dienone **27**. Only about 1 mg of the major product could be isolated from glpc owing to the significant overlap of this peak and that of **27**. A capillary tube nmr[27] of this sample, after standing at room temperature for several days, showed absorption regions at τ 3.4–4.9 ($\sim$4, =CH) and 6.7–8.2 ($\sim$6, CH$_2$C=O, =CCH$_2$ and =CCH$_2$C=). The fine structure of the nmr signals was not discernible. An ir spectrum of this sample displayed bands at 3020 (=CH), 1705 (C=O), and 1665 cm^{-1} (=CC=O). The absorption at 1705 cm^{-1} may indicate that some of **18** was present and was formed either on standing at room temperature or upon collection from the glpc. Since **18** was also found upon glpc analysis, it appears that the latter explanation is more plausible.

Lithium Aluminum Hydride Reduction of the Crude Acetate Mixture from 1,5-Cyclooctadiene (Formation of 2,5- and 2,6-Cyclooctadien-1-ol).—The crude acetate mixture (2 g, 12 mmol) derived from the 1,5-cyclooctadiene bromination product was reduced with a suspension of 0.6 g (15 mmol) of lithium aluminum hydride in 10 ml of anhydrous ether to give 0.72 g (48%) of a crude alcohol product which showed two major glpc components (EGA, 4 ft, 175°) in a 45:55 ratio, in order of their retention times. The ir spectra of samples of the minor and major peaks, collected from the glpc, were identical with those of compounds

(27) L. R. Provost and R. V. Jardine, *J. Chem. Educ.*, **45**, 675 (1968).

previously assigned the structures 2,5-cyclooctadien-1-ol and 2,6-cyclooctadien-1-ol, respectively.

Conversion of the Crude Alcohol Mixture into the Tosylates.—To a solution of the crude alcohol mixture (0.5 g) in 10 ml of cold pyridine was added 1.55 g of tosyl chloride. The mixture was isolated as described above to afford an ether solution of a crude tosylate mixture which was not further purified.

Lithium Aluminum Hydride Reduction of the Crude Tosylates.—The crude tosylate mixture was treated with a suspension of 0.3 g of lithium aluminum hydride in 10 ml of anhydrous ether in the usual way to afford two major products in a 56:44 ratio, in order of their retention times. The ir spectra of the major and minor products were identical with those of authentic samples of 1,4- and 1,5-cyclooctadiene, respectively.

Registry No.—**1**, 10095-82-6; **2**, 23346-35-2; **5**, 23359-88-8; **8**, 1122-07-2; **11**, 10095-81-5; **12**, 23346-37-4; **15**, 10095-79-1; **20**, 4734-90-1; **22**, 23359-89-9; **23**, 23346-40-9; **24**, 23346-41-0; **25**, 23346-42-1; **27**, 1460-21-5; bicyclo[3.3.0]octan-2-yl acetate, 23346-44-3; bicyclo[3.3.0]oct-3-en-2-ol, 23346-45-4; 2,6-cyclooctadien-1-ol, 10017-18-2; 2,5-cyclooctadien-1-ol, 10054-74-7.

Molecular Rearrangements. IX.[1a] The Synthesis and Rearrangements of 2-Chlorobicyclo[2.2.2]oct-2-ene Oxide

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The synthesis of 2-chlorobicyclo[2.2.2]oct-2-ene oxide (**4**) is reported. Neat, thermal rearrangement of **4** produces 89% 3-chlorobicyclo[2.2.2]octan-2-one (**8**) in addition to nine minor products. Acetolysis of **4** gives as major products **8** (45%) and 3-acetoxybicyclo[2.2.2]octan-2-one (**11**, 40%). Reaction of **4** with anhydrous hydrogen chloride in ether leads to the formation of **8** and 3,3-dichlorobicyclo[2.2.2]octan-2-ol (**10**). The formation of these products is compared with and contrasted to the results from similar studies with 2-chlorobicyclo-[2.2.1]hept-2-ene *exo*-oxide.

Our previous investigations of the mechanism of the epoxide–carbonyl rearrangements of α-chloro epoxides have involved peroxidations of α-chlorostilbenes,[2] the intermediacy of α-chloro epoxides being assumed, and studies with the relatively stable α-chloro epoxides, 1-chloro-*cis*- (**1**) and -*trans*-4-methylcyclohexene oxide (**2**),[3] and 2-chloronorbornene *exo*-oxide (**3**).[4,5] The results obtained from these latter α-chloro epoxides have led us to suggest that α-ketocarbonium ion–chloride ion pairs are the principal intermediates in their neat, thermal rearrangements.

A goal of our program in this area of molecular rearrangements has been to study the kinetics of rearrangement of a number of α-chloro epoxides as a function of solvent, added salts, etc., to help us to substantiate or refute the idea of such ion-pair intermediates. The mixture of **1** and **2** did not appear to be suitable for such kinetic studies, since we have been unable to rule out the possibility of a chloronium ion intermediate for the rearrangement of **1**.[3] α-Chloro epoxide **3** was also less suitable than desired, since in

neat, thermal rearrangements *ca.* 40% was converted into polymeric material.[4]

The present work reports the synthesis and certain rearrangement studies of 2-chlorobicyclo[2.2.2]octene oxide (**4**), which appears to be a reasonable candidate for the proposed kinetic studies. Epoxide **4** might also allow us to determine the effect of the bicyclic framework on the rearrangement of the analogous bicyclic epoxide, **3**, since **4** has considerably less angle strain than **3**.[6] The *exo–endo* geometric relationship present in **3** is absent in **4**.

