# The Oxymercuration of Cycloalkenes

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The hydroxymercuration and methoxymercuration reactions of the eight stable unsubstituted cycloalkenes from $C_4$ through $C_9$ are reported. Near-ir hydroxy shift measurements and nmr methoxy shift measurements were used to assign product configurations of the $\beta$-hydroxymercurials and $\beta$-methoxymercurials, respectively. While the six *cis*-cycloalkenes underwent clean trans addition of the reagents, both *trans*-cyclooctene and *trans*-cyclononene reacted in an exclusively cis fashion. The tendency of an olefin to oxymercurate *via* a trans mechanism can be directly related to its ability to form the normal anti transition state. If for either steric or twist-strain reasons this transition state is made energetically unfavorable, cis addition will prevail.

Of the simple cyclic alkenes, only a few have received attention in the literature with respect to their oxymercuration products. One special problem of this reaction has been to assign the stereochemistry of the resultant alkoxy- or hydroxy-substituted organomercurial.

The product from methoxymercuration of cyclohexene was identified as the trans isomer by X-ray diffraction,[1] deoxymercuration studies,[2] and pmr methoxy shift data.[3] The hydroxymercuration product of cyclohexene was likewise identified as the trans isomer by pmr spin–spin coupling data[4] as well as ir hydroxy shift data.[5] The latter technique also identified the trans $\beta$-hydroxyalkylmercurial from cyclopentene.[5] Finally, both the ir technique and chemical methods proved cis-methoxymercuration and -hydroxymercuration of *trans*-cyclooctene.[6]

Since the stereochemical outcome for oxymercuration of cyclic alkenes necessarily sheds light on the transition state for this unique reaction, it was decided to enlarge the above list to include all the stable cycloalkenes from $C_4$ to $C_9$. Thus, the six cis olefins plus *trans*-cyclooctene and *trans*-cyclononene were allowed to react with mercuric acetate in both acetone–water and methyl alcohol solvents. The ir hydroxy shift and pmr methoxy shift techniques were used to prove the stereochemistry of hydroxymercuration and methoxymercuration, respectively.

## Results

Table I outlines the results of the hydroxy- and methoxymercuration reactions for the $C_4$–$C_9$ unsubstituted cyclic alkenes.[7]

As noted in Table I, the *cis*-cycloalkenes from cyclobutene to cyclononene underwent both hydroxymercuration and methoxymercuration in an exclusively

### TABLE I

| Cycloalkene | Stereochemistry of hydroxymercuration | Near-ir value $\Delta_\nu(OH)$,[a] cm$^{-1}$ | Stereochemistry of methoxymercuration | Nmr value $\Delta_\nu$ (OCH$_3$),[b] cps |
|---|---|---|---|---|
| Cyclobutene | Trans | 11.9 | Trans | 7.2 |
| Cyclopentene | Trans[c] | 14.0 | Trans | 5.5 |
| Cyclohexene | Trans[c,d] | 12.0 | Trans[e] | 7.8 |
| Cycloheptene | Trans | 14.4 | Trans | 7.9 |
| *cis*-Cyclooctene | Trans | 20.7 | Trans | 8.5 |
| *trans*-Cyclooctene | Cis[f] | 20.3 | Cis[f] | 8.5 |
| *cis*-Cyclononene | Trans | 11.8 | Trans | 9.7 |
| *trans*-Cyclononene | Cis[g] | 11.8 | Cis[g] | 9.7 |

[a] See ref 5; $\pm 2.5$ cm$^{-1}$.   [b] See ref 3; $\pm 0.1$ cps.   [c] See also ref 5.   [d] See also ref 4.   [e] See also ref 1, 2, and 3.   [f] See also ref 6.   [g] See ref 9.

trans manner. Only the one product could be detected from each of the 12 reactions (eq 1).[8]



$$n = 2\text{–}7 \text{ and } R = H \text{ or } CH_3$$
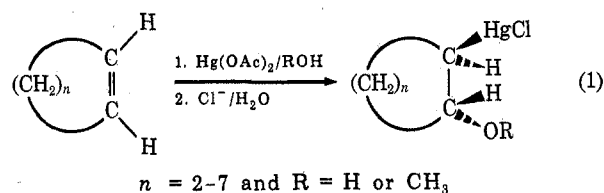
In contrast to the cis olefins, both *trans*-cyclooctene[6] and *trans*-cyclononene[9] reacted with both sets of reagents in an exclusively cis fashion. Also, in addition

(1) A. G. Brook and G. F. Wright, *Acta Crystallogr.*, **4**, 50 (1951).

