Molecular Rearrangements. VI.[1] A Study of the Rearrangements of 2-Chlorobicyclo[2.2.1]hept-2-ene *exo*-Oxide

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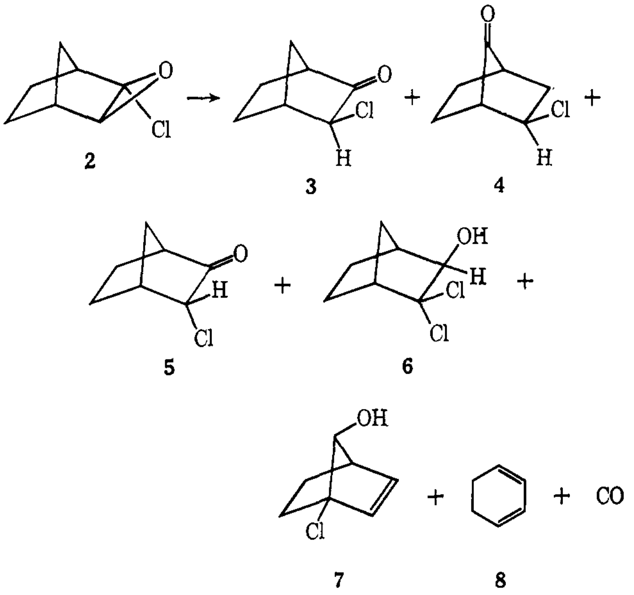
The synthesis of 2-chlorobicyclo[2.2.1]hept-2-ene *exo*-oxide (**2**) is reported. Neat, thermal rearrangement of **2** gives rise to two major products, *exo*-3-chlorobicyclo[2.2.1]heptan-2-one (**3**, 37.4%) and *exo*-2-chlorobicyclo-[2.2.1]heptan-7-one (**4**, 34.9%), in addition to seven minor products. Acetolysis of **2** gives a ratio of **4**/**3** of 2.7 along with acetoxy ketone product resulting from the addition of acetic acid to **2**. Reaction of **2** with anhydrous hydrogen chloride in ether leads to the unexpected addition product 3,3-dichlorobicyclo[2.2.1]heptan-*exo*-2-ol. Possible mechanistic pathways for these reactions are considered.

Our previous work in the rearrangements of 1-chloro-*cis*- and -*trans*-4-methylcyclohexene oxide led us to conclude that an α-ketocarbonium ion–chloride ion pair was produced as a common intermediate which yields *trans*-2-chloro-4-methylcyclohexanone exclusively.[1] To expand our knowledge of the rearrangements of α-chloro epoxides and, hopefully, substantiate further the ion pair intermediacy, we initiated an investigation into the synthesis and rearrangements of 2-chlorobicyclo-[2.2.1]hept-2-ene *exo*-oxide (**2**). It was felt that **2** served experimental purposes well for at least two reasons: (1) the rearrangements would be starting with a single epoxide rather than a mixture, and (2) the literature holds a wealth of information on the carbonium ion chemistry of this bicyclic system.[3]

2-Chlorobicyclo[2.2.1]hept-2-ene (**1**) was prepared by the Diels–Alder reaction of cyclopentadiene and *trans*-1,2-dichloroethylene, hydrogenation,[4] and the product dehydrochlorinated in good yield with potassium *t*-butoxide in *t*-butyl alcohol.[5] Epoxidation of **1** gave **2** in 65% yield. The assignment of the *exo* configuration to the epoxide is based upon the analogous epoxidation of bicyclo[2.2.1]hept-2-ene[6] and the observation that the nuclear magnetic resonance (nmr) spectrum of the epoxide shows a one-proton doublet at high field (τ 9.18) for the *anti*-7 hydrogen.[7]

A slow, neat, thermal rearrangement of the α-chloro epoxide **2** was conducted in a manner analogous to the thermal rearrangement of 1-chloro-4-methylcyclohexene oxide.[1] Analysis of the rearrangement mixture by gas chromatography (gc) with integration of the areas under the peaks showed two major components in addition to 11% of unrearranged epoxide and seven minor components. The two major components of the rearrangement were identified as *exo*-3-chlorobicyclo-[2.2.1]heptan-2-one (**3**, 37.4%) and *exo*-2-chlorobicyclo[2.2.1]heptan-7-one (**4**, 34.9%). Several minor products were as follows: *endo*-3-chlorobicyclo[2.2.1]heptan-2-one (**5**, 4.3%), a saturated alcohol whose nmr spectrum suggests the structure 3,3-dichlorobicyclo[2.2.1]heptan-*exo*-2-ol (**6**, 2.9%), a liquid unsaturated alcohol which from its infrared and nmr spectra is believed to be 1-chlorobicyclo[2.2.1]hept-2-en-*syn*-7-ol (**7**, 2.7%), 1,3-cyclohexadiene (**8**, 3.0%), and carbon monoxide (1.6%). The other two minor components (2.0% of total) were not identified.



Diene **8** and carbon monoxide were found to be arising from the thermal decomposition (during the gc analysis) of bicyclo[2.2.1]hept-2-en-7-one (**9**) present in the rearrangement mixture. The photolytic cleavage of **9** to give **8** and carbon monoxide has been reported.[8]

The isomeric chloro ketones **3** and **5** were identified by their gc retention times, and by collection and comparison of their infrared spectra with authentic samples. The *exo* isomer **3** was prepared independently by sulfuryl chloride chlorination of bicyclo[2.2.1]heptan-2-one. The *endo* isomer **5** was then obtained by base equilibration of the *exo* isomer.[9]

No report on the preparation of the chloro ketone **4** could be found in the literature. Walborsky and Loncrini[10] have reported that the major product upon treat-

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[1] For paper V in this series, see R. N. McDonald and T. E. Tabor, *J. Amer. Chem. Soc.*, **89**, 6573 (1967).

[2] NDEA Fellow, 1962–1965. This represents a portion of a dissertation presented by R. E. Tabor to the Graduate School of Kansas State University in partial fulfillment of the requirements for the Ph.D. Degree.

[3] Some recent reviews on this subject are (a) P. D. Bartlett, "Nonclassical Ions," W. A. Benjamin, Inc., New York, N. Y., 1965; (b) G. D. Sargent, *Quart. Rev.* (London), **20**, 301 (1966); (c) J. A. Berson, "Molecular Rearrangements," Vol. 1, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p 111.

[4] J. D. Roberts, F. O. Johnson, and R. A. Carboni, *J. Amer. Chem. Soc.*, **76**, 5692 (1954).

[5] N. A. LeBel, *ibid.*, **82**, 623 (1960).

[6] H. Kwart and T. Takeshita, *J. Org. Chem.*, **28**, 670 (1963).

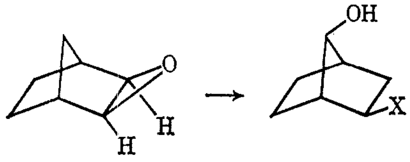
[7] K. Tori, K. Kitahonoki, Y. Takano, H. Tanida, and T. Tsuji [*Tetrahedron Lett.*, 559 (1964)] report this proton appears as a doublet at τ 9.30 in bicyclo[2.2.1]hept-2-ene *exo*-oxide.

[8] D. I. Shuster, F.-T. Lee, A. Padwa, and P. G. Gassman, *J. Org. Chem.*, **30**, 2262 (1965).

[9] (a) J. Meinwald, Y. C. Meinwald, and T. N. Baker, *J. Amer. Chem. Soc.*, **86**, 4074 (1964); (b) E. Tobler, D. E. Battin, and D. J. Foster, *J. Org. Chem.*, **29**, 2834 (1964).

[10] H. M. Walborsky and D. F. Loncrini, *ibid.*, **22**, 1117 (1957).

ment of bicyclo[2.2.1]hept-2-ene *exo*-oxide (**10**) with 48% hydrobromic acid is *exo*-2-bromobicyclo[2.2.1]heptan-*syn*-7-ol (**11a**). In the present study it was found that treatment of **10** with concentrated hydrochloric acid gave the corresponding chloro alcohol, *exo*-2-chlorobicyclo[2.2.1]heptan-*syn*-7-ol (**11b**). The properties of **11b** differed from those of *exo*- and *endo*-3-chlorobicyclo[2.2.1]heptan-*exo*-2-ol,[9b] *endo*-3-chlorobicyclo[2.2.1]heptan-*endo*-2-ol,[9b] and *syn*- and *anti*-7-chlorobicyclo[2.2.1]heptan-*exo*-2-ol.[4] The infrared and nmr spectra were in agreement with the structure **11b**.[11]



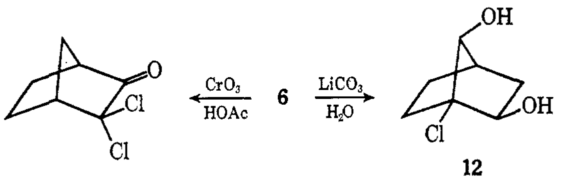
10 **11a**, X = Br
b, X = Cl

Oxidation of the chloro alcohol **11b** with chromium trioxide in acetic acid gave the desired chloro ketone **4**. This oxidation product was identical with the chloro ketone formed in 34.9% yield in the thermal rearrangement of **2**. The infrared spectrum of **4** showed carbonyl absorptions at 5.43 (m) and 5.62 (s) μ which are quite characteristic of bicyclo[2.2.1]heptan-7-ones.[12] In the nmr spectrum of **4** the *endo*-2 hydrogen appeared as a multiplet at τ 5.25 (1 H). This oxidation product also gave further support for the 7 position of the hydroxyl group in **11b**. Additional evidence for the 7-keto structure of **4** was afforded by conversion into its ethylene ketal, dehydrochlorination, and hydrolysis to the known bicyclo[2.2.1]hept-2-en-7-one (**9**).[12,13] Gc analysis of **9** gave 1,3-cyclohexadiene (**8**) and carbon monoxide.