Results

The synthesis of **4** began with the Diels–Alder reaction of cyclohexadiene and *trans*-1,2-dichloroethylene. This reaction had been reported by Hine, *et al.*,[7] who stated that "from the boiling point, method of preparation, and analysis, the mixture appeared to contain 5,6-dichlorobicyclo[2.2.2]oct-2-ene (**5**) and a somewhat larger amount of cyclohexadiene dimer." Indeed, separation of **5** from cyclohexadiene dimer was effected only after a careful distillation, and yields of **5** averaged *ca.* 20%. The halogens are believed to be *trans* by analogy to the stereochemistry of the product

(1) (a) Part VIII: R. N. McDonald and D. G. Hill, *Chem. Commun.*, 671 (1969). (b) NDEA Fellow, 1964–1967; NSF Cooperative Fellow, 1967–1968. (c) Taken from the Ph.D. Thesis of R. N. Steppel.

(2) R. N. McDonald and P. A. Schwab, *J. Amer. Chem. Soc.*, **85**, 820, 4004 (1963).

(3) R. N. McDonald and T. E. Tabor, *ibid.*, **89**, 6573 (1967).

(4) R. N. McDonald and T. E. Tabor, *J. Org. Chem.*, **33**, 2934 (1968).

(5) R. N. McDonald and R. N. Steppel, *J. Amer. Chem. Soc.*, **91**, 782 (1969).

(6) H. M. Walborsky, M. E. Baum, and A. A. Youssef, *ibid.*, **83**, 988 (1961).

(7) J. Hine, J. A. Brown, L. H. Zalkow, W. E. Gardner, and M. Hine, *ibid.*, **77**, 594 (1955).

obtained from cyclopentadiene and *trans*-1,2-dichloroethylene.[8]

Hydrogenation of **5** (usually as a mixture with dicyclohexadiene) over 5% palladium on carbon in ethyl alcohol gave *trans*-2,3-dichlorobicyclo[2.2.2]-octane (**6**) in yields of *ca.* 80%. Dehydrochlorination of **6** with potassium *t*-butoxide in *t*-butyl alcohol afforded 2-chlorobicyclo[2.2.2]octene (**7**) in *ca.* 85% yield. Epoxidation of **7** with *m*-chloroperbenzoic acid


5

6   **7**

4
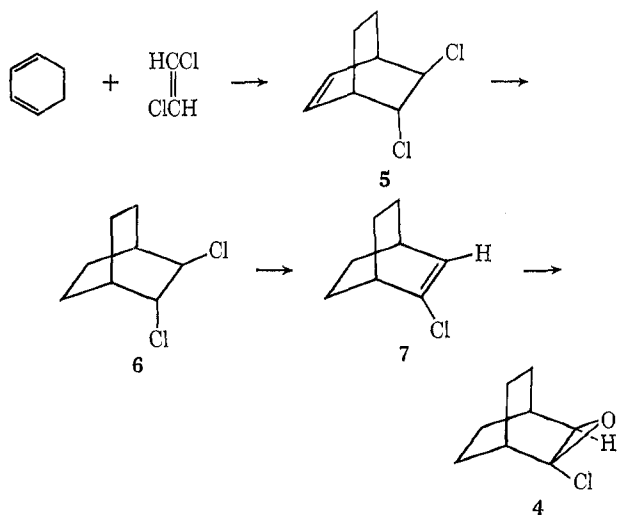
gave a 60% yield of **4** as a crystalline compound, mp 47–48°, which is a reasonably stable α-chloro epoxide.

Neat, thermal rearrangements of **4** were conducted in sealed tubes with a bath temperature of 100°. After 24 hr the samples had not colored and only traces of hydrogen chloride were evident when the tubes were opened. This is in marked contrast to similar attempts with **3** at 60°, where immediate darkening and facile rearrangement (sometimes explosively) occurred and relatively large quantities of hydrogen chloride were noted. The product mixture from **4** was shown by glpc to consist mainly of 3-chlorobicyclo-[2.2.2]octanone (**8**, 89.7%),[9] along with at least nine other components of unknown structure.


8
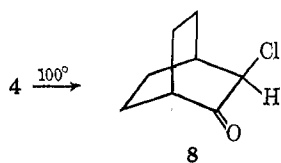
To verify the structure of the major product, **8**, bicyclo[2.2.2]octanone was chlorinated with sulfuryl chloride. From this reaction a mixture of **8** and 3,3-dichlorobicyclo[2.2.2]octanone (**9**) was obtained. When excess sulfuryl chloride was employed, **9** was the only product formed in 83% yield.


9
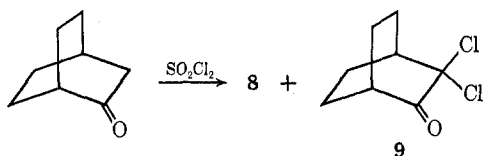
(8) J. D. Roberts, F. O. Johnson, and R. A. Carboni, *J. Amer. Chem. Soc.*, **76**, 5692 (1954).
(9) Glpc integrated per cent.

Treatment of **4** with anhydrous hydrogen chloride in ether gave a mixture of 3,3-dichlorobicyclo[2.2.2]-octan-2-ol (**10**) and **8** in a ratio of 2:1 as determined by nmr spectroscopy. Attempted separation and purification of this mixture by glpc or column chromatography on acidic alumina resulted in substantial or complete conversion of **10** into **8**. Chromic acid oxidation of the 1:2 mixture of **8** and **10** produced a mixture of **8** and **9** in a ratio of 7:3 as analyzed by glpc, thus establishing the presence of **10** in the original mixture. We believe that probably as much as 95% of the reaction between hydrogen chloride and **4** occurs by addition to form **10**, which then eliminates hydrogen chloride and ketonizes to yield **8** to some extent in the work-up.