(2) M. M. Kreevoy and F. R. Kowitt, *J. Amer. Chem. Soc.*, **82**, 739 (1960).

(3) W. L. Waters, *Tetrahedron Lett.*, No. 43, 3769 (1969).

(4) M. M. Anderson and P. M. Henry, *Chem. Ind. (London)*, No. 50, 2053 (1961).

(5) T. G. Traylor and A. W. Baker, *J. Amer. Chem. Soc.*, **85**, 2746 (1963).

(6) V. I. Sokolov, L. L. Troitskaya, and O. A. Reutov, *Dokl. Akad. Nauk SSSR*, 136 (1966).

(7) All attempts to oxymercurate cyclopropenes resulted in ring opening. Although the structures of the reaction products were not proven conclusively, it was definite that no simple $\beta$-hydroxy- or methoxycyclopropylmercury compounds were produced.

(8) In the case of methoxymercuration the raw $\beta$-methoxycycloalkylmercuric acetate was analyzed by nmr spectroscopy. Although it has been our experience that the easily exchangeable acetates on the mercury atom always produce one acetate line for a mixture of isomers, the methoxy singlet has been a reliable indication of isomeric purity.[3] Thus the area immediately adjacent to the observed methoxy singlet was carefully analyzed under increased spectrum amplitude conditions. Also, the total line shape of the methoxy singlet was noted. In each case not only were there no neighboring singlets to be seen but also the methoxy singlet itself was perfectly symmetrical and the peak at half-height approached natural line width.

As for the isomeric purity of the hydroxyoxymercuration products, only the recrystallized $\beta$-hydroxycycloalkylmercuric chloride products were subjected to ir measurement.[5] Although not a good indication of isomer distribution in the raw product, it should be noted that only one sharp hydroxyl peak could be seen in the ir of each of the reaction products listed. Isomeric purification to this extent by mere recrystallization seems unlikely.

(9) Professor Reutov's group has also found cis-oxymercuration in the case of *trans*-cyclononene. This and other results are the subject of a paper in preparation by V. I. Sokolov, L. L. Troitskaya, and O. A. Reutov.

to the usual $\beta$-hydroxy or $\beta$-methoxy products, $\beta$-acetoxy products were sometimes formed[10] (eq 2).
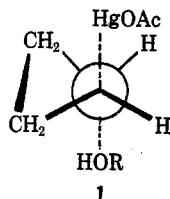


$$n = 6, 7 \text{ and } R = H \text{ or } CH_3$$
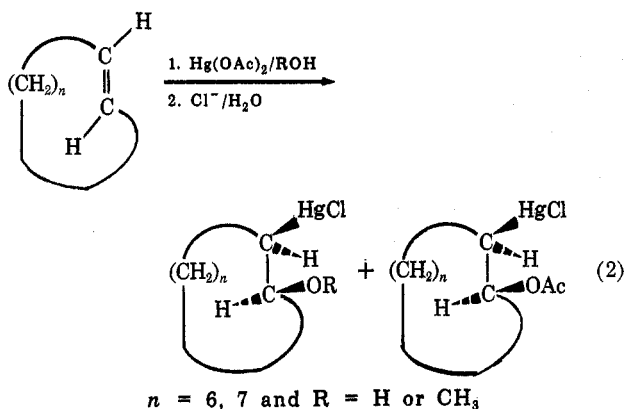
The strained cis-addition products can undergo immediate ring flipping to give the more stable trans conformers (eq 3). These compounds, once in their



$$R = H, CH_3, \text{ or } Ac$$
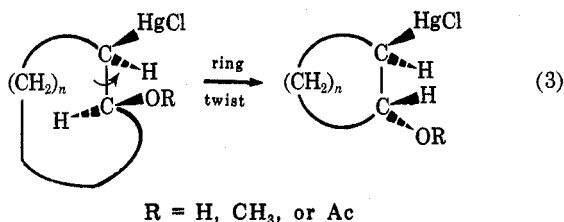
more stable trans conformations, are identical with the products from the cis olefins. Their structural and configurational assignments are therefore made extremely easily.

