Bicyclo[2.2.2]octeneboronic Acids and Their Reaction with Mercuric Chloride

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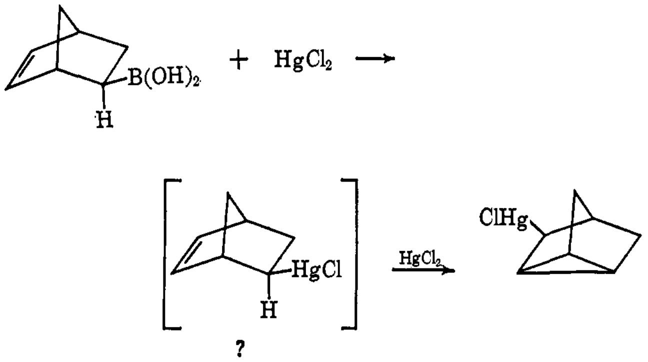
Abstract: The Diels–Alder reaction of cyclohexadiene with dibutyl vinylboronate yielded a 4:1 mixture of *endo*- and *exo*-dibutyl bicyclo[2.2.2]oct-2-ene-5-boronate, which was hydrolyzed to the boronic acids. Attempted separation of the isomers was unsuccessful. The *exo*- but not the *endo*-boronic acid reacted with mercuric chloride in the presence of sodium chloride and glycerol in buffered aqueous acetone to yield tricyclo[2.2.2.0^{2,6}]octyl-3-mercuric chloride, which isomerized to *exo*-bicyclo[2.2.2]oct-2-enyl-5-mercuric chloride in the presence of mercuric chloride. Under forcing conditions, the *endo*-boronic acid underwent slight conversion to the equilibrium-controlled bicyclic mercury compound. These results provide an additional example of electrophilic displacement with preferred inversion and show that the closure of the cyclopropane ring does indeed involve the displacement of boron and is not a subsequent rearrangement of the product. The bicyclooctenyl- and tricyclooctylmercuric chlorides decomposed on heating to yield *exo*-5-chlorobicyclo[2.2.2]oct-2-ene.

We have described an apparent example of preferred inversion in an electrophilic displacement at saturated carbon in the reaction of mercuric chloride with *exo*- and *endo*-norborneneboronic acid.[2] The proposed mechanism has been supported by the boron isotope effect[3] and a brief kinetic study.[4]

A major mechanistic question which cannot be resolved by the foregoing methods is the possibility that the initial step of these reactions is not the postulated transannular process but a direct displacement of boron by mercury, which is followed by rapid rearrangement of the initially formed norbornenylmercuric chloride to the more stable nortricyclylmercuric chloride.

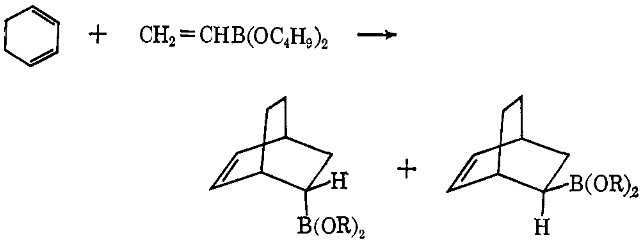


We have presented arguments against this mechanism, including the need for considerable homoallylic activation of the boron atom by unknown means,[2] but a rearrangement of a norbornenylmercury compound analogous to the second step is known.[5]

We undertook this study of the chemistry of the bicyclo[2.2.2]octeneboronic acids in the hope of resolving this question. Since bicyclo[2.2.2]octenes appear to be generally more stable than their tricyclo[2.2.2.0^{2,6}]octane isomers,[6] isolation of a tricyclooctylmercuric chloride from the mercuri-deboronation reaction would clearly indicate a concerted transannular displacement of boron.

Results

Dibutyl vinylboronate and 1,3-cyclohexadiene at 200° in a bomb yielded a mixture containing 80% dibutyl *endo*-bicyclo[2.2.2]oct-2-ene-5-boronate (Ia) and 20% of the *exo* isomer IIa.



Ia, R = C_4H_9
b, R = H

IIa, R = C_4H_9
b, R = H

Use of *t*-butyl vinylboronate in place of the *n*-butyl ester increased the *exo* content only slightly, to 24%. Isomer ratios were determined by deboronation with hydrogen peroxide and gas chromatography of the resulting bicyclooctenols.[7]

Attempts to separate the isomeric boronic acids Ib and IIb obtained by hydrolysis of the esters Ia and IIa were unsuccessful. Recrystallization of an 80% *endo* sample of boronic acid four times from aqueous acetone yielded material which was 93% *endo*, but the highest *exo* content of the boronic acid in the mother liquor was 22%. Chromatography on silica gel gave partial separation of very small quantities.