10
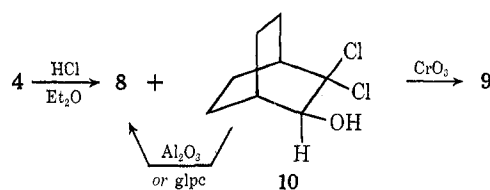
Acetolysis of **4** produced a mixture of at least 16 components as analyzed by glpc, of which only four integrated for more than 2.0% when a basic wash in the work-up was omitted. The two major products were identified as **8** (44.8%)[9] and 3-acetoxybicyclo[2.2.2]-octan-2-one (**11**, 39.5%).[9] 3-Hydroxybicyclo[2.2.2]-octanone (**12**) was obtained in 0.8%[9] yield, which increased to 12.7% when the acetolysis product was taken up in ether and washed with aqueous base.

11

12   **13**
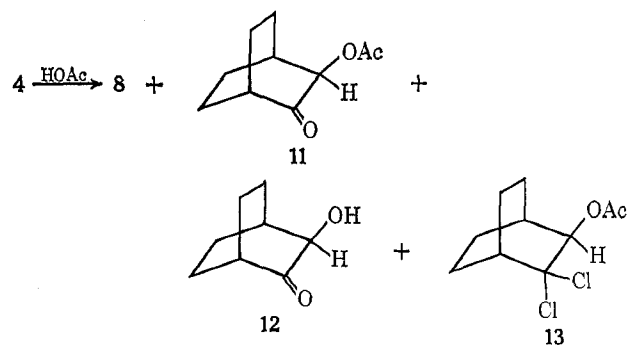
A second acetate was obtained as a minor product which, on the basis of its infrared and nmr spectra, was thought to be 2-acetoxy-3,3-dichlorobicyclo[2.2.2]-octane (**13**). Acetate **13** could have been formed by addition of hydrogen chloride (generated in the formation of **11**) to **4** to produce **10** followed by acid-catalyzed esterification.

The structures of **11** and **12** were verified by independent synthesis. α-Chloro ketone **8** was heated under reflux with aqueous potassium carbonate to give **12** in *ca.* 90% yield. Acetylation of **12** produced **11**.

Discussion

As pointed out above, the neat, thermal rearrangement of **4** proceeds far more cleanly than that of its [2.2.1] analog, **3**.[4] Little if any rearrangement of **4** to 8-ketobicyclo[3.2.1]oct-2-yl products was observed, whereas Wagner–Meerwein rearrangement of **3** under the same conditions was a major process.[4] These are summarized in Table I.

Rearrangement type	14	15	16	17
Neat, thermal	37.4	36.9[b]	89.7	c
HCl, ether	13.0	23.2	33.3[d]	0.0
HOAc	8.5	25.9	85.1	c

[a] X is Cl in neat, thermal, and HCl-catalyzed rearrangements, and Cl, OAc, and OH in acetolysis. [b] This includes 2.0% bicyclo[2.2.1]hept-2-en-7-one. [c] No products containing the [3.2.1] ring system were identified, but it seems likely that several are among the minor components. [d] It is not certain if any of 8 is formed directly or if it arises by dehydrochlorination of 10.

Solvolyses of bicyclo[2.2.2]octan-2-yl arenesulfonates[6,10] and deamination of 2-aminobicyclo[2.2.2]-octane[10] generally lead to mixtures of [2.2.2] and [3.2.1] products with the [2.2.2] product predominating. We were surprised to find a lack of rearrangement in the major isolated product, especially in the hydrogen chloride catalyzed rearrangement and acetolysis of 4, where the recovery of products is very good. These two reactions with 3 produced 15 to 14 ratios of 1.8 and 3.0, respectively. The exact ratios of 17 to 16 are unknown but are definitely inverted compared with 15 to 14 ratios, being less than 0.17.

At least two interpretations may be offered to explain this reduced amount of skeletal rearrangement from 4 compared with 3: (A) a change in mechanism, or (B) the greater stability of the 3-ketobicyclo[2.2.2]oct-2-yl cation relative to the 8-ketobicyclo[3.2.1]oct-2-yl cation compared with that of the 3- and 7-ketonorborn-2-yl cations.

In the neat, thermal rearrangement of 4, interpretation A could encompass several possibilities, including (a) hydride rather than chloride as the principal migrating group and (b) chlorine migrating *via* a chloronium ion, 18. Hydride shifts have been shown

18
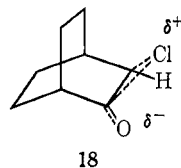
to be nonexistent in the related rearrangement of 1 and 2,[3] and to contribute less than 10% of the total rearrangement of 3 to *exo*-3-chloronorcamphor.[5,11] A chloronium ion intermediate is ruled out as a major process with 3 and also is not believed to be occurring in the rearrangement of the mixture of 1 and 2. Arguing from these analogies, we conclude that a gross change in mechanism in the rearrangement of 4 to 8 is unlikely.

Defense of interpretation B may be found in the comment by Sargent "that the rehybridization of C_2 from sp^3 to sp^2, necessitated by the generation of a carbonium ion, must result in a substantially greater increment in angle strain for the norbornyl system than for the bicyclo[2.2.2]octyl system."[12] It would appear that this reduced strain in the [2.2.2] system would become even more significant as we introduce two sp^2-hybridized carbons into an ethano bridge, as would be the case in the 3-ketobicyclo[2.2.2]oct-2-yl cation.[6,13] This explanation could account for the facts that (A) neat, thermal rearrangement of 3 leads to the formation of about equal amounts of *exo*-3-chloronorcamphor and *exo*-2-chloro-7-ketonorbornane[4] while similar treatment of 4 leads to primarily 8, and (B) acetolysis of 3 gives a small amount of *exo*-2-acetoxy-7-ketonorbornane as the only identified acetoxy ketone[4] while acetolysis of 4 produces a relatively large amount of acetoxy ketone 11. Chloro ketone 8 has been shown to be stable to the acetolysis conditions.