The combined data for the solid dichloro alcohol, assigned structure **6**, obtained as a minor product (2.9%) in the rearrangement of chloro epoxide **2** initially made a structural assignment somewhat perplexing. The alcohol was found to correspond to the molecular formula $C_7H_{10}Cl_2O$ as determined by its molecular weight and elemental analysis. This indicated that the alcohol was arising by addition of a molecule of hydrogen chloride to the α-chloro epoxide **2**. It was subsequently found that the dichloro alcohol was the major product (27.1%) when **2** was treated with hydrogen chloride in ether.

When the dichloro alcohol was oxidized with chromium trioxide in acetic acid, a solid ketone was obtained whose infrared spectrum showed carbonyl absorptions at 5.48 (m) and 5.62 (s) μ. These absorptions suggested that this ketone was a bicyclo[2.2.1]heptan-7-one, in view of the similar absorptions observed for *exo*-2-chlorobicyclo[2.2.1]heptan-7-one (**4**). However, Krieger[14] has reported that the carbonyl absorption of 3,3-dibromobicyclo[2.2.1]heptan-2-one appears at 1772 cm^{-1} (5.64 μ) compared to 1761 (5.68 μ) and 1758 cm^{-1} (5.69 μ) for *endo*- and *exo*-3-bromobicyclo[2.2.1]heptan-2-one, respectively. This then allowed for the possibility that the oxidation product was 3,3-dichlorobicyclo[2.2.1]heptan-2-one.

Hydrolysis of the dichloroalcohol with aqueous lithium carbonate gave 1-chlorobicyclo[2.2.1]heptane-*exo*-2,*syn*-7-diol (**12**). Diol **12** would be the expected hydrolysis product from either 1-*exo*-2-dichlorobicyclo[2.2.1]heptan-*syn*-7-ol (**13**)[15] or **6**, with the latter involving Wagner–Meerwein rearrangement.



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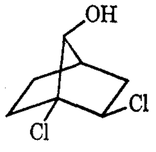

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The nmr spectrum allows a differentiation between **6** and **13**. In the latter structure two carbon-bound downfield protons should be observed since chlorine and hydroxyl have similar effective shielding constants;[16] only one is observed. The spectrum (CCl_4, TMS internal standard) can be reasonably interpreted in terms of structure **6** with the *endo*-C_2 proton as a singlet at τ 6.17 (indication of some splitting), the hydroxyl proton as a broad singlet at τ 6.83 (concentration dependent), the bridgehead C_4 proton as broad adsorption at τ 7.26,[17] and the bridgehead C_1 proton as a broad singlet at τ 7.77, which is not completely separated from the complex absorption from τ 7.8 to 9.0 for the six methylene protons.

The liquid unsaturated alcohol obtained as a minor product (2.7%) in the rearrangement of **2** was assigned the structure of 1-chlorobicyclo[2.2.1]hept-2-en-*syn*-7-ol (**7**) on the basis of its nmr spectrum. The complex absorption centered at *ca.* τ 4.0 was assigned to the two vinyl protons. The *anti*-7 proton appeared as a singlet at τ 6.29 and the hydroxyl proton appeared as a singlet at 7.10 (concentration dependent). The broad singlet at τ 7.23 was assigned to the lone bridgehead proton and the remaining four methylene protons gave rise to complex absorption in the region of τ 7.9–9.3. The assignments agree quite well with those reported for bicyclo[2.2.1]hept-2-en-*syn*-7-ol.[18]

As was mentioned previously, the dichloro alcohol **6** was the major product (27.1%) when the α-chloro epoxide **2** was treated with hydrogen chloride in ether. This reaction also gave rise to the chloro ketones **3** and **4** in 13.0 and 23.2% yields, respectively. Four other products (32.8% total) remain unidentified. Another component observed in the gc analysis of the reaction mixture integrated as 3.9%, and was indicated by its retention time to be unreacted epoxide. *endo*-3-Chloro-

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[11] The nmr spectral assignments agree with those of the acetate of **11b** reported by W. C. Baird [*J. Org. Chem.*, **31**, 2411 (1966)].

[12] P. G. Gassman and P. G. Pape, *ibid.*, **29**, 160 (1964).

[13] R. K. Bly and R. S. Bly, *ibid.*, **28**, 3165 (1963).

[14] H. Krieger, *Suomen Kemistilehti*, **31B**, 112 (1958); *Chem. Abstr.*, **52**, 13423*e* (1958).

[15] Reference 11 describes the analogous hydrolysis of *exo*-2-chloro-*syn*-7-acetoxybicyclo[2.2.1]heptane to bicyclo[2.2.1]heptane-*exo*-2,*syn*-7-diol.

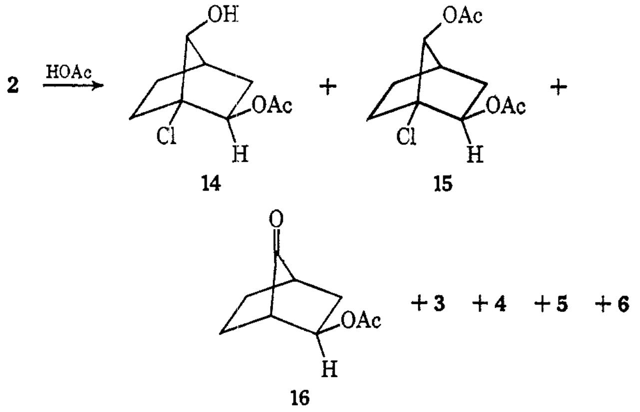
[16] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, Inc., New York, N. Y., 1959, p 59.

[17] The fact that this proton absorption is at lower field than is normally observed for bicyclo[2.2.1]heptanes (*ca.* τ 7.8) is explained as due to the deshielding effect of the two chlorines on C_3.

[18] R. R. Sauers and R. M. Hawthorne, *J. Org. Chem.*, **29**, 1685 (1964).

bicyclo[2.2.1]heptan-2-one (**5**) was indicated to be present in only a trace amount.

The reaction of α-chloro epoxide **2** with anhydrous acetic acid was carried out by the dropwise addition of **2** to a relatively large volume of acetic acid in order to determine whether any acetoxy ketone products as well as chloro ketone products would be formed. Gc analysis of the crude product of this reaction showed the presence of at least 14 products. The major product of the reaction was found to be a hydroxyacetate whose structure is indicated to be 1-chloro-*exo*-2-acetoxybicyclo[2.2.1]heptan-*syn*-7-ol (**14**, 24.5% by integration). Other products of this reaction are given in Table I. In addition, there were seven other minor components (18.3% total) which were unidentified, except that one of these (1.7%) was indicated by its retention time to be unreacted epoxide.



14 **15** **16**

Table I

Compound	% yield
1-Chloro-*exo*-2-*syn*-7-diacetoxybicyclo[2.2.1]heptane (**15**)	14
exo-2-Acetoxybicyclo[2.2.1]heptan-7-one (**16**)	12.6
exo-2-Chlorobicyclo[2.2.1]heptan-7-one (**4**)	13.3
exo-3-Chlorobicyclo[2.2.1]heptan-2-one (**3**)	5.0
endo-3-Chlorobicyclo[2.2.1]heptan-2-one (**5**)	3.5
3,3-Dichlorobicyclo[2.2.1]heptan-*exo*-2-ol (**6**)	8.9

Compounds **3**–**6** were identified by their retention times and by collection of each component from the gas chromatogram and comparison of their infrared spectra with those of known samples. The acetoxy ketone **16** was collected from the gas chromatogram and identified by comparison of its infrared spectrum with that of a known sample.[19]

The major product of the acetolysis, **14**, was collected from the gas chromatogram. The elemental analysis and molecular weight were in agreement with the formula $C_9H_{13}ClO_3$. Its structural assignment as **14** is based on the interpretation of its nmr spectra and conversion into a known compound. The placement of the acetoxyl group at C-2 is argued from mechanistic considerations. The diacetate **15** likewise was collected from the gas chromatogram and could also be prepared by acetylation of **14**.

