anticipated, trans-cyclooctene from 5 was formed by a 100% syn mechanism. Elimination of the trans 2-d_1 salt 6 showed the cis-olefin was also formed by a 100% syn pathway. More importantly, however, 100% (within experimental error) of the deuterium initially present in the starting salts 5 and 6 was found in the isolated olefins or the dimethylbutyl-

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(4) N. A. LeBel, *Advan. Alicyclic Chem.*, 195 (1971).

(5) (a) The starting materials were prepared according to the method of Coke.[2] The elimination reactions were carried out as described by Wittig[3] using potassium metal in liquid ammonia. The deuterium content of the starting materials and products was analyzed by mass spectrometry (11–14 eV). The mixture of cis- and trans-cyclooctene was separated by gas chromatography and each pure olefin was analyzed for deuterium. (b) Dimethylbenzylamine (21% d_1, 79% d_0) in NH_3 for 5 hr in the presence of KNH_2 lost 51% of its deuterium.

(6) The isotope effects for the formation of both cis- and trans-2-butene from 3-deuterio-2-bromobutane by an anti E_2 mechanism were found to be the same within experimental error: R. A. Bartsch, *J. Amer. Chem. Soc.*, 93, 3683 (1971).

Table I

	% cis-cyclooctene[a]	% trans-cyclooctene	Syn k_H/k_D	Amine
1 (cyclooctyl, $\overset{+}{N}(Me)_2Cl^-$, $CH_2C_6H_5$, D) $\xrightarrow[\text{NH}_3(1)]{\text{KNH}_2}$	95.4 (59.5% d_1;[b] 40.5% d_0)	4.6[c]	1.47[d,e]	26.9% d_1; 73.1% d_0
2 (cyclooctyl, $\overset{+}{N}(Me)_2Cl^-$, $CH_2C_6H_5$, D) $\xrightarrow[\text{NH}_3(1)]{\text{KNH}_2}$	97.1 (100% d_1; 0% d_0)	2.9		1.0% d_1; 99.0% d_0
3 (cyclooctyl, $\overset{+}{N}(Me)_3I^-$, D) $\xrightarrow[\text{NH}_3(1)]{\text{KNH}_2}$	22.2 (67.4% d_1; 32.6% d_0)	77.8 (98.3% d_1; 1.7% d_0)	2.07[e]	
4 (cyclooctyl, $\overset{+}{N}(Me)_3I^-$, D) $\xrightarrow[\text{NH}_3(1)]{\text{KNH}_2}$	36.9 (100% d_1; 0% d_0)	63.1 (85.5% d_1; 14.5% d_0)	5.89[f]	
5 (cyclooctyl, $\overset{+}{N}(Me)_2I^-$, $n\text{-}C_4H_9$, D) $\xrightarrow[\text{NH}_3(1)]{\text{KNH}_2}$	28.7 (60.4% d_1; 39.6% d_0)	71.3 (100% d_1; 0% d_0)	1.53[e]	12.5% d_1; 87.5% d_0
6 (cyclooctyl, $\overset{+}{N}(Me)_2I^-$, $n\text{-}C_4H_9$, D) $\xrightarrow[\text{NH}_3(1)]{\text{KNH}_2}$	37.3 (100% d_1; 0% d_0)	62.7 (71.7% d_1; 28.3% d_0)	2.53[f]	17.8% d_1; 82.2% d_0

[a] Reaction time was 5 hr. [b] All values are corrected for the isotopic purity of the N,N-dimethylcyclooctylamines. All samples had 83.3% d_1 or greater. The accuracies of the deuterium measurements are within ±1.5%. [c] The cis/trans ratios for unlabeled **1**, **3**, and **5** were 97/3, 23.8/76.2, and 32.4/67.6, respectively. The trans-olefin was shown to be stable to the reaction conditions. [d] Secondary isotope effects were neglected. [e] Isotope effect for the formation of cis-cyclooctene. [f] Isotope effect for the formation of trans-cyclooctene.

amine. This striking result would tend to preclude an α-elimination reaction, an E1cb intermediate with hydrogen exchange, both E1 and E2 reaction pathways, and the exchange of hydrogen in the dimethylbutylamine with solvent. Thus, both cis- and trans-cyclooctene are formed via a 100% α', β elimination mechanism. These results strongly suggest that the same mechanism is operating with the dimethylbenzyl- and trimethylcyclooctylammonium salts, **1-4**.

Our results clearly indicate that the reaction conditions in NH₃–NH₂⁻ elicit markedly different results from the Hofmann pyrolysis reaction. Indeed this is the first reported example of a strained olefin being formed by a ylide mechanism. The intervention of the α', β mechanism is much less prevalent in the Hofmann pyrolysis.[7] Our data also provide an explanation for the interesting observation by Cope[8] that an asymmetric (at nitrogen) Hofmann elimination reaction afforded the opposite enantiomer of trans-cyclooctene in liquid ammonia from that obtained in the pyrolysis reaction. A syn E2 process was presumably operating in the latter case.