Another factor which may be of importance in comparing the rearrangements of 3 and 4 is that, when chloride departs from 3, it leaves from the *endo* face of the [2.2.1] system and must rebond from the *exo* face to give the major products of neat, thermal rearrangement, 14 (*exo*-X = Cl) and 15 (X = Cl).[4,5] Skeletal rearrangement of the suggested intermediate 3-keto- to the 7-ketonorbornyl cation–chloride ion pair could then compete with collapse to products. No such timing delay or motion for chloride ion migration is required in the rearrangement of 4 to 8 in the [2.2.2] system.

Formation of a nonclassical ion pair in the [2.2.1] system and not in the [2.2.2] system is yet another explanation which cannot be ruled out.[5] A more definitive explanation must await further work in this and related systems.

Experimental Section[14]

trans-5,6-Dichlorobicyclo[2.2.2]oct-2-ene (5).—In a Carius tube a mixture of 24 g (0.3 mol) of 1,3-cyclohexadiene, 38.8 g (0.4 mol) of *trans*-1,2-dichloroethylene, 200 mg of hydroquinone, and 200 ml of diphenylamine was heated at 180–200° for 30 hr. After cooling to room temperature the tube was opened carefully, since hydrogen chloride is normally present. The excess dichloroethylene was removed in a trap-to-trap distillation under reduced pressure, leaving a dark green residue (ca. 35 g) composed mainly of 5 and dicyclohexadiene.

A number of such reaction mixtures were combined and distilled using a 30-cm Vigreux column, collecting the material boiling above 45° (1 mm). Redistillation of 50 ml of this crude product using a Teflon annular spinning-band column gave 7.94 g of pure 5, bp 56° (1 mm) [lit.[7] bp 90–93° (10 mm)], along with 7.93 g of 84.5% pure product. The yields averaged 20%. The infrared spectrum (neat) of 5 exhibited a broad olefinic absorption at 5.9–6.4 μ with strong absorptions at 3.34, 12.0, 13.4, and 14.7 μ, while the nmr spectrum (CCl₄, internal TMS) showed absorptions centered at τ 3.68 (m, 2), 6.15 (m, 2), 7.23 (m, 2), and 7.7–9.2 (m, 4).

(10) H. L. Goering and M. F. Sloan, *J. Amer. Chem. Soc.*, 83, 1397 (1961).
(11) Multiple hydride shifts (*endo*-3,5, *exo*-5,6, and *endo*-6,2) have been shown to contribute to the extent of 3.1% in the neat, thermal rearrangement of 3: R. N. Steppel, unpublished results.

(12) G. D. Sargent, *Quart. Rev.* (London), 20, 301 (1966); see p 361.
(13) For discussion of the greater stability of bicyclo[2.2.2]octene compared with norbornene, see R. B. Turner, W. R. Meador, and R. E. Winkler, *J. Amer. Chem. Soc.*, 79, 4116 (1957); H. L. Goering and M. F. Sloan, *ibid.*, 83, 1992 (1961).
(14) All melting points were taken on a Kofler hot stage (in sealed capillaries) and are corrected; boiling points are uncorrected. Infrared absorption spectra were determined using a Perkin-Elmer Model 137 double-beam recording spectrometer and nmr spectra were obtained using a Varian A-60 recording spectrometer. Gas chromatographic analyses were performed on an F & M Model 500 temperature-programmed gas chromatograph. Microanalyses were determined by Galbraith Laboratories, Inc., Knoxville, Tenn.

trans-2,3-Dichlorobicyclo[2.2.2]octane (6).—A mixture of 41 g of Diels–Alder product containing 37% 5 and dicyclohexadiene dissolved in 60 ml of absolute ethanol was hydrogenated using 3.0 g of 5% palladium on carbon at room temperature in a glass-lined bomb (Magna Dash) with an initial hydrogen pressure of 1100 psi. After 12 hr, the catalyst was removed by filtration and most of the ethanol was distilled under reduced pressure in a short-path distillation (excessive heating causes decomposition). Upon cooling, 16 g of white, crystalline product was obtained. Drying in a desiccator over calcium chloride and sublimation at 50° (5 mm) gave 15.1 g (99%) of pure *trans*-2,3-dichlorobicyclo-[2.2.2]octane, mp 118.5–119.5°. Similar results were obtained using prereduced platinum oxide in a Parr apparatus with yields of about 80%. The infrared spectrum (Nujol) had characteristic, strong absorptions at 10.4, 11.96, 12.25, 12.51, and 14.58 μ (broad). The nmr spectrum (CDCl₃, internal TMS) exhibited absorptions at τ 5.81 (s, 2), and 7.8–8.8 (m, 10).

2-Chlorobicyclo[2.2.2]octene (7).—Potassium *t*-butoxide was prepared by treating 400 ml of *t*-butyl alcohol with 27.9 g (0.71 g-atom) of potassium. To this stirred solution was added 85.0 g (0.48 mol) of 6 and the mixture was heated under reflux for 40 hr. After cooling, 300 ml of water was added and the mixture was extracted with five 100-ml portions of pentane. The combined pentane extracts were washed with four 500-ml portions of water and dried (MgSO₄), and the pentane was removed by distillation. The residue was distilled using a semimicro spinning-band column, which afforded 58.3 g (86%) of 7, bp 108° (102 mm). The infrared spectrum (neat) had characteristic absorptions at 6.18, 9.71, and 14.35 μ, and the nmr spectrum (CCl₄, internal TMS) exhibited absorptions at τ 3.68 (d of d, 1, J = 7.2 and 2.2 Hz), 7.37 (br s, 2), and 7.8–9.2 [m (a spike at 8.5), 8].