Attempted reduction of **14** with lithium aluminum hydride gave only recovered starting material probably due to the initial formation of an insoluble alkoxide intermediate. Reduction of the diacetate **15** with lithium aluminum hydride proceeded readily at room temperature to yield 1-chlorobicyclo[2.2.1]heptane-*exo*-2, *syn*-7-diol (**12**). No ketal formation was realized by treating **12** with acetone and *p*-toluenesulfonic acid in benzene. However, using the ketal exchange method by reaction of **12** with 2,2-dimethoxypropane and *p*-toluenesulfonic acid catalyst in benzene gave a small amount of material believed to be the cyclic ketal in addition to considerable recovered diol. Both the infrared and nmr spectra indicated the presence of the geminal dimethyl group in this product. Molecular models indicate that there are considerable steric interactions involved in the ketal, which might explain the difficulties in its preparation and its apparent ease of cleavage during purification attempts. The indication that the ketal could be formed, however, was added support for the *exo-syn* relationship of the hydroxyl groups in the diol **12**.

To establish completely the structure of the diol as **12**, it was first treated with sodium in refluxing glyme followed by reaction with dimethyl sulfate. Three major products were isolated from this reaction mixture and all were dimethyl ethers. The mass and nmr spectral data and mechanistic considerations suggest that these products are 1-chloro-*exo*-2,*syn*-7-dimethoxybicyclo[2.2.1]heptane (33%), *exo*-2,*syn*-7-dimethoxybicyclo[2.2.1]heptane (**17**, 20%), and 1-methyl-*exo*-2, *syn*-7-dimethoxybicyclo[2.2.1]heptane (43%). Compound **17** was identified by comparison of its infrared spectrum with that of a known sample prepared by a similar treatment of bicyclo[2.2.1]heptane-*exo*-2,*syn*-7-diol.[20]

Although neither *exo*-3-acetoxybicyclo[2.2.1]heptan-2-one nor its *endo* isomer was isolated from the acetolysis of α-chloro epoxide **2**, the presence of these compounds could not be excluded since seven minor products of this reaction were not isolated and identified. Several unsuccessful attempts were made to prepare these compounds.[2]

Discussion

The formation of products in the rearrangements of α-chloro epoxide **2** can be interpreted by the two different sets of processes shown in Scheme I. No data are available to allow one to say if and where equilibrating classical carbonium ions or their nonclassical counterparts are involved in these pathways.

Some criticism of the process on the right-hand half of Scheme I can be offered. It does not involve chlorine as the migrating group to form α-chloro ketone product, which is contrary to our previous finding[1,21] and those of others,[22] and requires a 3,2-*endo* hydride shift to produce *exo*-3-chlorobicyclo[2.2.1]heptan-2-one. A rebuttal to the first part of this criticism might be that the bicyclo[2.2.1]heptane system is so prone to Wagner–Meerwein rearrangements that this takes precedence over the normal processes found in acyclic and alicyclic α-chloro epoxides. The C_{1-6} or C_{4-5} σ

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[19] The infrared spectra of **16** and the *endo* isomer were kindly furnished by Professor P. G. Gassman.

[20] K. Alder, F. H. Flock, and H. Wirtz, *Chem. Ber.*, **91**, 609 (1958).

[21] (a) R. N. McDonald and P. A. Schwab, *J. Amer. Chem. Soc.*, **85**, 4004 (1963); (b) *J. Org. Chem.*, **29**, 2459 (1964).

[22] A. Kirrman, P. Duhamel, and R. Nouri-Bimorghi, *Bull. Soc. Chim. Fr.*, 3264 (1964); *Ann.*, **691**, 33 (1966); R. Nouri-Bimorghi, *C. R. Acad. Sci.* (Paris), *Ser. C*, **262**, 759 (1966); G. A. Razuvaev, V. S. Etlis, and N. N. Trofimov, *Zh. Org. Khim.*, **1**, 2128 (1964) [*Chem. Abstr.*, **64**, 11145*e* (1966)].

orbitals appear from models to be spatially well arranged in **2** for participation in C–O bond fissions as has been argued for bicyclo[2.2.1]hept-*exo*-2-yl tosylate. Such an argument, however, should also lead to the conclusion that the rearrangements of **2** and bicyclo[2.2.1]heptene *exo*-oxide should occur with similar facility. This is obviously *not* the case when the present work is compared with that of Crandall.[23]

The second part of the criticism is possibly the more serious since most reactions which could involve 3,2-*endo* shifts of hydrogen or other atoms or groups take alternate paths in this bicyclic ring system.[24] Such a 3,2-*endo* migration appears as an attractive possibility for the formation of bicyclo[2.2.1]heptan-2-one as a major product during attempted gc purification of bicyclo[2.2.1]heptene *exo*-oxide.[23] No proof of such a process has, however, been offered.

The yield of *exo*-3-chlorobicyclo[2.2.1]heptan-2-one is somewhat larger than that of *exo*-2-chlorobicyclo[2.2.1]heptan-7-one and much greater than that of any products formed by 6,2-hydride shift (not established as even present) in the neat thermal rearrangement of **2**. This would then mean that the rate of *endo*-3,2 hydride shift is essentially equal to that of Wagner–Meerwein rearrangement and far greater than that of 6,2-hydride shift. This is exceedingly difficult to accept in light of the nmr study of the norbornyl cation by Saunders, Schleyer, and Olah[25a] in mixed SbF_5–SO_2–SO_2F_2 solvent who calculated that at −120° the 3,2-hydride shift is slower than 6,2-hydride shift and Wagner–Meerwein rearrangement by a minimum of $10^{8.8}$. Berson and coworkers[25b] have found that the *exo*-3-methylbicyclo[2.2.1]hept-2-yl cation does not undergo the *endo*-3,2 hydride shift despite the large thermodynamic driving force for such a process. However, such an *endo*-3,2 hydride shift has recently been established in the pinacol rearrangement of *endo*-3-phenyl-2,3-*exo,cis*-bornanediol.[26,27]

The authors believe that a concerted *endo*-3,2 hydride shift with epoxide ring opening is ruled out from strain and stereoelectronic considerations just as a concerted 1,2-chlorine shift was argued unreasonable in certain other α-chloro epoxide rearrangements[21a] and would not account for the stereospecificity in product formation in the neat thermal rearrangement of 1-chloro-*cis*- and -*trans*-4-methylcyclohexene oxide.[1]

The significant difference between the right and left hand sides of Scheme I is that each side yields a different enantiomer of *exo*-3-chlorobicyclo[2.2.1]heptan-2-one if optically active α-chloro epoxide **2** is used. Such studies are presently underway and should allow us to determine the extent to which both C_2–O and C_3–O bond fissions occur.

Experimental Section[28]

***trans*-5,6-Dichlorobicyclo[2.2.1]hept-2-ene.**—The Diels–Alder adduct from cyclopentadiene and *trans*-1,2-dichloroethylene was obtained in 67% yield: bp 80.0–76.6° (17.0–14.5 mm); $n^{20}D$ 1.5123 (lit.[4] 34%, bp 76–78° (18 mm), $n^{25}D$ 1.5101).

***trans*-2,3-Dichlorobicyclo[2.2.1]heptane.**—Hydrogenation of *trans*-5,6-dichlorobicyclo[2.2.1]hept-2-ene according to the published procedure,[4] except using palladium on carbon rather than platinum oxide as the catalyst, gave *trans*-2,3-dichlorobicyclo-[2.2.1]heptane in 96% yield: bp 85° (17.5 mm), $n^{20}D$ 1.5040 (lit.[4] 85% yield, bp 85–86° (18 mm), $n^{25}D$ 1.5015).

2-Chlorobicyclo[2.2.1]hept-2-ene (1).—Dehydrochlorination of *trans*-2,3-dichlorobicyclo[2.2.1]heptane was carried out using the procedure of LeBel[5] with potassium *t*-butoxide in *t*-butyl alcohol. 2-Chlorobicyclo[2.2.1]hept-2-ene was obtained in 60% yield: bp 69.5–71.5° (67.5–68.0 mm), $n^{21}D$ 1.4896 (lit.[4] bp 64–66° (52 mm), $n^{25}D$ 1.4880).

2-Chlorobicyclo[2.2.1]hept-2-ene *exo*-Oxide (2).—A solution of 40.0 g (0.311 mol) of 2-chlorobicyclo[2.2.1]hept-2-ene in 25 ml of methylene chloride was treated with a solution of 72.0 g of *m*-chloroperbenzoic acid (82% minimum purity) in 700 ml of methylene chloride for 10 hr. After work-up, vacuum distillation through a short path column gave 34.9 g (77.7%) of crude epoxide containing a small amount of methylene chloride. Redistillation (semimicro spinning-band column) gave 29.4 g (65.4%) of pure 2-chlorobicyclo[2.2.1]hept-2-ene *exo*-oxide: bp 52.2–53.4° (5.1–5.2 mm), $n^{26}D$ 1.4886. The epoxide could be stored under Dry Ice for periods of several weeks with little or no rearrangement, but samples left at room temperature and atmospheric pressure soon underwent a violent exothermic rearrangement with evolution of hydrogen chloride fumes. Elemental analysis was not attempted because of this facile decomposition.