Reaction of 20% *exo*-bicyclo[2.2.2]oct-2-ene-5-boronic acid (IIb) with mercuric chloride in acetone in the presence of calcium carbonate for 1 day at room temperature yielded 20% (based on total boronic acid) of *exo*-bicyclo[2.2.2]oct-2-enyl-5-mercuric chloride (IV). When the *exo* content of the starting boronic acid was reduced to 7%, the yield of mercury compound (IV) was 7%. Pure *endo*-boronic acid (Ib), recovered from these treatments with mercuric chloride, did not react

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[1] (a) We thank the National Science Foundation for financial support, Grant No. GP-2953. (b) Abstracted from the Ph.D. thesis of M. L. Talbot, 1966. (c) Preliminary communication: D. S. Matteson and M. L. Talbot, *Chem. Ind.* (London), 1378 (1965).

[2] D. S. Matteson and J. O. Waldbillig, *J. Am. Chem. Soc.*, 86, 3778 (1964).

[3] D. S. Matteson, J. O. Waldbillig, and S. W. Peterson, *ibid.*, 86, 3781 (1964).

[4] D. S. Matteson and M. L. Talbot, *ibid.*, 89, 1119 (1967).

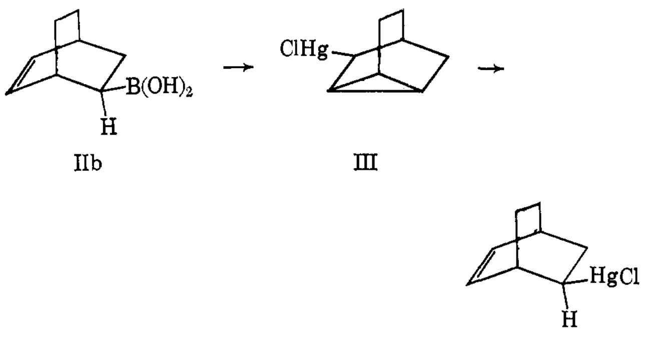
[5] K. C. Pande and S. Winstein, *Tetrahedron Letters*, 3393 (1964).

[6] N. A. LeBel and J. E. Huber, *J. Am. Chem. Soc.*, 85, 3193 (1963).

[7] D. S. Matteson and J. O. Waldbillig, *J. Org. Chem.*, 28, 366 (1963).

detectably with mercuric chloride under these conditions.

Since it was suspected that the bicyclooctenylmercuric chloride (IV) resulted from rearrangement of the original product, sodium chloride was added to inhibit rearrangement and glycerol to activate the boronic acid leaving group, a technique reported previously.[8] The solvent was aqueous acetone and the base sodium acetate. These conditions yielded tricyclo[2.2.2.0^{2,6}]-octyl-3-mercuric chloride (III), which could be isomerized to the bicyclooctenylmercuric chloride (IV) by treatment with mercuric chloride under the reaction conditions used in the previous experiments.



IIb III IV

Refluxing the *endo*-boronic acid (Ib) (98.8%) with mercuric chloride and calcium carbonate in acetone for a week did yield 5.8% of bicyclooctenylmercuric chloride (IV) and a 73% recovery of unreacted boronic acid Ib. It was not possible to detect any reaction of the *endo* isomer Ib when sodium chloride and glycerol were included in the reaction mixture.

The reaction of *exo*-bicycloocteneboronic acid (IIb) with mercuric chloride appeared to be slower than that of *endo*-norborneneboronic acid. Rate studies with the latter in the presence of sodium chloride but without glycerol showed extensive reaction in a few days at 25°,[4] but no evidence of reaction was obtained with the *exo*-bicyclooctenyl compound (IIb) under these conditions.