2-Chlorobicyclo[2.2.2]oct-2-ene Oxide (4).—An ice-cold solution of 7.1 g (0.05 mol) of 2-chlorobicyclo[2.2.2]oct-2-ene in 100 ml of methylene chloride was treated with 13.0 g (0.06 mol) of 80%) *m*-chloroperbenzoic acid. After 1 hr the precipitated *m*-chlorobenzoic acid was filtered and washed with small portions of cold methylene chloride. After 48 hr, additional *m*-chloro-benzoic acid was again filtered and similarly washed. The filtrate was washed with cold, saturated aqueous sodium bicarbonate and water and dried over magnesium sulfate. After most of the methylene chloride had been removed under reduced pressure, 150 ml of hexane was added and the work-up was repeated. Careful removal of the hexane under reduced pressure afforded a semisolid, crude product weighing 7.4 g, which was dissolved in 30 ml of hexane and divided into three approximately equal portions. Each portion was chromatographed on 50 g of activity II, neutral alumina. Rapid elution with hexane gave a total of 4.74 g (60%) of 4 after the solvent had been removed by rotatory evaporation (avoiding excessive heating) and evaporation of the last traces of solvent at room temperature and atmospheric pressure (the liquid only crystallizing slowly after the solvent has evaporated), mp 47–48° after sublimation at 40° (100 mm). Column chromatography of larger amounts of epoxide on larger columns resulted in major losses owing to molecular rearrangement during chromatography. 3-Chloro-bicyclo[2.2.2]octan-2-one (8) was the major rearrangement product and was eluted with benzene.

The infrared spectrum (neat) of 4 had strong characteristic absorptions at 9.28, 10.05, 10.34, 10.88, 12.0, 12.06, and 13.65 μ. The nmr spectrum (CDCl₃, internal TMS) exhibited absorptions centered at τ 6.56 (d, 1, J = 4.5 Hz) and 7.5–9.0 (m, 10).

Anal. Calcd for C₈H₁₁OCl: C, 60.57; H, 6.99. Found: C, 60.30; H, 6.84.

Neat, Thermal Rearrangement of 2-Chlorobicyclo[2.2.2]oct-2-ene Oxide.—Two glass tubes (8-mm bore) were treated with cleaning solution (Na₂Cr₂O₇–H₂SO₄), distilled water, ammonium hydroxide, and distilled water, in that order. After drying in an oven at 100° the tubes were allowed to cool in a desiccator. Into each tube was placed 150 mg (95 mmol) of 4, and the tubes were flushed and evacuated several times under nitrogen and sealed under vacuum while cooling the epoxide with a Dry Ice–isopropyl alcohol bath. The two tubes were placed in a bath maintained at 100 ± 0.5°. The epoxide melted immediately. After 24 hr, the tubes were removed and allowed to cool. Upon opening, moist indicator paper signified the presence of a trace amount of hydrogen chloride, which could not be detected by smell. Comparison of the infrared spectrum of the rearrangement mixture with that of 3-chlorobicyclo[2.2.2]oct-2-one indicated the predominance of that compound. Glpc analysis on a 0.25

in. × 12 ft 10% Carbowax 20M on 60–80 Chromosorb W column showed ten peaks. The peaks, retention times (minutes), and integrated percentages follow: 1, 1.3, 0.7%; 2, 1.4, 1.4%; 3, 2.4, 0.5%; 4, 2.7, 0.3%; 5, 3.0, 0.7%; 6, 3.4, 0.4%; 7, 4.2, 1.6%; 8, 5.1, 89.7%; 9, 7.2, 2.5%; and 10, 8.0, 2.2%.

Component 8 was collected and identified as 3-chlorobicyclo-[2.2.2]octan-2-one (8) by comparison of the infrared and nmr spectra and retention time with those of an authentic sample. No attempt was made to identify the smaller components.

The second tube, containing rearrangement products, gave identical results on glpc analysis.

3-Chlorobicyclo[2.2.2]octan-2-one (8).—In an nmr spectral tube were placed 100 mg (0.9 mmol) of bicyclo[2.2.2]octan-2-one, 0.5 ml of carbon tetrachloride, 200 mg of sulfuryl chloride, and *ca.* 10 mg of azobisisobutyronitrile. The nmr spectrum of this reaction mixture just after combining the reagents indicated immediate formation of 3-chlorobicyclo[2.2.2]octan-2-one. After 1.5 hr, analysis by glpc indicated the presence of bicyclo[2.2.2]-octan-2-one, 8, and 3,3-dichlorobicyclo[2.2.2]octan-2-one (9) in the ratio of 3.3:33.3:63.4, respectively. Collection gave 15 mg (36%) of 8 and 55 mg (58%) of 9.

After sublimation at 69° (10 mm), the sample of 8 had mp 133.5–134° and its 2,4-dinitrophenylhydrazone had mp 151–152°, recrystallized from ethanol. The infrared spectrum (Nujol) of 8 had characteristic absorptions of 5.75 (CO), 9.4, 11.6, 11.88, 12.46, and 13.1 μ. The nmr spectrum (CHCl₃, internal TMS) exhibited absorptions at τ 5.85 (d of d, 1, J = 2.9 and 1.0 Hz) and 7.5–8.6 [m (major peaks at 7.68 and 8.14, 10].

Anal. Calcd for C₈H₁₁OCl: C, 60.57; H, 6.99. Found: C, 60.58; H, 7.07.