A strong band at 11.54 μ was observed in the infrared spectrum and is believed to be due to the epoxide ring vibration. The nmr spectrum (CCl_4, TMS internal standard) exhibited absorptions at τ 6.86 (singlet, 1, epoxide ring), 7.38 (multiplet, 1, bridgehead C_1), 7.53 (multiplet, 1, bridgehead C_4), 8.2–8.9 (multiplet, 5, C_5, C_6, and *syn*-C_7), and 9.18 (broad doublet, 1, *anti*-C_7).

Neat Thermal Rearrangement of 2-Chlorobicyclo[2.2.1]hept-2-ene *exo*-Oxide.—A 4.1-g sample of epoxide **2** was placed in a 10 ml distillation flask connected to a semimicro spinning-band column and brought to reflux at reduced pressure, bp 51.0° (4.9 mm), with a wax bath maintained at 80°. These conditions are essentially those used for distillation of the epoxide in which only slight rearrangement occurred over a period of several hours. After heating for 46 hr the sample was still refluxing at 51.0° (4.9 mm). At the end of 187.5 hr the head temperature had decreased to 39.5° (4.9 mm) and refluxing had slowed considerably. After a total of 260.5 hr refluxing had completely ceased and the head temperature had dropped to 30.0° (4.9 mm). At this point heating was discontinued, and the flask was cooled, removed, and stored under Dry Ice.

During the rearrangment the sample had slowly discolored and by the end of the rearrangement had become dark red. About 60% of the mixture is volatile, the remaining 40% being polymeric material. The infrared spectrum of the rearrangement mixture showed intense carbonyl absorption at 5.63, weak carbonyl absorption at 5.41 and weak hydroxyl absorption at 2.87 μ. Also, a weak epoxide absorption at 11.52 μ indicated that the rearrangement still had not proceeded to completion.

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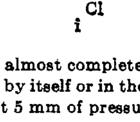
[23] J. K. Crandall, *J. Org. Chem.*, **29**, 2830 (1964).

[24] D. C. Kleinfelter and T. E. Dye, *J. Amer. Chem. Soc.*, **88**, 3174 (1966).

[25] (a) M. Saunders, P. von R. Schleyer, and G. A. Olah, *ibid.*, **86**, 5680 (1964); (b) J. A. Berson, J. H. Hammons, A. W. McRowe, R. G. Bergman, A. Remanick, and D. Houston, *ibid.*, **89**, 2590 (1967).

[26] A. W. Bushell and P. Wilder, *ibid.*, **89**, 5721 (1967).

[27] Referees have suggested that **3** may be formed by *endo* capture of chloride by the α-ketocarbonium ion, or possibly by an *endo*-2,3 chloride shift from i, followed by acid-catalyzed isomerization. That this does not occur



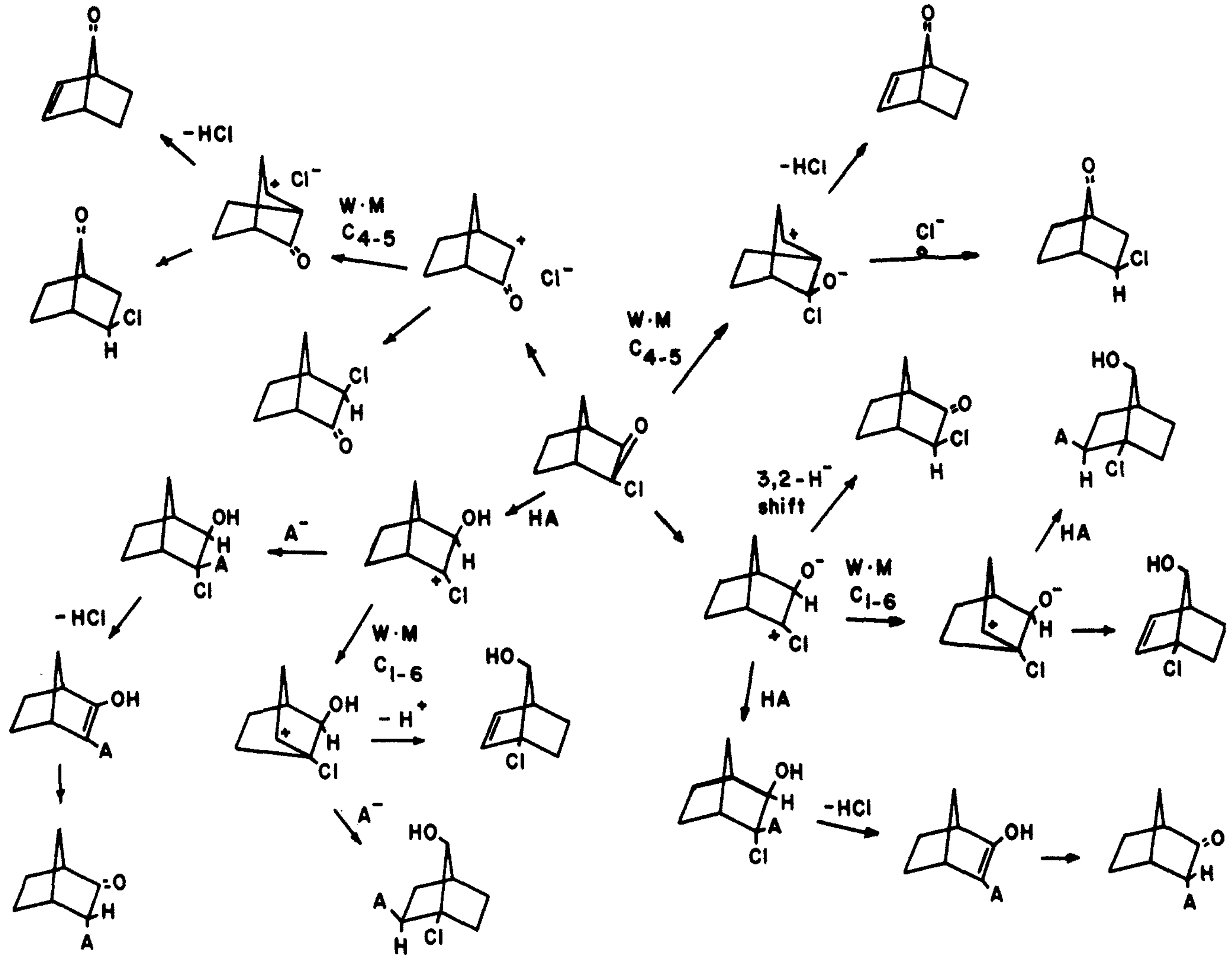
i

is shown by the fact that **3** is almost completely uneffected when placed in a rearrangement of **2**, as well as by itself or in the presence of hydrogen chloride when placed in sealed tubes at 5 mm of pressure and heated in a bath at 80° for the same length of time as a rearrangement: R. N. Steppel, unpublished results. A maximum of about 2% of **3** might be produced by this route. It is also interesting to note that the same products in about the same distribution are produced on "gc analysis" of **2** with the injection port at 250°; some unrearranged **2** is evident under these conditions.

[28] All melting points were taken on a Kofler hot stage and are corrected. Boiling points are uncorrected. Infrared spectra were determined on a P-E Model 137 or 237 spectrophotometer; nmr spectra were determined on a Varian A-60 spectrometer, and mass spectra were determined with a Bendix time-of-flight mass spectrometer. Molecular weights were obtained either mass spectrometrically or with an osmometer, Model 301A. Gc analyses were performed using an F & M Model 500 gas chromatograph. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

SCHEME I

POSSIBLE MECHANISTIC PATHWAYS FOR THE REARRANGEMENTS OF 2



Gc analysis of the volatile portion of the rearrangement mixture using a 0.25 in. × 6 ft 20% Carbowax 20M on 60/80 Chromosorb W column at 200° showed the presence of ten major components. The peak numbers, retention times, and integrated percentages were as follows: no. 1, 0.23 min, 1.6%; no. 2, 0.41 min, 3.0%; no. 3, 1.70 min, 1.2%; no. 4, 2.04 min, 11.0%; no. 5, 3.15 min, 0.8%; no. 6, 4.20 min, 2.7%; no. 7, 4.80 min, 37.4%; no. 8, 5.66 min, 34.9%; no. 9, 6.16 min, 4.3%; and no. 10, 9.68 min, 2.9%.