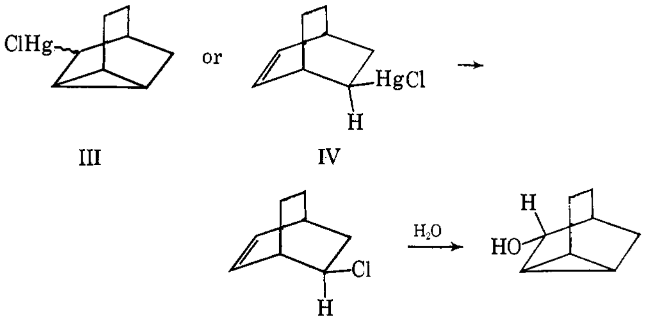
Structural Evidence. The structure of *endo*-bicyclo-[2.2.2]oct-2-ene-5-boronic acid (Ib) was confirmed by deboronation with alkaline hydrogen peroxide to *endo*-bicyclo[2.2.2]oct-2-en-5-ol, which was compared with an authentic sample[9] (purified by gas chromatography) by nmr and infrared spectra. The infrared and nmr spectra of the boronic ester and acid I were consistent with the assigned structures, and catalytic hydrogenation of 80% *endo*-butyl ester yielded dibutyl bicyclo[2.2.2]-octane-2-boronate.

Evidence for the *exo*-bicyclooctenylboron compounds II in mixtures with the *endo* isomers I includes the already described reaction with mercuric chloride. Bicyclooctenols derived from the boronic acid mixture (in 94% yield) showed infrared evidence of the *exo* isomer, especially the very strong *exo* band at 14.4 μ, which was absent from the spectrum of the pure *endo* isomer. Gas chromatography yields the same retention time for this component as for *exo*-bicyclo[2.2.2]-oct-2-en-5-ol prepared by acid-catalyzed isomerization of tricyclo[2.2.2.0^{2,6}]octan-3-ol, described in a following paragraph.

The unsaturation of *exo*-bicyclo[2.2.2]oct-2-enyl-5-mercuric chloride (IV) was revealed by the multiplet at τ 3.7–3.9 in the nmr. The infrared C=C stretching band was very weak, and an attempted hydrogenation failed due to catalyst poisoning. The *exo* configuration is supported by bromo-demercuration in pyridine, which generally proceeds with retention,[10] and in this case yielded *exo*-5-bromobicyclo[2.2.2]oct-2-ene. This reactive halide has not been characterized in pure form, but was identified by solvolysis to tricyclo[2.2.2.0^{2,6}]-octan-3-ol.[11] Further confirmation of the carbon skeleton of the mercury compound IV was provided by lithium aluminum hydride reduction to bicyclo[2.2.2]-octene.

The nmr spectrum indicated tricyclo[2.2.2.0^{2,6}]-octyl-3-mercuric chloride (III) to be saturated, but the complexity precluded further interpretation. Attempted bromo-demercuration yielded almost nothing, though infrared spectral evidence was obtained for tricyclooctanol in the oily solvolysis product. Lithium aluminum hydride reduction yielded not tricyclooctane but bicyclo[2.2.2]octene.

Tricyclo[2.2.2.0^{2,6}]octyl-3-mercuric chloride (III) decomposed in a few days at room temperature or rapidly at its melting point (90°) to yield metallic mercury and *exo*-5-chlorobicyclo[2.2.2]oct-2-ene (V), a low-melting solid showing the usual infrared and nmr evidence for the double bond. Like the corresponding arenesulfonates[6] and bromo compound,[11] this substance solvolyzed to "*endo*"-tricyclo[2.2.2.0^{2,6}]octan-3-ol (VI).



III IV V VI

Bicyclooctenylmercuric chloride (IV) also decomposed at its melting point, 150°, to yield chlorobicyclooctene (V).

Isomerization of the acetate of the tricyclooctyl alcohol VI and its epimer to *exo*-bicyclo[2.2.2]oct-2-en-5-yl acetate has been reported.[6] We obtained a sample of *exo*-bicyclo[2.2.2]oct-2-en-5-ol by refluxing the tricyclic alcohol VI with 0.01 *M* acid. Gas chromatography indicated that this isomerization required several days. Neither *endo*-bicyclo[2.2.2]oct-2-en-5-ol nor its most probable interconversion product, *exo*-bicyclo-[3.2.1]oct-3-en-2-ol,[2] isomerized under these conditions.

Discussion

Proof that the boron atom is not displaced before the step which closes the cyclopropane ring is pro-

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(8) D. S. Matteson and R. A. Bowie, *J. Am. Chem. Soc.*, 87, 2587 (1965).

(9) H. L. Goering, R. W. Greiner, and M. F. Sloan, *ibid.*, 83, 1391 (1961).

(10) F. R. Jensen and L. H. Gale, *ibid.*, 82, 148 (1960); F. R. Jensen, L. D. Whipple, D. K. Wedegaertner, and J. A. Landgrebe, *ibid.*, 82, 2466 (1960).