The relatively low syn k_H/k_D of 1.47–2.07 for the formation of cis-cyclooctene by an α', β mechanism suggests that the transition state either comes very early or very late on the reaction coordinate.[9] However, the

near-maximum syn k_H/k_D (5.89) for formation of trans-cyclooctene from **4** is consistent with a mechanism where the C–H bond is approximately 50% broken in the transition state. This isotope effect differs significantly from that observed for the formation of trans-olefin from **6** (2.53). Thus, a rational correlation of the isotope effects with the cis/trans ratio of olefins formed in these reactions based upon the extent of proton transfer in the transition state according to the Westheimer[10] model is not in evidence.[11] Similarly, steric effects[12] do not appear to play a dominant role in determining the cis to trans ratio of olefins formed in these reactions. However, the conformation of the ring and the strength of the base involved in removing the diastereotopic β hydrogens provide one explanation for the observed cis/trans ratios. With a stabilized ylide derived from dimethylcyclooctylsulfonium iodide[13] or the benzyl salt **1**, the base is more discriminant than with highly reactive ylides and chooses the path of lowest activation energy affording the cis-olefin.

(7) J. L. Coke and M. P. Cooke, Jr., J. Amer. Chem. Soc., **89**, 6701 (1967).

(8) A. C. Cope, W. R. Funke, and F. N. Jones, ibid., **88**, 5693 (1966).

(9) The Cope elimination of N,N-dimethylcyclooctylamine oxide afforded cis-cyclooctene by a 100% syn elimination, as expected, with a syn k_H/k_D = 3.57 at 100°. Elimination of cyclooctyl tosylate under these conditions affords cis-cyclooctene by a >90% syn pathway with an isotope effect of 1.9; unpublished results.

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(11) A correlation of kinetic isotope effects with extent of proton transfer in a transition state has recently been questioned: F. G. Bordwell and W. J. Boyle, J. Amer. Chem. Soc., **93**, 512 (1971).

(12) The cis/trans ratios observed with N-methyl-N-cyclooctylpiperidinium iodide and N-methyl-N-cyclooctylpyrrolidium iodide were 27/73 and 20/80, respectively; unpublished results with K. Bair.

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The Absolute Configuration of 1,2-Cyclononadiene and *cis*-3-Acetoxycyclononene
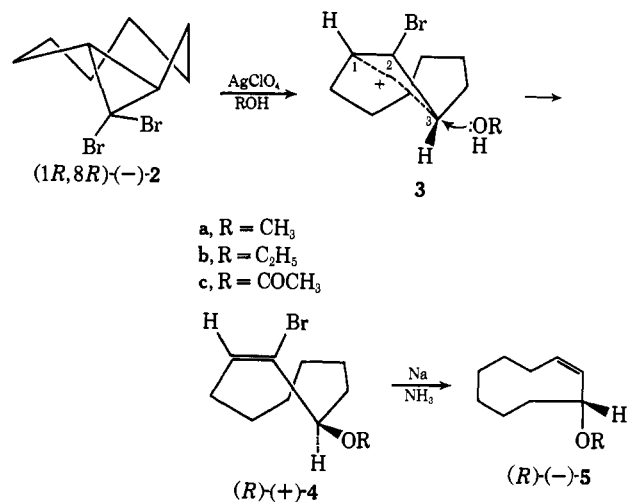
Sir:

We recently reported the hydroxymercuration[1] and alkoxymercuration[1,2] of optically active 1,2-cyclononadiene[3] to afford optically active products *via* a mercurinium ion[4] intermediate. We now wish to report the absolute configuration of 1,2-cyclononadiene and the products of its oxymercuration. We also wish to present evidence for the intermediacy of a chiral carbonium ion in a cyclopropyl–allyl rearrangement.

The key intermediates in our assignment of the stereochemistry of these compounds are the (+) and (−) enantiomers of 9,9-dibromo-*trans*-bicyclo[6.1.0]nonane (1 and 2). The (−) enantiomer of *trans*-cyclooctene was treated with $CHBr_3$ and $KOC(CH_3)_3$ in pentane at 0° affording optically pure 1, $[\alpha]^{25}D$ +44.2° (*c* 2.49, CH_2Cl_2), mp 51.5–53°.[3] An X-ray study[5] on the tetragonal crystals of 1 showed this compound to exist in a distorted crown conformation. This structure determination established the absolute configuration of (+)-1, (1*S*,8*S*) and corroborated the assignment[6] of the absolute configuration of (−)-*trans*-cyclooctene as *R*.