Peak no. 4 was indicated to be unrearranged epoxide by comparison of retention times and also by the fact that this peak had essentially disappeared after the rearranged sample had been standing for several weeks. The component could not be collected for identification as the epoxide, because the epoxide was found to undergo rearrangement in the detector block under these conditions.

Peaks no. 7 and 9 had retention times corresponding to *exo*- and *endo*-3-chlorobicyclo[2.2.1]heptan-2-one, respectively. Collection of each of these components from the gc and comparison of the infrared spectra with authentic samples confirmed the assignments.

Collection of peak no. 8 from the gc followed by infrared analysis showed this component to be identical with *exo*-2-chlorobicyclo[2.2.1]heptan-7-one prepared independently by the oxidation of *exo*-2-chlorobicyclo[2.2.1]heptan-*syn*-7-ol.

When collections were attempted on peak no. 1, it was found that no material would condense in the Dry Ice–isopropyl alcohol cooled receiver. Peak no. 2 was obtained as a volatile, colorless liquid whose nmr spectrum was found to be identical with that of an authentic sample of 1,3-cyclohexadiene. This suggested that peak no. 1 might be carbon monoxide. When investigated, peak no. 1 did give a positive test for carbon monoxide using a U. S. Safety Service Co., No. CO-100 indicating tube for SAF-CO-METER carbon monoxide indicator.

The infrared spectrum of a low boiling fraction obtained by distillation of another sample of the rearrangement mixture strongly indicated the presence of bicyclo[2.2.1]hept-2-en-7-one by the intense carbonyl absorption at 5.62, a medium intense carbonyl absorption at 5.42, a weak carbon–carbon double bond absorption at 6.18, and vinyl hydrogen absorption at 3.23 (w) and 14.27 μ (s), in good agreement with the report of Bly and Bly.[13] A 2,4-dinitrophenylhydrazone recrystallized twice from 95% ethanol, melted at 136.0–137.5° (lit.[12] mp 136–137°). When the sample containing this ketone was subjected to gc analysis under the conditions employed above, two components were observed at the same retention times as peaks no. 1 and 2 in the rearrangement mixture and were identified as carbon monoxide and 1,3-cyclohexadiene.

Collection of peak no. 10 from the gc gave a white crystalline solid, which melted at 104–107° after vacuum sublimation. An osmometric molecular weight in ethanol gave a value of 182.8, which indicated the addition of a molecule of hydrogen chloride to the epoxide. The structure of this solid is assigned as 3,3-dichlorobicyclo[2.2.1]heptan-*exo*-2-ol.

Anal. Calcd for $C_7H_{10}Cl_2O$: C, 46.44; H, 5.77; mol wt, 181.06. Found: C, 46.75; H, 5.60.

Peak no. 6 was collected as a clear, colorless liquid and assigned the structure of 1-chlorobicyclo[2.2.1]hept-2-en-*syn*-7-ol on the basis of its spectral data and mechanistic considerations.

Insufficient quantities of peaks no. 3 and 5 were obtained for determination of their structures.

exo-**3-Chlorobicyclo[2.2.1]heptan-2-one (3).**—A 25.0-g (0.227 mol) sample of bicyclo[2.2.1]heptan-2-one was placed in a 100-ml, three-necked flask equipped with a condenser, an addition funnel, and a magnetic stirrer. The flask was heated until all of the solid ketone melted, and then 30.7 g (0.227 mol) of sulfuryl chloride was added dropwise. A vigorous gas evolution ensued, and heating was continued until the evolution ceased. After cooling, the light yellow reaction mixture weighed 34.8 g. Gc analysis using a 0.25 in. × 6 ft 20% Carbowax 20M on 60/80 Chromosorb W column at 225° showed the presence of six peaks. The yield of **3** was 77%. Distillation (semimicro spinning-band column) gave pure *exo*-3-chlorobicyclo[2.2.1]heptan-2-one: bp 85.3° (4.8 mm); $n^{20}\text{D}$ 1.4976 (lit.[9a] bp 88–89° (4.5 mm), $n^{28.5}\text{D}$ 1.4941). The infrared and nmr spectra were in agreement with those reported.[9]

***endo*-3-Chlorobicyclo[2.2.1]heptan-2-one (5).**—A mixture of 6.02 g (0.0417 mol) of *exo*-3-chlorobicyclo[2.2.1]heptan-2-one, 12.0 g of potassium carbonate, and 50 ml of water was heated under reflux for 20 hr. After cooling, the reaction mixture was extracted continuously with ether overnight. The ether extract was dried and the ether was removed under reduced pressure leaving 5.5 g of a light brown liquid residue. Gc analysis using a 0.25 in. × 6 ft 20% Carbowax 20M on 60/80 Chromosorb W column at 225° showed two major components which were identified as *exo*-3-chlorobicyclo[2.2.1]heptan-2-one (40.8%) and *endo*-3-chlorobicyclo[2.2.1]heptan-2-one (59.2%), respectively. Gc collections gave the *endo* isomer as a waxy solid, mp 55.5–60.5° (lit. mp 53–56°,[9a] lit. mp 50–53° [9b]). The infrared and nmr spectra were in agreement with the reported data.[9]

Bicyclo[2.2.1]hept-2-ene *exo*-Oxide (10).—A solution of 25.0 g (0.265 mol) of bicyclo[2.2.1]hept-2-ene in 25 ml of methylene chloride was treated with a solution of 61.3 g of *m*-chloroperbenzoic acid (82% minimum purity) in 650 ml of methylene chloride for 8 hr. After work-up, vacuum distillation through a short path column gave 21.2 g (72.6%) of crude epoxide as a white crystalline solid. After recrystallization twice for hexane, the epoxide showed mp 139–142° in a sealed capillary (lit.[29] mp 125.5–126.5°).

***exo*-2-Chlorobicyclo[2.2.1]heptan-*syn*-7-ol (11b).**—This compound was prepared in a manner quite similar to that described by Walborsky and Loncrini[10] for the preparation of *exo*-2-bromobicyclo[2.2.1]heptan-*syn*-7-ol. To 50 ml of concentrated hydrochloric acid cooled to below 10° was added 12.96 g (0.117 mol) of bicyclo[2.2.1]hept-2-ene *exo*-oxide at such a rate that the temperature did not rise above 15°. The mixture was allowed to stir for an additional 1 hr with cooling and then was added to 100 ml of water. The aqueous mixture was extracted with four 50-ml portions of ether, and the combined ether extracts were washed with 25 ml of 10% sodium carbonate solution and 25 ml of water, and dried. Removal of the ether under reduced pressure gave 12.6 g of a light yellow liquid residue. Gc analysis using a 0.25 in. × 6 ft 20% Carbowax 20M on 60/80 Chromosorb W column at 190° showed the presence of three peaks. The center peak (50.7%) was collected as a white crystalline solid, which after recrystallization from hexane had mp 52.2–53.2°.

Anal. Calcd for $C_7H_{11}ClO$: C, 57.34; H, 7.56. Found: C, 57.45; H, 7.72.

In the infrared spectrum the hydroxyl group exhibited strong absorption at 3.07 μ, while in the nmr spectrum (CCl_4, TMS internal standard) absorptions occurred at τ 6.0 (complex, 2, *endo*-C_2 and *anti*-C_7), 7.07 (singlet, 1, hydroxyl), 7.8 (complex, 4, bridgeheads and C_3), and 8.0–9.1 (complex, 4, C_5 and C_6).

***exo*-2-Chlorobicyclo[2.2.1]heptan-7-one (4).**—To a solution of 0.860 g (5.87 mmol) of *exo*-2-chlorobicyclo[2.2.1]heptan-*syn*-7-ol in 4 ml of glacial acetic acid was added slowly a solution of 0.464 g (4.6 mmol) of chromium trioxide in 12 ml of glacial acetic acid. The exothermic reaction was moderated with a water bath at room temperature. After stirring at room temperature for 2 hr, the reaction mixture was added to 20 ml of water, followed by extraction with four 20-ml portions of pentane. The combined pentane extracts were washed with 10 ml of 10% sodium carbonate solution, 10 ml of water, and dried. Removal of the pentane under reduced pressure left a light yellow liquid residue. The infrared spectrum of the crude product showed carbonyl absorptions at 5.44 (m), 5.64 (s), and 5.77 (s) μ. A medium intense hydroxyl absorption at 2.94 μ indicated the presence of some starting material. Column chromatography using Woelm acid-washed alumina, activity grade 1, gave a clear liquid, eluted with methylene chloride, which showed carbonyl absorptions at 5.43 (m) and 5.62 (s) μ, but no hydroxyl absorption.

Purification by gc collections using a 0.25 in. × 6 ft 20% Carbowax 20M on 60/80 Chromosorb W column at 175° gave pure *exo*-2-chlorobicyclo[2.2.1]heptan-7-one in low yield.

Anal. Calcd for C_7H_9ClO: C, 58.14; H, 6.27. Found: C, 58.09; H, 6.40.