(11) N. A. LeBel, J. E. Huber, and L. H. Zalkow, *ibid.*, 84, 2226 (1962).

vided by the isolation of tricyclooctylmercuric chloride (III) from the reaction of *exo*-bicycloocteneboronic acid (IIb) with mercuric chloride. Since the tricyclic mercury compound III isomerizes to *exo*-bicyclooctenylmercuric chloride (IV), the latter cannot be an intermediate. These results support the direct transannular displacement mechanism for the conversion of the norborneneboronic acids to nortricyclylmercuric chloride.[2,4] Although the instability of tricyclooctylmercuric chloride (III) precludes its isolation from the sluggish reaction of *endo*-bicycloocteneboronic acid (Ib), it (or its epimer) is the probable intermediate in the formation of the bicyclic product IV.

It is evident that *exo*-bicycloocteneboronic acid (IIb) reacts much faster than its *endo* isomer Ib with mercuric chloride. From the high yield of bicyclooctenylmercuric chloride (IV) after 21 hr in acetone with calcium carbonate at 20–25°, the half-life of the *exo*-boronic acid could hardly exceed 7 hr and may be much less. Recovery of 73% of the *endo*-boronic acid after refluxing a week with the same reagents indicates a half-life of 2 or more weeks. A minimal temperature coefficient[4] would make this 30 weeks at 25°. Thus, the apparent *exo*/*endo* rate ratio is more than 700 and probably several thousand. However, the stability of the mercuric chloride solution for the entire period of the *endo* run has not been proved, and the *endo* reaction could be faster than it appears.

The epimeric configuration of the chloromercuri group in tricyclooctylmercuric chloride (III) has not been definitely established. The facile conversions to *exo*-bicyclo[2.2.2]octene derivatives are consistent with either possibility.[6] Opening a π complex of mercury(II) in the transition state of the mercuri-deboronation which yields III would involve a nucleophilic displacement on carbon,[4] which would favor the "*exo*"[6] position for the mercury. However, steric hindrance dominates the outcome of oxymercurations in bicyclic systems[12] and directs the relatively small water molecule to the "*endo*" side (toward the 1-carbon bridge) of the carbonium ion in the formation of tricyclooctanol (VI).[6] It therefore seems likely that the tricyclic mercury compound III is the *endo* epimer, analogous to the alcohol VI.

Attack of mercury(II) at the *endo* side of the double bond would be sterically hindered in *endo*-bicycloocteneboronic acid (Ib), which would contribute to the extreme sluggishness of reaction of this isomer.

Experimental Section

Dibutyl Bicyclo[2.2.2]oct-2-ene-5-boronates (Ia and IIa). A mixture of 115 g of dibutyl vinylboronate,[13] 50 g of cyclohexadiene, 20 ml of *n*-butyl alcohol, and 0.5 g of phenothiazine under nitrogen in a bomb of the type used for hydrogenations was heated 30 hr at 195–205° under autogenous pressure. Distillation yielded 118 g (71%) of dibutyl bicyclo[2.2.2]oct-2-ene-5-boronates, bp 73–74° (0.05 mm), n^{22}D 1.4638. Characteristic absorptions due to the unsaturated group appeared in the infrared at 3.30 and 6.22 μ and in the nmr at τ 3.6–4.2. The isomer content was found to be 80% *endo* and 20% *exo* by the analytical method used previously in the norbornene series,[7] oxidation of the boronic acids with alkaline hydrogen peroxide followed by gas chromatography on a Ucon polar column.

Anal. Calcd for $C_{16}H_{29}BO_2$: C, 72.72; H, 11.06; B, 4.10. Found:[14] C, 72.50; H, 11.19; B, 3.96.

80% *endo*-Bicyclo[2.2.2]oct-2-ene-5-boronic Acid (Ib and IIb). A sample of the dibutyl ester and two parts by weight of water were concentrated at 15 mm to yield 90% of solid boronic acid residue (80% *endo*). The analytical sample was recrystallized twice from water–ethanol and dried 20 min at 0.1 mm, mp 86–90° dec, unstable to air if dried too long.

Anal. Calcd for $C_8H_{13}BO_2$: C, 63.21; H, 8.62; B, 7.12. Found: C, 63.01; H, 8.50; B, 7.44.