## Discussion

Several contributing factors which can control the stereochemistry of electrophilic addition reactions were considered in some detail by Traylor.[11] Of these, the "twist–strain" theory[11] most adequately explains the results for oxymercuration of the simple cis-cycloalkenes. This theory deals with the transition-state stereochemistry for electrophilic addition and predicts that *only* cyclopropene of all the cis-cycloalkenes should undergo cis-oxymercuration.[7] In the case of a three-membered carbon ring the necessary anti transition state for normal addition is prohibited. However, cyclobutene, the next higher homolog, should accommodate the necessary 180° coplanar transition state as pictured in **1**, and should even



**1**

reflect a relief of ring strain compared to the parent olefin.[11]

The results listed in Table I for the $C_4$–$C_9$ cis-cycloalkenes support the twist–strain theory fully. Whenever there are no other interceding factors, *e.g.*, steric, etc., and whenever there is a decrease—or at least *no increase*—in the strain of a system when going from olefin to an anti transition state, the oxymercuration reaction will occur exclusively *via* a trans mechanism

In contrast to the cis-cycloalkenes, it can be noted that both *trans*-cyclooctene and *trans*-cyclononene undergo oxymercuration in an exclusively cis fashion. Although it might be argued that the increased strain involved in the anti transition state for these olefins prevents trans addition, the overriding factor is probably one of steric control. The back side of the $\pi$ bond, and hence the back side of any intermediate mercurinium ion, is completely shielded toward attack by a nucleophile. Hence, addition can only be exo and cis to cycloalkenes such as these.

In light of the above, one would predict an increasing amount of trans-oxymercuration with larger and larger *trans*-cycloalkenes. In these olefins, the carbon skeletons would be much less rigid, thereby reducing ring strain and virtually eliminating any steric effect. In support of this expectation, Sokolov reports competing cis- *and* trans-oxymercuration for *trans*-cyclodecene and exclusive trans-oxymercuration for *trans*-cyclododecene.[12]

Unfortunately, this work does not settle any of the questions currently being raised about mercurinium ions.[13] However, when added to the results for the rigid and semirigid bicyclic olefins,[11] it does present a unified and very useful stereochemical picture of the overall oxymercuration reaction. Thus, the reaction involves the trans stereospecific addition of a mercury salt and alcohol or water solvent across a carbon–carbon multiple bond *except* in cases where an anti transition state is prohibited by steric and/or "twist–strain" reasons. The dividing lines for these two limitations appear to be *trans*-cyclodecene[12] and bicyclooctene,[13,14] respectively.

## Experimental Section

Melting points were taken on a Thomas-Hoover and Mel-Temp melting point apparatus and are uncorrected. Infrared spectra were taken on Perkin-Elmer Infracord 137B and Beckman IR-33, IR-5A, and IR-7 spectrophotometers. Overtone hydroxyl stretching frequencies in the near-ir were measured with a Cary 14 recording spectrophotometer. Nuclear magnetic resonance spectra were obtained with Varian HR-60, A-60, and HA-60 instruments. Vapor phase chromatography (vpc) was performed with Varian A-700 and 1720 gas chromatographs.

**Oxymercuration of Cycloalkenes. General Procedure.**—To a solution of $1 M$ Hg (OAc)$_2$ in 25% acetone–water or methanol was added an equimolar amount of the cycloalkene (*ca*. 1–10 mmol). The reaction mixture was stirred at room temperature until a test portion failed to give a precipitate of HgO on treatment with $2 M$ NaOH. The reaction mixture was then neutralized by pouring it into an aqueous solution of excess NaCl and NaHCO$_3$, and the $\beta$-hydroxy- (or methoxy-) cycloalkylmercuric chloride was isolated by filtration or CHCl$_3$ extraction. The raw solid (or oily) product was then analyzed by ir or nmr spectroscopy to determine isomeric purity.[8] Simple recrystallization from an appropriate

(10) Professor Reutov's group also noted the $\beta$-acetoxy products: ref 6 and V. I. Sokolov, L. L. Troitskaya, and O. A. Reutov, *J. Organometal. Chem.*, **17**, 323 (1969). The authors believe that the initial oxymercuration products of *trans*-cycloalkenes are the $\beta$-acetoxy compounds, which then react with water or alcohol to give the $\beta$-hydroxy- or $\beta$-alkoxycycloalkyl-mercurials.