The nmr spectrum (neat, TMS external standard) exhibited absorptions at τ 5.25 (multiplet, 1, *endo*-C_2) and 6.8–8.3 (complex, 8).

This ketone gave a 2,4-dinitrophenylhydrazone which melted at 140.0–142.0°.

***exo*-2-Chlorobicyclo[2.2.1]heptan-7-one Ethylene Ketal.**—The procedure of Meinwald, Meinwald, and Baker[9a] was employed, using ethylene glycol, benzene solvent, and *p*-toluenesulfonic acid catalyst. A 0.805-g (5.57 mmol) sample of *exo*-2-chlorobicyclo[2.2.1]heptan-7-one gave 0.778 g of the crude ketal after distillation through a short path column. The yield of the ketal based on gc integration was 63.5%.

Bicyclo[2.2.1]hept-2-en-7-one Ethylene Ketal.—To a refluxing solution of potassium *t*-butoxide in *t*-butyl alcohol, prepared from 0.675 g (0.173 g-atom) of potassium and 10 ml of dry *t*-butyl alcohol, was added a solution of 0.778 g (85.7% pure, 3.54 mmol) of *exo*-2-chlorobicyclo[2.2.1]heptan-7-one ethylene ketal in 10 ml of dry *t*-butyl alcohol. The reaction mixture immediately began to turn cloudy and after refluxing for an additional 28 hr a white solid had precipitated. The reaction mixture was cooled, added to 50 ml of water, and extracted continuously with ether overnight. After drying, the ether solution was concentrated by distillation at atmospheric pressure, leaving 1.26 g of a light yellow liquid residue. Gc collection of the product gave 0.408 g (76%). The nmr spectrum (neat, TMS external standard) exhibited absorptions at τ 3.48 (triplet, 2, vinyl), 5.78 (multiplet, 4, dioxolane), 7.13 (quintet, 2, bridgeheads), 7.66 (multiplet, 2, *exo*-C_5 and *exo*-C_6), and 8.65 (multiplet, 2, *endo*-C_5 and *endo*-C_6).

Bicyclo[2.2.1]hept-2-en-7-one (9).—A 0.400-g (0.00263 mol) sample of bicyclo[2.2.1]hept-2-en-7-one ethylene ketal was hydrolyzed with 5% sulfuric acid according to the method of Gassman and Pape.[12] After work-up, there was obtained 0.550 g of a clear, colorless liquid containing some solvent (pentane). The infrared spectrum of this crude product was in agreement with that reported[12,13] for bicyclo[2.2.1]hept-2-en-7-one, showing carbonyl absorptions at 5.36 (m) and 5.60 (s), carbon double bond absorption at 6.17 (w), and vinyl carbon hydrogen absorptions at 3.28 (w) and 14.27 μ (s).

Gc analysis using a 0.25 in. × 7.5 ft 20% Carbowax 20M column at 100° showed decomposition of the ketone to give carbon monoxide and 1,3-cyclohexadiene. The ketone could be converted into its 2,4-dinitrophenylhydrazone, which melted at 138.5–139.2° (lit.[12] mp 136–137°).

Reaction of 2-Chlorobicyclo[2.2.1]hept-2-ene *exo*-Oxide with Hydrogen Chloride in Ether.—Anhydrous hydrogen chloride gas was bubbled through 25 ml of anhydrous ether at room temperature for *ca.* 15 min. A solution of 2.067 g (0.0143 mol) of 2-chlorobicyclo[2.2.1]hept-2-ene *exo*-oxide in 10 ml of anhydrous ether was added slowly and the mixture allowed to stir at room temperature for 3.5 hr. The solution was then concentrated under reduced pressure to give 2.293 g of a clear, colorless liquid which developed a light pink color upon standing.

Gc analysis using a 0.25 in. × 6 ft 20% Carbowax 20M on 60/80 Chromosorb W column at 200° showed the presence of eight major components. The retention times and integrated percentages were as follows: peak no. 1, 1.71 min, 3.9%; peak no. 2, 3.35 min, 7.9%; peak no. 3, 3.60 min, 3.2%; peak no. 4, 3.90 min, 13.0%; peak no. 5, 4.59 min, 23.2%; peak no. 6, 4.98 min, 12.4%; peak no. 7, 7.54 min, 27.1%; and peak no. 8, 13.27 min, 9.3%.

Peak no. 1 was indicated to be unreacted epoxide by its retention time only. Peaks no. 2 and 3 were not identified. Peak no. 4 was identified as *exo*-3-chlorobicyclo[2.2.1]heptan-2-one (**3**) by its retention time. Peak no. 5 was identified as *exo*-2-chlorobicyclo[2.2.1]heptan-7-one (**4**) by its retention time and by collection and comparison of its infrared spectrum with that of an authentic sample. The retention time of peak no. 6 suggested it to be *endo*-3-chlorobicyclo[2.2.1]heptan-2-one (**5**), but after collection of this component the infrared spectrum showed only a weak, sharp carbonyl absorption at 5.66 and a strong hydroxyl absorption at 2.90 μ. Thus, this peak from the gc is an unknown compound probably containing a small amount of **5**.

Peak no. 7 was identified as 3,3-dichlorobicyclo[2.2.1]heptan-*exo*-2-ol (**6**) by its retention time and by collection and comparison of its infrared spectrum with that of the same material obtained in the thermal rearrangement of the epoxide. A collected sample, after vacuum sublimation and recrystallization from hexane, melted at 103.0–109.0° (sealed capillary). The melting points of samples of this alcohol appeared to vary somewhat depending upon length of exposure to the atmosphere.

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(29) S. B. Soloway and S. J. Cristol, *J. Org. Chem.*, **25**, 327 (1960).

Collection of peak no. 8 gave a tan waxy solid. Vacuum sublimation of the collected material gave a white waxy solid, which melted at 85–92°. This material was not identified, but the infrared spectrum showed major absorptions at 2.98 (s), 5.73 (m), and 6.15 (w) μ.

Reaction of 3,3-Dichlorobicyclo[2.2.1]heptan-*exo*-2-ol with Chromium Trioxide in Acetic Acid.—The method described previously for the oxidation of *exo*-2-chlorobicyclo[2.2.1]heptan-*syn*-7-ol was employed. A 0.119-g (0.657 mmol) sample of the dichloro alcohol in 2 ml of glacial acetic acid was treated with a solution of 0.064 g (0.64 mmol) of chromium trioxide in 6 ml of glacial acetic acid for 7 hr at room temperature. After work-up there was obtained 0.116 g of a tan solid whose infrared spectrum showed no hydroxyl absorption, but did show carbonyl absorptions at 5.48 (m) and 5.62 (s) μ, initially suggesting a 7-keto structure. Recrystallization of the crude product from hexane followed by vacuum sublimation gave 0.032 g (27.2%) of a white crystalline solid, mp 101.5–102.5°, which is indicated to be 3,3-dichlorobicyclo[2.2.1]heptan-2-one. Repeated attempts to prepare an ethylene ketal by the method of Meinwald, Meinwald, and Baker[9a] were unsuccessful.

The infrared spectrum had absorptions at 5.48 (m) and 5.62 (s) μ for the carbonyl group while the nmr spectrum (CCl$_4$, TMS internal standard) exhibited absorptions at τ 6.94 (multiplet, 1, C$_4$), 7.18 (multiplet, 1, C$_1$), and 7.4–8.5 (complex, 6).

Hydrolysis of 3,3-Dichlorobicyclo[2.2.1]heptan-*exo*-2-ol.—This compound was hydrolyzed according to the procedure described by Baird.[11] A mixture of 0.108 g (0.596 mmol) of 3,3-dichlorobicyclo[2.2.1]heptan-*exo*-2-ol, 0.238 g of lithium carbonate, and 10 ml of water was heated to reflux for 32 hr. After cooling, the reaction mixture was filtered, and the filtrate was extracted continuously with ether for 12 hr. The ether extract was dried and concentrated to give 0.060 g of a light yellow liquid residue. In addition to a strong hydroxyl absorption at 3.00 μ the infrared spectrum showed fairly strong absorption in the carbonyl region at 5.74 μ.

The crude product was taken up in ether and washed with 10 ml of 40% sodium bisulfite solution. After drying and removal of the ether under reduced pressure, 0.023 g of a viscous, yellow-brown liquid remained. Vacuum sublimation gave a white semisolid material, which was recrystallized from cyclohexane to give a low yield of 1-chlorobicyclo[2.2.1]heptane-*exo*-2,*syn*-7-diol (**12**) as a white crystalline solid, mp 170–192° (sealed capillary). The melting point of the diol varied somewhat upon exposure to the moist atmosphere. The infrared spectrum of this product was identical with that of the diol (mp 200–202°) obtained by the lithium aluminum hydride reduction of 1-chloro-*exo*-2,*syn*-7-diacetoxybicyclo[2.2.1]heptane (**15**).