Di-*t*-butyl Bicyclo[2.2.2]oct-2-ene-5-boronates. Heating 48 g of di-*t*-butyl vinylboronate[15] with 25 g of cyclohexadiene and 0.5 g of phenothiazine for 2 days at 200° yielded 46.6 g (68%) of di-*t*-butyl bicyclooctaneboronates, bp 57–58° (0.08 mm), shown to be 76% *endo* and 24% *exo* by oxidation and gas chromatography.[7] A satisfactory analytical sample was not obtained, but the structure was proved by transesterification with *n*-butyl alcohol, which yielded the *n*-butyl ester (Ia and IIa), identity checked by infrared and nmr.

Dibutyl Bicyclo[2.2.2]octane-2-boronate. Dibutyl bicyclo[2.2.2]-oct-2-ene-5-boronate (5 g) in 25 ml of absolute ethanol was hydrogenated at 3 atm over 1.0 g of 30% palladium on charcoal in 10 min to yield 4.2 g of the saturated product, bp 85–86° (0.1 mm), n^{26}D 1.4580.

Anal. Calcd for $C_{16}H_{31}BO_2$: C, 72.18; H, 11.74; B, 4.06. Found: C, 71.97; H, 11.47; B, 4.36.

Bicyclo[2.2.2]octane-2-boronic Acid. The butyl ester was hydrolyzed in the usual manner, and the product was recrystallized from ethanol–water, mp 150–152°.

Anal. Calcd for $C_8H_{15}BO_2$: C, 62.38; H, 9.82; B, 7.02. Found: C, 62.15; H, 9.89; B, 6.85.

***exo*-Bicyclo[2.2.2]oct-2-enyl-5-mercuric Chloride (IV).** The crude boronic acid prepared from 5.0 g of dibutyl bicyclo[2.2.2]-oct-2-ene-5-boronate (20% *exo*) was stirred with 5.15 g of mercuric chloride, 1.5 g of calcium carbonate, and 100 ml of acetone for 21 hr at room temperature under nitrogen. The excess calcium carbonate was filtered, and the filtrate was diluted with 300 ml of water, which precipitated 1.30 g (20% based on total boronic ester, 100% based on *exo* content) of *exo*-bicyclo[2.2.2]oct-2-enyl-5-mercuric chloride. The nmr showed a multiplet between τ 3.7 and 3.9 which integrated to 1.9/11 of the total proton signal and was attributed to the unsaturated group. The analytical sample was recrystallized from acetone, needles, mp 149–150° dec, strongest infrared bands (in CS_2) at 3.40 and 14.18 μ, others at 3.28, 3.49, 7.32, 7.50, 7.91, 8.27, 8.59, 8.81, 9.42, 9.52, 10.05, 10.45, 11.05, 11.55, and 12.5 μ.

Anal. Calcd for $C_8H_{11}HgCl$: C, 27.99; H, 3.23; Hg, 58.45; Cl, 10.33. Found: C, 28.03; H, 3.45; Hg, 58.17; Cl, 10.44.

Dibutyl *endo*-Bicyclo[2.2.2]oct-2-ene-5-boronate (Ia). The filtrate from the precipitation of *exo*-bicyclo[2.2.2]oct-ene-5-mercuric chloride, preceding paragraph, was saturated with hydrogen sulfide. The mercuric sulfide was filtered, and the solution was concentrated at 15 mm to yield 2.3 g (80%) of *endo*-bicyclo[2.2.2]oct-2-ene-5-boronic acid, shown to be free of *exo* isomer by the usual analysis. Treatment with butanol and distillation yielded the butyl ester, bp 64–65° (0.1 mm), n^{22}D 1.4635, infrared C=C band at 6.22 μ, strong fingerprint bands at 14.3 and 15.0 μ.

Anal. Found: C, 72.47; H, 10.82; B, 4.30.

Tricyclo[2.2.2.0^{2,6}]octyl-3-mercuric Chloride (III). The boronic acid from 10.0 g of dibutyl bicyclo[2.2.2]oct-2-ene-5-boronate (20% *exo*) was stirred with 105 ml of acetone, 45 ml of water, 10 ml of glycerol, 4.5 g of sodium chloride, 3 g of sodium acetate, and 2.1 g (equivalent to *exo*-boronic acid) of mercuric chloride for 12 hr at room temperature under nitrogen. Addition of 400 ml of water precipitated 1.9 g (73% based on *exo*-boronic acid) of tricyclo-[2.2.2.0^{2,6}]octyl-3-mercuric chloride (III), mp 91–93° dec. The analytical sample was recrystallized twice from cold acetonitrile–water and twice from cold acetone–water, then dissolved in carbon disulfide, filtered to remove a dark contaminant, and evaporated under a stream of nitrogen to yield the pure solid, mp 89–90° dec. The nmr spectrum consisted of a complex absorption between τ 7.5 and 8.6 with weaker bands to τ 7.0 and 9.3. The infrared spectrum (in CS_2) showed peaks at 3.30 (m), 3.42 (s), 3.50 (s), 7.60 (mw), 8.25 (m), 8.66 (m), 8.77 (ms), 8.84 (s), 9.85 (m), 10.09 (mw), 11.0 (mw), 12.91 (ms), 13.44 (ms), and 14.07 (s) μ.