(11) T. G. Traylor, *Accounts Chem. Res.*, **2**, 152 (1969).

(12) Personal communication from V. I. Sokolov, L. L. Troitskaya, and O. A. Reutov, INEOS, Moscow, U. S. S. R. (paper in preparation).

(13) See, for example, R. D. Bach and R. F. Richter, *J. Amer. Chem. Soc.*, **94**, 4747 (1972).

(14) T. G. Traylor, *J. Amer. Chem. Soc.*, **86**, 244 (1964).

solvent yielded the desired mercury compound suitably pure for elemental analysis or mass spectroscopic studies.

**Configurational Assignment of Hydroxymercuration Products.**—Approximately 2 mmol of the $\beta$-hydroxycycloalkylmercuric chloride was added to *ca.* 30 mmol of NaBH$_4$ in 25 ml of water and stirred overnight at room temperature. The aqueous mixture of the parent alcohol and elemental mercury was then extracted with ether, the extract was dried over MgSO$_4$, and the solvent was removed on a rotary evaporator.

The first overtone hydroxyl stretching frequencies of the alcohols and hydroxymercurials were determined with *ca.* 0.02 *M* CH$_2$Cl$_2$ solutions of the sample in 1-cm silica cells. Scale expansion and slow scanning speeds were used to ensure large symmetrical peaks. All overtone frequencies were calibrated relative to phenol, using 7013.1 cm$^{-1}$ as an arbitrary standard reference value. Finally, the cis and trans assignments were made by the generalization that the *trans*-$\beta$-hydroxymercurials have $\Delta\nu_{OH}$ values (compared to the parent alcohol) of 10–25 cm$^{-1}$, while the *cis*-$\beta$-hydroxymercurials have $\Delta\nu_{OH}$ values in the range of 29–35 cm$^{-1}$.[15]

**Configurational Assignment of Methoxymercuration Products.**—Approximately 2 mmol of the $\beta$-methoxycycloalkylmercuric chloride was dissolved in *ca.* 10 ml of 0.5 *M* NaOH at 0°. To the stirred basic solution was added an equivalent amount of NaBH$_4$ as a 1 *M* solution in 0.5 *N* NaOH. After 15 min of additional stirring the product cycloalkyl methyl ether was extracted with *ca.* 1 ml of CCl$_4$, washed repeatedly with H$_2$O until neutral, and dried over MgSO$_4$. To the clear CCl$_4$ solution of the cycloalkyl methyl ether was added a small amount of the $\beta$-methoxycycloalkylmercuric chloride and an nmr spectrum was then taken of the mixture (each compound *ca.* 2%). The frequency difference of the two methoxy lines was measured with a frequency counter on an expanded sweep width spectrum. Finally, the cis and trans assignments were made by the generalization that the trans-methoxymercuration products of cyclic olefins have $\Delta\nu_{OCH_3}$ values of 3–10 cps, while the *cis*-$\beta$-methoxycycloalkylmercurials have $\Delta\nu_{OCH_3}$ values of 10–13 cps.[3]

**Cycloalkenes. Cyclobutene** was prepared by the method of Cope[16] from the pyrolysis of the adduct[17] of acetylenedicarboxylic acid methyl ester to cyclooctatriene. The cyclobutene was condensed into a cold trap at −80° and used directly by recondensing it into a reaction solution at −80°. It should be noted that in some cases pyrolysis of the Diels–Alder adduct also produced 1,3-butadiene in about 10% yield.

**Cyclopentene, cyclohexene, cycloheptene, and cyclooctene** were obtained commercially (Aldrich Chemical Co.) and used without any further purification.

*trans*-**Cyclooctene** was prepared by pyrolysis of cyclooctyltrimethylammonium hydroxide, as described by Cope.[18] The olefin, separated by extraction with 20% aqueous AgNO$_3$, was shown to be pure by vpc analysis on a 20 ft × 0.375 in. 20% DEGS column and by comparison of its ir spectrum with that reported.[18] Yield of the trans olefin was 33% of theory.