Reaction of 2-Chlorobicyclo[2.2.1]hept-2-ene *exo*-Oxide with Anhydrous Acetic Acid.—A 6.97-g (0.0482 mol) sample of 2-chlorobicyclo[2.2.1]hept-2-ene *exo*-oxide in a Dry Ice cooled addition funnel was added dropwise with stirring to 75 ml of anhydrous acetic acid at room temperature. The temperature of the reaction mixture increased to 32.3° during the addition and then gradually decreased again. After stirring for a total of 18 hr, the reaction mixture was taken up in ether and cooled in an ice bath while the acetic acid was neutralized by the addition of a cold saturated sodium bicarbonate solution. The ether layer was separated, washed with water, and dried. Concentration under reduced pressure gave 6.59 g of a light yellow liquid residue.

Gc analysis of the crude product using a 0.25 in. × 6 ft 20% Carbowax 20M on 60/80 Chromosorb W column at 200° showed the presence of fourteen major components besides some solvent. The retention times and integrated percentages were as follows: peak no. 1, 0.99 min, 0.7%; peak no. 2, 1.70 min, 1.7%; peak no. 3, 2.98 min, 2.7%; peak no. 4, 3.33 min, 3.0%; peak no. 5, 3.59 min, 0.6%; peak no. 6, 3.88 min, 5.0%; peak no. 7, 4.56 min, 13.3%; peak no. 8, 4.95 min, 3.5%; peak no. 9, 6.09 min, 12.6%; peak no. 10, 6.90 min, 4.1%; peak no. 11, 7.52 min, 8.9%; peak no. 12, 13.20 min, 5.5%; peak no. 13, 14.66 min, 24.4%; and peak no. 14, 15.97 min, 14.0%. These integrated percentages are only approximate owing to the overlap of some of the peaks.

Peak no. 2 was indicated to be unreacted epoxide by its retention time. Peaks no. 6 and 8 were identified as *exo*- and *endo*-3-chlorobicyclo[2.2.1]heptan-2-one, respectively, by comparison of retention times, and by collection of the components and comparison of their infrared spectra with those of known samples. Peak no. 7 was identified as *exo*-2-chlorobicyclo[2.2.1]heptan-7-one by its retention time and by the infrared spectrum of a collected sample. In the same manner peak no. 11 was identified as 3,3-dichlorobicyclo[2.2.1]heptan-*exo*-2-ol. Peak no. 9 was collected and identified as *exo*-2-acetoxybicyclo[2.2.1]heptan-7-one by comparison of its infrared spectrum with that of an authentic sample.[19]

Collection of peak no. 13 from the gc gave a white crystalline solid, which after recrystallization from hexane melted at 70.7–71.7°. An osmometric molecular weight determination in ethanol gave a value of 196.8, suggesting the addition of a molecule of acetic acid to epoxide **2**. The infrared spectrum exhibited absorptions at 3.03 (s) (O–H), 5.75 (s) and 8.12 μ (s) (acetate). The nmr spectrum (CCl$_4$, TMS internal standard) exhibited absorptions at τ 5.14 (triplet, 1, *endo*-C$_2$), 6.17 (multiplet, 1, *anti*-C$_7$), 7.45 [doublet (J = 4.5 cps), 1, hydroxyl], and 7.5–9.1 (multiplet, 10) with an intense singlet at τ 7.97 due to the methyl of the acetoxyl substituent. After treatment of the sample with deuterium oxide, the doublet at τ 7.45 was gone and the multiplicity at 6.17 was simplified. From mechanistic considerations the structure 1-chloro-*exo*-2-acetoxybicyclo[2.2.1]heptan-*syn*-7-ol (**14**) is assigned.

Anal. Calcd for $C_9H_{13}ClO_3$: C, 52.82; H, 6.40; mol wt, 204.66. Found: C, 52.57; H, 6.37.

Collection of peak no. 14 from the gc also gave a white crystalline solid, which after recrystallization from hexane melted at 92.5–93.0°. An osmometric molecular weight determination in ethanol gave a value of 250.7. The infrared spectrum contained absorptions at 5.73 (s) and 8.00 μ (s) for the acetates and the nmr spectrum (CCl$_4$, TMS internal standard) exhibited absorptions at τ 5.13 (complex, 2, *endo*-C$_2$ and *anti*-C$_7$) and 7.5–8.8 (complex, 13, methyl absorptions at τ 7.96 and 8.00). These data are in accord with the structure of 1-chloro-*exo*-2,*syn*-7-diacetoxybicyclo[2.2.1]heptane (**15**).

Anal. Calcd for $C_{11}H_{15}ClO_4$: C, 53.56; H, 6.13; mol wt, 246.69. Found: C, 53.85; H, 6.21.

Owing to poor separation for collections, insufficient quantities of the remaining peaks (no. 1, 3, 4, 5, 10, and 12) could be obtained for identification. These six components account for a total of 16.6% of the products. No further attempts were made to identify these peaks.

Acetylation of 1-Chloro-*exo*-2-acetoxybicyclo[2.2.1]heptan-*syn*-7-ol.—A mixture of 0.062 g (0.303 mmol) of 1-chloro-*exo*-2-acetoxybicyclo[2.2.1]heptan-*syn*-7-ol, 1 ml of pyridine, and 0.5 ml of acetic anhydride was allowed to stir at room temperature for several days. The mixture was then added to *ca.* 25 ml of water, and, while cooling in an ice bath, 10% hydrochloric acid was added dropwise until the pyridine odor had nearly disappeared. The resulting mixture was extracted with four 6-ml portions of pentane, and the combined pentane extracts were washed with two 10-ml portions of 5% hydrochloric acid and 10 ml of water and dried. Removal of the pentane by distillation left 0.076 g (100%) of a tan crystalline solid, mp 91.0–92.5°. Gc analysis of an ether solution of the solid showed only one component (besides ether) whose retention time was identical with that of 1-chloro-*exo*-2,*syn*-7-diacetoxybicyclo[2.2.1]heptane (**15**). Recrystallization from hexane gave 0.035 g of white crystals, mp 91.5–92.0°, whose infrared spectrum was identical with that of **15**.

Reduction of 1-Chloro-*exo*-2,*syn*-7-diacetoxybicyclo[2.2.1]heptane with Lithium Aluminum Hydride.—To a well-stirred mixture of 0.335 g (8.83 mmol) of lithium aluminum hydride in 8 ml of anhydrous ether was added dropwise a solution of 0.400 g (1.62 mmol) of 1-chloro-*exo*-2,*syn*-7-diacetoxybicyclo[2.2.1]heptane in 4 ml of ether. After stirring at room temperature for 1 hr, the excess lithium aluminum hydride was destroyed by the cautious addition of water followed by moist sodium sulfate. The mixture was extracted with ether and the ether extracts were dried and concentrated to give 0.302 g of a light yellow, gummy, solid residue. Vacuum sublimation yielded 0.221 g of a white crystalline solid, which after recrystallization from hexane gave 0.180 g (68.3%) of 1-chlorobicyclo[2.2.1]heptane-*exo*-2,*syn*-7-diol (**12**), mp 200–202° (sealed capillary) with prior sublimation. The infrared spectrum showed strong absorption at 2.97 μ while the nmr spectrum (CDCl$_3$, TMS internal standard) exhibited absorptions at τ 6.1 (complex, 4, hydroxyls, *endo*-C$_2$, *anti*-C$_7$) and 7.5–9.1 (complex, 7).

O-Isopropylidene Derivative of 1-Chlorobicyclo[2.2.1]heptane-*exo*-2-*syn*-7-diol.—A mixture of 0.270 g (1.66 mmol) of the diol, 0.587 g (5.64 mmol) of 2,2-dimethoxypropane, 10 ml of anhydrous benzene, and several small crystals of *p*-toluenesulfonic acid monohydrate was heated under reflux. Then the benzene was distilled off very slowly through a 12-cm, vacuum-jacketed Vigreux column until *ca*. 5 ml of a brown liquid remained. Then several milliliters of a solution of sodium methoxide in methanol was added which turned the mixture to an intense yellow color. Distillation was then continued until the volume had been reduced to about 3 ml. The residue was dissolved in 25 ml of ether, washed with three 10-ml portions of water, and dried. Concentration of the ether solution gave 0.336 g of a yellow-orange liquid residue. The infrared spectrum of the crude product showed absorptions at 3.01 (m), 6.23 (m), 7.25 (s), 7.34 μ (s), and bands in the 8.0–9.5-μ region characteristic of ketals. The absorptions of 7.25 and 7.34 μ are suggestive of a geminal dimethyl group.