3,3-Dichlorobicyclo[2.2.2]octan-2-one (9).—A solution of 0.9 g (7.36 mmol) of bicyclo[2.2.2]octan-2-one in 5 ml of carbon tetrachloride was treated with 4 ml of sulfuryl chloride. Upon addition an exothermic reaction took place with the evolution of a gas. After stirring overnight the excess sulfuryl chloride and carbon tetrachloride were removed under reduced pressure in a trap-to-trap distillation which left a slightly yellow solid. The solid was sublimed at 60° (0.2 mm), which gave a slightly brown-tinted, white solid. The material was resublimed twice and afforded 1.14 g (80%) of 9, mp 190–191°.

The infrared spectrum (CS₂) had characteristic absorptions at 5.68 (CO), 5.72 (CO), 12.0, and 14.5 μ (broad). The nmr spectrum (CDCl₃, internal TMS) exhibited absorptions at τ 7.0–8.4 (m with two major peaks centered at 7.4 and 8.2).

Anal. Calcd for C₈H₁₀OCl₂: C, 49.78; H, 5.22. Found: C, 49.88; H, 5.33.

Acetolysis of 2-Chlorobicyclo[2.2.2]octene Oxide.—A solution of 1.1 g (7 mmol) of 4 in 25 ml of glacial acetic acid was stirred at room temperature for 3 days. The acetic acid was removed by a short-path distillation under reduced pressure, leaving a colorless, liquid reaction product. Analysis by nmr spectroscopy (CDCl₃, internal TMS) indicated downfield resonances centered at τ 4.87 and 5.77, with a shoulder on the upfield side of the τ 5.77 peak in the approximate ratio of 3.4:6.2 (including shoulder), as well as other absorptions which included two high-field singlets at τ 7.84 and 7.97. Estimation of the value of the shoulder gave the ratio of 35.4:45.2:19.4 for the two downfield peaks and the shoulder, respectively. The reaction components corresponding to the absorptions at τ 4.87 and the shoulder at τ 5.84 were assigned the structures of 3-acetoxybicyclo[2.2.2]octan-2-one (11) and 3-chlorobicyclo[2.2.2]octan-2-one (8), respectively (see below).

The reaction mixture was taken up in ether, washed with 5% aqueous sodium hydroxide and water, and then dried over magnesium sulfate. The ether was removed under reduced pressure, leaving 0.96 g of reaction product. Analysis of the nmr spectrum (CDCl₃, internal TMS) revealed downfield resonances at τ 4.87, 5.84, and 6.03 [assigned as the C₃H in 3-hydroxybicyclo[2.2.2]octan-2-one (see below)], while the peak at τ 5.77, present before base treatment, had completely disappeared. Integration gave the approximate ratio of the three respective peaks as 1.2:10:2.6; these values are only approximate because the integration was not very good. The singlet at τ 7.79 also disappeared, which suggested that it was due to an acetate which had been saponified, since no acid proton could be found. Analysis by glpc on a 0.25 in. × 12 ft 10% Carbowax 20M column showed the presence of six major components and at least eight minor components. The peaks, retention times (min), and integrated percentages follow: 1, 3.05, 0.1%; 2,

3.37, 0.1%; 3, 3.7, 0.3%; 4, 3.9, 0.3%; 5, 5.95, 1.0%; 6, 6.5, 0.4%; 7, 7.1, 4.2%; 8, 8.3, 0.8%; 9, 10.2, 12.7%; 10, 12.8, 60.2%; 11, 17.0, 0.9%; 12, 17.9, 11.6%; 13, 19.2, 2.8%; and 14, 20.8, 4.3%.

Groups of the above peaks were collected and then reinjected under appropriate conditions to effect the separation and collection of several of the individual components. In this manner peaks 9 and 10 were shown to be 3-hydroxy- (12) and 3-chlorobicyclo[2.2.2]octan-2-one (8), respectively, by comparison of their infrared and nmr spectra with those of authentic samples. Reinjection of 12 (peak 9) showed that it partially decomposed to a yellow solid whose nmr spectrum was identical with that for peak 11.

Peaks 11 and 12 were rechromatographed on a 0.25 in. × 6 ft 10% diisodecylphthalate column. An unidentified yellow solid, corresponding to peak 11, was obtained whose infrared spectrum was characterized by two strong absorptions at 5.73 and 5.81 μ. Its nmr spectrum (CDCl₃, internal TMS) exhibited absorptions centered at τ 7.2 (br s) and 7.98 (t, *J* = 1.5 Hz) in a 1:4 ratio. Peak 12 was collected as a white solid and shown to be 3-acetoxybicyclo[2.2.2]octan-2-one (11) by comparison of its infrared and nmr spectra with those of an authentic sample.

Peak 13 remained unassigned but may have been 3-acetoxy-3,3-dichlorobicyclo[2.2.2]octane (13) based on the strong carbonyl (5.82 μ) and strong acetoxyl (8.12 μ) absorptions in the infrared spectrum, while the nmr spectrum (CHCl₃, internal TMS) had absorptions at τ 4.72 (d, *J* = 2.2 Hz) and 7.4–8.8 (broad multiplet with a singlet absorption at τ 7.82). Reinjection of this material on glpc indicated that either the sample was impure or decomposition was taking place.

A 10-ml aliquot was removed from a second identical acetolysis run. The acetic acid was again removed under reduced pressure, leaving 310 mg of reaction product which was dissolved in 5 ml of acetone. Jones reagent[15] was added at 20–25° until the orange color of the oxidizing reagent persisted. Only a few drops were required, much less than would have been required if an oxidizable secondary alcohol would have been present in any significant amount based on a comparison of the oxidation of 320 mg of bicyclo[2.2.2]octan-2-ol to bicyclo[2.2.2]octan-2-one. After the mixture had stirred for 10 min, 10 ml of water was added to it, followed by saturation with sodium chloride. The mixture was extracted with 100 ml of ether in three portions and the combined extracts were washed with 5% aqueous sodium bicarbonate and water and dried over magnesium sulfate. Removal of the ether left 320 mg of reaction product. Analysis of the nmr spectrum before oxidation again clearly showed the peaks at τ 4.78 and 5.77 with a definite upfield shoulder on the τ 5.77 peak, the size of the τ 4.87 peak being just slightly smaller than the combined τ 5.77 peak and shoulder. Analysis of the nmr spectrum after oxidation indicated that the only discernible missing peak was the one absorbing at τ 5.77. The size of the shoulder (peak now centered at τ 5.84) had increased such that it was now just slightly larger than the peak at τ 4.87.