*cis*-**Cyclononene** was prepared by P. G. Marsh using the method of Gardner.[19] Catalytic hydrogenation was chosen as the method for reduction of 1,2-cyclononadiene. The ir spectrum of the product was identical with that reported in the literature.[20]

*trans*-**Cyclononene** was prepared by the method of Cope.[21] P. G. Marsh prepared cyclonononylamine hydrochloride from dimethyl azelate. The amine hydrochloride was then converted to the usual tetraalkylammonium hydroxide and pyrolyzed at 100° (1 mm). The raw product mixture contained 98% *trans*-cyclononene by vpc analysis using a 10 ft × 0.25 in. 20% DEGS column. The trans olefin was purified by preparative vpc using a 20 ft × 0.375 in. DEGS column. The ir spectrum of the product matched that in the literature.[20]

**Oxymercuration Reactions. Cyclobutene.**—Hydroxymercu-

ration of cyclobutene under conditions described above gave a 33% yield of crude *trans*-2-chloromercuricyclobutanol. Recrystallization from chloroform-*n*-heptane gave a white, crystalline solid, mp 95.5–96.0°. *Anal.* Calcd for C$_4$H$_7$OHgCl: C, 15.64; H, 2.30; Hg, 65.31. Found: C, 15.75; H, 2.56; Hg, 63.57. The first overtone of the hydroxyl stretching frequency appeared at 7028.3 cm$^{-1}$ (±1.5 cm$^{-1}$). Reduction of the organomercurial with NaBH$_4$ as outlined above gave cyclobutanol. Its ir spectrum was identical with that of an authentic sample,[17] and its first overtone hydroxyl frequency was found at 7040.2 cm$^{-1}$.

Methoxymercuration of cyclobutene gave a 65% yield of *trans*-1-methoxy-2-chloromercuricyclobutane, oil at room temperature: mass spectrum molecular ion at *m/e* 320; nmr (CDCl$_3$) $\tau$ 5.73 (m, 1), 6.73 (s, 3), 6.9–7.6 (m, 1), 7.8–8.2 (m, 4); spin decoupling *via* saturation at $\tau$ 8.0 produced a singlet at $\tau$ 5.73, therefore $J[C(OMe)H-C(HgX)H] \cong 0$, and $\angle$CH–CH $\cong 90°$. Reduction of the organomercurial with NaBH$_4$ gave cyclobutyl methyl ether (nmr, ir), whose methoxy line (nmr) had shifted 7.2 cps upfield compared to the parent organomercurial.

Contaminating 1,3-butadiene (noted above) produced 1,4-dichloromercuri-2,3-dimethoxybutane (nmr), mp 162.5–165.0° dec, from CHCl$_3$ (lit.[22] mp 165–166°), which separated quickly from all recrystallization solvents.

**Cyclopentene.**—Hydroxymercuration of cyclopentene gave *trans*-2-chloromercuricyclopentanol as described previously.[5] Reduction of the organomercurial with NaBH$_4$ yielded cyclopentanol (ir) with $\Delta\nu_{OH} = 14.0$ cm$^{-1}$.

Methoxymercuration of cyclopentene gave an 85% yield of *trans*-1-methoxy-2-chloromercuricyclopentane: mp 83.0–83.5° from EtOH–H$_2$O (lit.[23] mp 83.3–83.7°); mass spectrum molecular ion at *m/e* 334; nmr (CCl$_4$) $\tau$ 5.89 (m, 1), 6.73 (s, 3), 7.29 (m, 1), 7.7–8.7 (m, 6). NaBH$_4$ reduction gave cyclopentyl methyl ether (ir, nmr) with $\Delta\nu_{OCH_3} = 5.5$ cps.

**Cyclohexene.**—Hydroxymercuration of cyclohexene gave *trans*-2-chloromercuricyclohexanol as described previously.[5] NaBH$_4$ reduction gave cyclohexanol (ir) with $\Delta\nu_{OH} = 12$ cm$^{-1}$.

Methoxymercuration of cyclohexene gave an 89% yield of *trans*-1-methoxy-2-chloromercuricyclohexane: mp 113.5–114.5° from EtOH–H$_2$O (lit.[24] mp 113.5–114.5°); mass spectrum molecular ion at *m/e* 348; nmr (CDCl$_3$) $\tau$ 6.66 (s, 3), 6.70 (m, 1), 7.18–9.10 (m, 8). NaBH$_4$ reduction gave cyclohexyl methyl ether (ir, nmr) with $\Delta\nu_{OCH_3} = 7.8$ cps.