The silver perchlorate induced ring expansion of 9,9-dibromo-*cis*-bicyclo[6.1.0]nonane in methanol affording *trans*-2-bromo-3-methoxycyclononene has recently been reported.[7] The stereospecificity observed in this series of reactions led these authors to suggest that a free allylic cation was *not* involved in the solvolytic process. Orbital symmetry considerations[8] predict that the silver ion promoted ring expansion of the *trans*-dibromocarbene adduct 2 would proceed by a concerted disrotatory process affording the *cis,trans*-allyl cation 3. Attack by solvent at C_1 would afford *trans*-2-bromo-3-alkoxycyclononene while attack at C_3 would result in the cis isomer 4 (Scheme I).

Treatment of 2, $[\alpha]^{25}D$ −43.7°, with an excess of silver perchlorate in anhydrous methanol at 25° for 10 min resulted in quantitative conversion to *cis*-2-bromo-3-methoxycyclononene (4a), $[\alpha]^{25}D$ +42.6°. Reduction of 4a with sodium in liquid ammonia (1 hr) afforded 5a (55%) that had $[\alpha]^{25}D$ −13.1°. The methoxy ether 5a was identical, except for its optical activity,

Scheme I

a, R = CH_3
b, R = C_2H_5
c, R = $COCH_3$

with an authentic sample prepared by methoxymercuration–demercuration of 1,2-cyclononadiene.[1] The cyclopropyl–allyl transformation with 2 in anhydrous ethanol required 4 hr affording 4b, $[\alpha]^{25}D$ +36.0° (92%). Similarily, treatment of 4b with sodium in liquid ammonia afforded the pure cis isomer 5b[2] that had $[\alpha]^{25}D$ −20.2°. Acetolysis of 2 with excess silver perchlorate in glacial acetic acid for 30 min afforded 4c (80% conversion) that had $[\alpha]^{25}D$ +8.1°. Reduction of 4c with lithium aluminum hydride gave *cis*-2-bromo-3-hydroxycyclononene, $[\alpha]^{25}D$ +9.3°. Esterification of this alcohol with optically pure *O*-methylmandelyl chloride and nmr analysis using the method of Raban and Mislow[9] showed this compound to be of low optical purity (*ca.* 5%).

The above results preclude the possibility of a long-lived achiral carbonium ion. The rate of racemization of 4a–4c under the reaction conditions is too slow to account for the observed loss of optical activity and a concerted solvolysis of 2 may also be excluded.[10] We may, therefore, conclude that an optically active product arises by preferential attack by solvent on the chiral carbonium ion 3 from the least hindered side. Examination of molecular models clearly indicates that the developing carbonium ion 3 is more accessible to attack from the "outside" of the ring since the opposite approach is effectively shielded by the methylene chain. Since 2 has C_{2v} symmetry, (*R*)-(+)-4 would be formed regardless of which of the two asymmetric centers in 2 (C-1 or C-8) becomes the asymmetric carbon atom in 4.

The optical stability of 3 derives from steric inhibition to free rotation of the methylene chain that comprises the ring. Racemization of 3 requires overcoming the steric inhibition to rotation of the planar allyl moiety through the ring. Since the strained *trans,trans*-allyl cation derived from 9,9-dibromo-*cis*-bicyclo[6.1.0]-nonane[7] maintained its stereochemical integrity, in all probability the allyl moiety in 3 does not undergo cis,-

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(2) R. D. Bach, *J. Amer. Chem. Soc.*, 91, 1771 (1969).
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(4) G. A. Olah and P. R. Clifford, *ibid.*, 93, 1261, 2320 (1971); R. D. Bach and H. F. Henneike, *ibid.*, 92, 5589 (1970).
(5) We are indebted to Drs. S. H. Simonsen and B. J. Bowen for the X-ray analysis; B. J. Bowen, Ph.D. Thesis, University of Texas, Austin, Tex., 1969.
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(9) M. Raban and K. Mislow, *Top. Stereochem.*, 2, 199 (1967).
(10) The optical purity of 5a and 5b cannot be greater than 86 and 48% since these compounds prepared by oxymercuration of 6 (48% optically pure) had $[\alpha]^{25}D$ +7.3° and $[\alpha]^{25}D$ +15.3°,[1] respectively. This is based upon a maximum rotation of 175° for 1,2-cyclononadiene.[11] Doubling the reaction time for the solvolysis of 2 gave rotations of $[\alpha]^{25}D$ +41.3, +30.4, and +7.6°, for 4a, 4b, and 4c, respectively.
(11) W. R. Moore, R. D. Bach, and T. M. Ozretich, *J. Amer. Chem. Soc.*, 91, 5918 (1969).