The crude product, insoluble in Skellysolve B, was dissolved in a small amount of benzene and chromatographed through a column of Woelm basic alumina, activity grade 1. The major portion of the sample was eluted in the second fraction with benzene as a solvent. Concentration of this fraction gave 0.082 g of a light yellow oil, whose infrared spectrum was very similar to the crude product except that the hydroxyl absorption at 3.01 μ had disappeared. Elution of the column with methanol gave 0.055 g of recovered diol. An additional 0.059 g of the diol was recovered after extraction of the above aqueous wash with ether. The nmr spectrum of the chromatographed product indicated the sample to be quite impure, but it did show a pair of methyl singlets at τ 8.48 and 8.54, and the complex absorption at *ca*. 6.0 expected for the *endo*-2 and *anti*-7 protons of the desired product.

In another reaction, gc collections were attempted on the crude product using a 0.25 in. × 6 ft 20% Carbowax 20M on 60/80 Chromosorb W column at 200°. The results indicated that cleavage of the product was occurring on the column. From 0.092 g of crude product was isolated 0.004 g of a waxy white solid, mp 37.5–47.5°, whose infrared spectrum was essentially identical with that of the crude product. No further attempts were made at isolation or purification of the product of this reaction.

Bicyclo[2.2.1]heptane-*exo*-2-*syn*-7-diol.—This compound was prepared according to the procedure of Walborsky and Loncrini.[30] Performic acid oxidation of a 10.0-g (0.106 mol) sample of bicyclo-[2.2.1]hept-2-ene, followed by basic hydrolysis of the intermediate hydroxyformate, gave 10.6 g (77.7%) of crude diol as a yellow, sticky solid. Attempted purification by the method of Crandall[23] gave 6.0 g (44%) of a white crystalline solid as the carbon disulfide soluble fraction. A portion of this material was recrystallized from cyclohexane and sublimed under vacuum to give bicyclo[2.2.1]heptane-*exo*-2,*syn*-7-diol, mp 178–184.5° (sealed capillary), with prior sublimation (lit.[23] mp 175.5–181°).

To check the purity of the carbon disulfide soluble material, a sample was converted into the diacetate using acetic anhydride and pyridine. Gc analysis of the crude diacetate, using a 0.25 in. × 6 ft 20% Carbowax an 60/80 Chromosorb W column at 200°, showed three components besides ether and some acetic anhydride. The retention times and integrated percentages of these three peaks were as follows; peak no. 1, 4.37 min, 1.9%; peak no. 2, 5.20 min, 14.7%; and peak no. 3, 5.78 min, 83.4%. The 14.7% impurity is most likely the diacetate of bicyclo[2.2.1]-heptane-*exo*-2,*anti*-7-diol.[23]

***exo*-2-*syn*-7-Dimethoxybicyclo[2.2.1]heptane (17).**—To a refluxing mixture of 0.440 g (0.0191 g-atom) of sodium metal and 20 ml of dry 1,2-dimethoxyethane was added a solution of 0.511 g (3.99 mmol) of bicyclo[2.2.1]heptane-*exo*-2,*syn*-7-diol (of *ca*. 83% purity) in 10 ml of dry 1,2-dimethoxyethane. A tan solid soon began to precipitate, and after heating under reflux for an additional 1 hr, the excess sodium was still present. Then a solution of 2.0 g (15.8 mmol) of dimethyl sulfate in 5 ml of 1,2-dimethoxyethane was added dropwise, and the tan solid present largely disappeared and was finally replaced by a white solid precipitate. After another 4 hr of heating, the mixture was cooled and treated with 10 ml of dilute ammonium hydroxide to destroy the excess dimethyl sulfate. Then an additional 10 ml of water and 20 ml of ether were added, the mixture was stirred well, and the layers were separated. The aqueous layer was extracted with three 20-ml portions of ether, and the combined ether solutions were dried. Concentration under reduced pressure left 0.517 g of a yellow-orange liquid residue.

Gc analysis of the crude product using a 0.25 in. × 6 ft 20% Carbowax 20M on 60/80 Chromosorb W column at 150° showed two major components. The first of these was collected as a colorless liquid (64% of product). The infrared spectrum showed an ether linkage at 8.96 μ (s), while the nmr spectrum ($CDCl_3$, TMS internal standard) exhibited absorptions at τ 6.51 (multiplet, 2, *endo*-C_2 and *anti*-C_7), 6.72 (singlet, 6, methoxyl), 7.65 and 7.82 (broad singlets, 2, C_1 and C_4), and 8.1–9.2 (complex, 6). This shows its identity to be the dimethyl ether **17**.

The second major gc component (25% of product) is one of the monomethyl ethers of the starting diol as evidenced by infrared absorptions at 2.90 (m) (OH) and 9.02 μ (s) (ether). The nmr spectrum (CCl_4, TMS internal standard) also agreed with this assignment of structure exhibiting absorptions at τ 6.15–6.59 (complex, 2, *endo*-C_2 and *anti*-C_7), 6.59 (singlet, 3, methoxyl), 7.36 (singlet, 1, hydroxyl), 7.6–8.1 (complex, 2, C_1 and C_4), 8.1–9.2 (complex, 6). It is, of course, reasonable that both possible monomethyl ethers are present in this single gc fraction.[20]

Reaction of 1-Chlorobicyclo[2.2.1]heptane-*exo*-2-*syn*-7-diol with Sodium and Then Dimethyl Sulfate.—This reaction was conducted in the same manner as described above for the preparation of *exo*-2,*syn*-7-dimethoxybicyclo[2.2.1]heptane. To a mixture of 0.422 g (0.0184 g-atom) of sodium metal and 20 ml of dry 1,2-dimethoxyethane heated under reflux was added a solution of 0.320 g (1.97 mmol) of 1-chlorobicyclo[2.2.1]heptane-*exo*-2,-*syn*-7-diol in 10 ml of dry 1,2-dimethoxyethane. A white solid precipitated and gradually turned to a tan color. After refluxing for an additional 1 hr, a solution of 2.0 g (15.8 mmol) of dimethyl sulfate in 5 ml of 1,2-dimethoxyethane was added dropwise. The tan precipitate nearly disappeared during the addition, but was soon replaced by a white precipitate. After refluxing for another 4 hr, the mixture was cooled and worked up as described above to give 0.434 g of crude product as a light yellow liquid. Gc analysis of this material showed three major peaks. One of these (20% of product) was identified as dimethyl ether **17** by collection and comparison of its infrared spectrum with that of authentic material.

The second major peak (33% of product) was collected as a clear, colorless liquid. Its infrared spectrum contained absorptions at 8.94 (s) (ether) and 13.44 μ (m) (carbon–chlorine) with none for hydroxyl. The nmr spectrum (CCl_4, TMS internal standard) exhibited absorptions in the region of τ 6.7 (complex, 8, methoxyls, *endo*-C_2, and *anti*-C_7) (with the methyl singlets at τ 6.58 and 6.65) and 7.7–9.3 (complex, 7). The mass spectrum of this compound (mol wt 190.67) did not show a parent ion, but the peak *m/e* 158 indicates the loss of methanol to give the parent ion of the corresponding olefin.[31] These data lead one to conclude that the structure of this compound is 1-chloro-*exo*-2,*syn*-7-dimethoxybicyclo[2.2.1]heptane.

The third major component was collected as a colorless liquid. Its infrared spectrum also showed absorption at 9.08 μ (s) (ether). The nmr spectrum (CCl_4, TMS internal standard) exhibited absorptions at τ 6.75 and 6.84 (singlets, 6, methoxyls), 7.00 (complex, 2, *endo*-C_2 and *anti*-C_7), 7.84 (broad singlet, 1, C_4), 8.1–9.1 (complex, 6, C_3, C_5, and C_6), and 8.95 (singlet, 3, methyl at C_1). The mass spectrum of this compound (mol wt 170.25) likewise did not show a parent ion, but the peak at *m/e* 138 again indicated fragmentation with loss of methanol to give the parent ion of the olefin.[29] These data lead one to conclude that the structure of this compound is 1-methyl-*exo*-2,*syn*-7-dimethoxybicyclo[2.2.1]heptane.

Registry No.—**2**, 16709-75-4; **4**, 16031-39-3; **6**, 16808-48-3; **11b**, 16709-78-7; **12**, 16720-16-4; **14**, 16709-79-8; **15**, 16709-80-1; **17**, 13921-80-7; bicyclo[2.2.1]hept-2-en-7-one ethylene ketal, 1491-12-9; 3,3-dichlorobicyclo-[2.2.1]heptan-2-one, 16720-17-5; *o*-isopropylidene derivative of 1-chloro[2.2.1]heptane-*exo*-2-syn-7-diol, 16709-84-5; 1-chloro-*exo*-2-*syn*-7-dimethoxybicyclo[2.2.1]heptane, 16709-85-6; 1-methyl-*exo*-2-*syn*-7-dimethoxybicyclo[2.2.1]heptane, 16709-83-4.

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(30) H. M. Walborsky and D. F. Loncrini, *J. Amer. Chem. Soc.*, **76**, 5396 (1954).

(31) Such ether cleavages are known to occur; see K. Biemann, "Mass Spectrometry, Organic Chemical Applications," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 116.