Finally, glpc (as above) on the remainder of the second acetolysis run after most of the acetic acid had been removed under reduced pressure showed the presence of at least 16 components, not including acetic acid, listed as follows with retention times (min), integrated percentages, and assigned structure where possible: 1, 2.4, 1.9%; 2, 4.1. 0.09%; 3, 4.6, 0.14%; 4, 5.2, 0.14%; 5, 8.6, 0.19%; 6, 9.8, 0.2%; 7, 10.6, 0.18%; 8, 13.1, 0.6%; 9, 16.3, 0.8%, 3-hydroxybicyclo[2.2.2]octan-2-one (12); 10, 21.4, 44.8%, 3-chlorobicyclo[2.2.2]octan-2-one (8); 11, 23.1, 39.5%, 3-acetoxybicyclo[2.2.2]octan-2-one (11); 12, 32.2, 5.3%; 13, 34.2, 3.1%; 14, 48.1, 0.7%; 15, 51.1, 1.1%; and 16, 52.4, 1.8%.

3-Hydroxybicyclo[2.2.2]octan-2-one (12).—One gram (6.4 mmol) of 3-chlorobicyclo[2.2.2]octan-2-one (8) was added to a solution of 7.2 g of potassium carbonate and 60 ml of water. The reaction mixture was heated to a gentle reflux for 3 hr under a nitrogen atmosphere. The α-chloro ketone gradually collected on the condenser and was washed back into the basic medium with a small amount of water. Upon termination of the reaction, 0.26 g of unreacted 8 was removed from the condenser. Ether extraction of the reaction mixture followed by distillation of the ether afforded 0.62 g of a 81:19 mixture of 12 and 8, respectively,

as analyzed by glpc. The yield of 12 was 93% based on converted 8. Although the unreacted 8 could be removed by fractional sublimation at a bath temperature of 50° (100 mm), by crystallization from ether–hexane, and by glpc, the resulting α-hydroxy ketone, 12, always contained varying amounts of another substance, apparently its dimer, as shown by the attenuated carbonyl absorption in the infrared spectrum and a change in the pattern of the nmr spectrum. Complete reversal of the dimerization process could be induced by heating a sample dissolved in chloroform to 60° as detected by nmr spectroscopy. The infrared spectrum (KBr) of 12 contained characteristic absorptions at 3.02 (OH), 5.82 (CO), 9.12, and 9.42 μ. The nmr spectrum (CDCl₃, internal TMS) exhibited absorptions at τ 6.03 ("d of d," 1, *J* = 3 and 1 Hz), 6.41 (OH, washed out with D₂O, 1), and 7.5–8.9 (m, 10).

Treatment of 0.79 g (5.0 mmol) of 8 with 10.0 g of potassium carbonate and 30 ml of water under reflux for 3 days gave 0.62 g (89%) of 12. The α-hydroxy ketone was allowed to stand at room temperature for a number of days before work-up and the product was isolated mostly in the dimerized form.

3-Acetoxybicyclo[2.2.2]octan-2-one (11).—To a solution of 2 ml of pyridine and 1.2 ml of acetic anhydride was added 160 mg (1.14 mmol) of 3-hydroxybicyclo[2.2.2]octan-2-one. After standing for 8 hr at 0°, the reaction mixture was decanted onto a small amount of ice and extracted with three 10-ml portions of ether. The ether extracts were washed with 5% hydrochloric acid, aqueous sodium bicarbonate (saturated), and water. After drying over magnesium sulfate, the ether was removed by rotatory evaporation, leaving 190 mg of crude product consisting of a 12.9:87.1 mixture of 12 and 11 as analyzed by glpc. The yield of 11 was 94.4% based on converted 12. Glpc collection, recrystallization from ether, and sublimation at a bath temperature of 60° (10 mm) afforded a pure sample of the acetate as a white, crystalline solid, mp 72–73°. The infrared spectrum (KBr) had characteristic absorptions at 5.80 (CO) and 8.08 μ (OAc). The nmr spectrum (CDCl₃, internal TMS) exhibited absorptions at τ 4.91 (m, 1) and 7.58–8.67 [m (7.90 for methyl singlet), 10].

Anal. Calcd for C₁₀H₁₄O₃: C, 65.91; H, 7.74. Found: C, 66.21; H, 7.91.

Hydrochlorination of 2-Chlorobicyclo[2.2.2]oct-2-ene Oxide.—Anhydrous hydrogen chloride was bubbled into 100 ml of dry ether (distilled from calcium hydride) for 15 min. A solution of 1.0 g of 4 in 10 ml of ether was added dropwise. After stirring for 9 days at room temperature the ether was removed under reduced pressure in a short-path distillation, leaving *ca.* 1.1 g of a white solid. Analysis of the nmr spectrum (CDCl₃, internal TMS) indicated a mixture of 3,3-dichlorobicyclo[2.2.2]octan-2-ol (10) and 3-chlorobicyclo[2.2.2]octan-2-one (8) in the approximate ratio of 2:1 with absorptions at τ 5.87 (C₂ H and C₃ H of the two respective compounds overlapping), 7.14 (s, OH of 10), and 7.4–8.8 (br). Analysis by glpc showed two peaks in the ratio of 64.8:35.2. The first peak was identified as 8, while the second peak was assigned the structure of 10. Reinjection of 10 showed that this compound partially decomposed to 8. However, the infrared and nmr spectra of the 10 indicated the absence of α-chloro ketone 8. The infrared spectrum (KBr) had characteristic absorptions at 3.1 (OH) and 11.9 μ. The nmr spectrum (CDCl₃, internal TMS) exhibited absorptions at τ 5.84 (m, C₂ H, 1), 7.25 (m, OH, 1), and 7.5–9.0 (m, 10).