**Cycloheptene.**—Hydroxymercuration of cycloheptene gave *trans*-2-chloromercuricycloheptanol in 64% yield, mp 78.0–78.5° from chloroform-*n*-heptane. *Anal.* Calcd for C$_7$H$_{13}$OHgCl: C, 24.07; H, 3.75; Hg, 57.44. Found: C, 24.14; H, 4.02; Hg, 57.51. The first overtone of the hydroxyl stretching frequency appeared at 7025.4 cm$^{-1}$. NaBH$_4$ reduction gave cyclopentanol (ir), having a first overtone hydroxyl frequency of 7039.8 cm$^{-1}$.

Methoxymercuration of cycloheptene gave an 80% yield of *trans*-1-methoxy-2-chloromercuricycloheptane: mp 45.0–45.5° from hexane; mass spectrum molecular ion at *m/e* 362; nmr (CCl$_4$) $\tau$ 6.70 (m, 1), 6.78 (s, 3), 7.25 (m, 1), 7.8–8.8 (m, 10). NaBH$_4$ reduction gave cycloheptyl methyl ether (ir, nmr) with $\Delta\nu_{OCH_3} = 7.9$ cps.

*cis*- **and** *trans*-**Cyclooctene.**—Hydroxymercuration of *cis*- and *trans*-cyclooctene gave *trans*-2-chloromercuricyclooctanol in 59 and 83% yields, respectively, mp 96.5–97.0°[25] from chloroform-*n*-heptane (lit.[6] mp 96–97°). *Anal.* Calcd for C$_8$H$_{15}$OHgCl: C, 26.45; H, 4.16; Hg, 55.22. Found: C, 26.44; H, 4.35; Hg, 55.19. Ir spectra (CS$_2$) of the products from the two reactions were identical. The first overtones of the hydroxyl stretching frequencies appeared at 7022.5 cm$^{-1}$ for the product from cis olefin and 7022.9 cm$^{-1}$ for the product from *trans*-cyclooctene. NaBH$_4$ reduction gave cyclooctanol (ir), having a first overtone hydroxyl frequency of 7043.2 cm$^{-1}$.

Methoxymercuration of *cis*- and *trans*-cyclooctene gave *trans*-1-methoxy-2-chloromercuricyclooctene in 65 and 70% yields, respectively: mp 58.0–59.5° from EtOH–H$_2$O (lit.[6] mp 60–61°); mass spectrum molecular ion at *m/e* 376; nmr (CCl$_4$) $\tau$ 6.50

(15) The first overtone differences are approximately twice the primary frequency differences listed in ref 5.

(16) Method of W. R. Moore, private communication adapted from A. C. Cope, A. C. Haven, F. L. Rump, and E. R. Trumbull, *J. Amer. Chem. Soc.*, **74**, 4867 (1952).

(17) Generously supplied by W. R. Moore.

(18) A. C. Cope, R. A. Pike, and C. F. Spencer, *J. Amer. Chem. Soc.*, **75**, 3212 (1953).

(19) P. D. Gardner and M. Narayana, *J. Org. Chem.*, **26**, 3518 (1961).

(20) A. T. Bloomquist, L. H. Liu, and J. C. Bohrer, *J. Amer. Chem. Soc.*, **74**, 3643 (1952).

(21) A. C. Cope, K. Banholzer, H. Keller, B. A. Pawson, J. J. Whang, and H. J. S. Winkler, *J. Amer. Chem. Soc.*, **87**, 3644 (1965).

(22) K. H. McNeely and G. F. Wright, *J. Amer. Chem. Soc.*, **77**, 2553 (1955).

(23) A. Brook, R. Donovan, and G. Wright, *Can. J. Chem.*, **31**, 535 (1953).

(24) A. Rodgman and G. Wright, *J. Org. Chem.*, **18**, 1617 (1953).

(25) It should be noted that recrystallization of the organomercurial from chloroform gave a white, crystalline solid, mp 93.5°. Remelting of this melting point sample occurred at 96.5–97.0°. A careful ir and thermal study of this compound revealed the existence of two crystalline polymorphic forms, the higher melting one being the more stable.

(m, 1), 6.68 (s, 3), 7.08 (m, 1), 7.7–8.8 (m, 12). NaBH₄ reduction gave cyclooctyl methyl ether (ir, nmr) with $\Delta\nu_{OCH_3}$ = 8.5 cps.

In the nmr spectrum of the raw β-methoxycyclooctylmercuric chloride, some β-acetate product was seen. Although investigation of this minor constituent was not carried out, it is certainly the identical product as isolated by Sokolov.[6]

*cis-* and *trans-*Cyclononene.—Hydroxymercuration of *cis-* and *trans-*cyclononene gave *trans-*2-chloromercuricyclononanol in 25 and 57% yields, respectively, mp 127–128° from chloroform-pentane. Anal. Calcd for C₉H₁₇OHgCl: C, 28.65; H, 4.54. Found: C, 28.53; H, 4.27. Ir spectrum (CHCl₃) of the products from the two reactions were identical. The first overtone hydroxyl stretching frequency was 7020.2 cm⁻¹ for both products. NaBH₄ reduction gave cyclononanol (ir), having a first overtone hydroxyl frequency of 7032.0 cm⁻¹.

Methoxymercuration of *cis-* and *trans-*cyclononene gave *trans-*1-methoxy-2-chloromercuricyclononane in 54 and 65% yields, respectively: mp 86.5–87.5° from CH₃OH–H₂O; ir spectra (KBr) of the products from the two reactions were identical; mass spectrum molecular ion at *m/e* 490; nmr (CCl₄) τ 6.37 (m, 1), 6.64 (s, 3), 7.02 (m, 1), 7.7–8.6 (m, 14). NaBH₄ reduction gave cyclononyl methyl ether (ir, nmr) with $\Delta\nu_{OCH_3}$ = 9.7 cps.

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# A Direct ¹H and ¹⁹F Nuclear Magnetic Resonance Study of Boron Trifluoride Complexes with Cycloalkanones[1]

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A direct ¹H and ¹⁹F nmr study of BF₃ complexes of several cycloalkanones (cyclobutanone through cyclodecanone) has been completed. At temperatures below −80°, exchange is slow enough to permit the observation of separate sets of resonance signals for coordinated and bulk ketone molecules. The appearance of the α-CH₂ pmr peaks of coordinated cyclohexanone and cycloheptanone reflect the slowing of an additional kinetic process, possibly cis–trans isomerization at the carbonyl oxygen. The ¹⁹F nmr signals of mixtures of the cycloalkanones with BF₃ were used to evaluate the relative basicities of this series of molecules. The basicities decreased in the order C₈ > C₅ > C₇ > C₆ ≃ C₉ > C₁₀ ≫ C₄, a trend which was interpreted primarily in terms of steric effects.

Boron trihalide mixtures with a variety of organic bases have been studied by calorimetric[3–7] and spectroscopic[8–17] techniques to evaluate the energetics and structural features of the complexes formed. The organic bases involved in several representative studies of BF₃ adducts include pyridines,[3,11] alkyl ethers, amines, and sulfides,[4] dimethyl sulfoxide and ethyl acetate,[5] cyclic ketones,[6] triethylamine,[7] ethers,[8] dimethylformamide,[9] benzophenone,[10] ureas and thioureas,[12] water,[13] trimethylamine,[14] diethyl ketone,[15]

aromatic amine 1-oxides,[16] and benzaldehydes.[17] In most of the nuclear magnetic resonance (nmr) studies, the components were mixed in a 1:1 mole ratio, and the ligand chemical shifts were compared to pure base.

Recently, a direct, low-temperature nmr technique has been refined and applied to studies of boron trihalide complexes.[18–24] In the presence of excess base, and at temperatures low enough to reduce the rate of ligand exchange, it is possible to observe separate resonance signals for bulk and coordinated ligand molecules. This observation leads to an accurate measure of the ¹H, ¹¹B, ¹⁹F, and even ¹³C[25] chemical shifts produced by complex formation, the stoichiometry of the complex, steric hindrance to complex formation, and the ligand preference of a boron trihalide in a system containing more than one base. These features have been evaluated for amines and

(1) Presented at the 163rd National Meeting of the American Chemical Society, Boston, Mass., April 1972.

(2) To whom correspondence should be addressed.

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