Attempted separation of the two compounds by recrystallization from pentane or by sublimation failed. Column chromatography of 100 mg of the mixture on 5 g of acid-washed, activity III alumina gave *ca.* 20 mg of slightly impure 10 still containing a small amount of 8. Rechromatography of the 20-mg sample did not improve the purity.

To 2 ml of stock dichromate solution (prepared from 117.5 g of potassium dichromate, 54.5 ml of 96% sulfuric acid, and 600 ml of water) and 1 ml of acetone was added 200 mg of the hydrochlorination mixture. The temperature rose to 31° and the color darkened. After stirring for 1 hr the reaction mixture was extracted several times with ether. The combined extracts were washed and dried over magnesium sulfate. The ether was removed under reduced pressure in a short-path distillation, leaving *ca.* 200 mg of white solid. Analysis by glpc showed two components in the ratio of 69.3:30.7, which, after collection, were identified as 8 and 3,3-dichlorobicyclo[2.2.2]octan-one (9), respectively, by comparison of their infrared and nmr spectra with those of authentic samples.

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Conformational Analysis. LXVI. Some Studies Involving the 3-*t*-Butylcyclooctyl Ring System[1]

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3-*t*-Butylcyclooctyl tosylate (one stereoisomer) was prepared and solvolyzed in acetic acid and in 80% ethanol, and the solvolysis rates of this compound and related compounds were measured. Very little transannular hydride transfer was observed. Of the olefins obtained, 3-*t*-butylcyclooctene predominated strongly over the 4 isomer, and this predominance appears to result from a subtle steric effect. The other stereoisomer of 3-*t*-butyl-cyclooctanol could not be obtained in spite of many attempts. Reaction of the tosylate with tetramethylammonium acetate under conditions known to give mainly inversion of configuration with other compounds (including other cyclooctyl compounds) here appeared to give largely retention of configuration (plus much elimination) presumably *via* an SN mechanism.

The relatively unusual physical and chemical properties of the eight-membered ring have long been known, and are considered to be largely due to conformational effects.[3] Actual definitive evidence concerning the conformation of cyclooctane derivatives is scarce, however. From crystallographic studies, it is known that a boat–chair conformation is preferred in two particular cases.[4] The most detailed theoretical calculations carried out to date on the cyclooctane ring suggest that this conformation is either the one of lowest energy, or very close to it.[5] There are two other conformations which have calculated energies within 2 kcal of that of the boat–chair in the case of cyclooctane itself, and it seems likely that these conformations will be observed in due course in substituted molecules.

Cope and coworkers found many years ago[6] that cyclooctane rings undergo transannular reactions, in which hydride ions were observed to migrate 1,5 across the ring when an electron-deficient center was generated, and, in the case of acid-catalyzed ring openings of cyclooctane epoxides, both 1,5 and 1,3 hydride transfers were observed. Additional studies have shown that *cis*-5-*t*-butylcyclooctyl tosylate solvolyzes at a very much faster rate than does cyclooctyl tosylate itself, and, during the solvolysis, nearly 100% transfer of a hydride from C-5 to C-1 occurs.[7] Models show very clearly that it is quite easy for the hydrogen at C-5, which is *trans* to the leaving group, to move over and displace the leaving group in an inversion process. Models also show that it is quite difficult to obtain a

reaction of this sort in a simply substituted cyclooctane ring from a hydride at C-3. Cope[8] determined the percentages of 1,5 *vs.* 1,3 hydride transfer in the ring opening of 5,6-*d*₂-*cis*-cyclooctene oxide, which were found to be 61 and 39%, respectively. However, the epoxides are highly deformed cyclooctanes, and their behavior is not necessarily that to be expected from simply substituted cyclooctanes.

That the hydride transfer observed with *cis*-5-*t*-butylcyclooctyl tosylate occurs from C-5 rather than from C-3 can be interpreted in terms of the stability of the carbonium ion formed after the hydride has migrated. If the migration occurs from C-5, the resulting carbonium ion is tertiary, whereas, if the hydride ion had migrated from C-3, the carbonium ion would have been secondary. That the hydride migrates exclusively from C-5, therefore, can be understood easily enough quite apart from the details of the conformational properties of the ring.

Since models suggest that a hydride transfer from C-3 is not sterically so feasible as it would be from C-5, one might ask what results would be expected from the solvolysis of 3-*t*-butylcyclooctyl tosylate. Carbonium ion stability indicates that hydride transfer from C-3 should occur, but the steric situation in the molecule suggests that this is not feasible, and, on that basis, participation would not be expected. The actual situation was investigated in the present work by means of a rate and product study.

Discussion

2-Cyclooctene-1-one[9] underwent conjugate addition of *t*-butylmagnesium chloride to furnish 3-*t*-butyl-cyclooctanone (I) in 74% yield. Lithium aluminum hydride reduced the ketone I to 3-*t*-butylcyclooctanol (II) in 84% yield. The latter, after distillation and recrystallization from pentane, showed a melting point of 43–44°.

When the *p*-nitrobenzoate of II was prepared, recrystallized, and then hydrolyzed to give back the

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