Anal. Calcd for $C_8H_{11}HgCl$: C, 27.99; H, 3.23; Hg, 58.45; Cl, 10.33. Found: C, 27.86; H, 3.43; Hg, 58.14; Cl, 10.04.

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[12] T. G. Traylor and A. W. Baker, *J. Am. Chem. Soc.*, **85**, 2746 (1963); T. G. Traylor, *ibid.*, **86**, 244 (1964).

[13] D. S. Matteson, *ibid.*, **82**, 4228 (1960); *Organometal. Chem. Rev.*, **1**, 1 (1966).

[14] Galbraith Laboratories, Knoxville, Tenn.

[15] D. S. Matteson, *J. Org. Chem.*, **27**, 3712 (1962).

Reaction of *endo*-Bicyclooctenebnoronic Acid with Mercuric Chloride. The boronic acid from 4.5 g of 98.8% *endo*-dibutyl bicyclo[2.2.2]oct-2-ene-5-boronate was stirred with 4.6 g of mercuric chloride, 3.0 g of calcium carbonate, and 72 ml of acetone under reflux and nitrogen atmosphere for 7 days. Addition of 400 ml of water precipitated 0.34 g (5.8%) of *exo*-bicyclo[2.2.2]oct-2-enyl-5-mercuric chloride. The unreacted boronic acid recovered from the solution weighed 1.90 g (73%), identity checked by infrared.

Bromo-Demercurations.[10] A solution of 3.90 g of *exo*-bicyclo-[2.2.2]oct-2-enyl-5-mercuric chloride (IV) in 35 ml of anhydrous pyridine (distilled from *p*-toluenesulfonyl chloride) was stirred at −40° under nitrogen during the dropwise addition of 1.8 g of bromine in 15 ml of pyridine over a period of 15 min. The solution was stirred 1 hr at −40°, mixed with 40 ml of cold hexane, and treated with 100 ml of cold water. The pyridine–mercuric bromide complex was filtered; yield 4.5 g (100%). The hexane solution was purified by further washings with water, acid, and sodium bicarbonate, and the hexane was distilled through an efficient column. The oily residue of bicyclooctenyl bromide was refluxed 3 days with 1.0 g of lithium carbonate in 50 ml of water and 4 ml of dioxane. Ether extraction yielded tricyclo[2.2.2.$0^{2,6}$]octan-3-ol, sublimed twice at 55° (0.1 mm), 0.38 g (28%), mp 122–123° (lit.[11] mp 125–127.1°), correct carbon and hydrogen analyses. Similar attempts to obtain tricyclooctanol from tricyclooctylmercuric chloride led to a small amount of oil which showed infrared absorption characteristic of the tricyclic alcohol.

Demercurations with Lithium Aluminum Hydride. A solution of 5.0 g of bicyclo[2.2.2]oct-2-enyl-5-mercuric chloride in 75 ml of ether was stirred under nitrogen at 0° during the dropwise addition of 2.2 g of lithium aluminum hydride in 50 ml of ether, then stirred at room temperature overnight. The mixture was cooled with an ice bath, the excess hydride decomposed with water, and the solid removed by filtration and washed with ether. The combined ether phase was distilled, and the residue sublimed at 15 mm to yield 0.40 g (26%) of bicyclo[2.2.2]octene, mp 114–115° (lit. mp 113–114.5°,[11] 116.4–117.5°[16]). Similar treatment of 4.0 g of tricyclo-[2.2.2.$0^{2,6}$]octyl-3-mercuric chloride with 5 g of lithium aluminum hydride, improved in the work-up stages by the use of sodium hydroxide to dissolve the aluminum hydroxide and by careful fractionation of the ether, yielded 0.56 g (45%) of bicyclo[2.2.2]octene, mp 114–115.5°. The nmr spectrum showed a multiplet at τ 3.6–4.1 which integrated to 2.0/12 of the total proton signal.

***exo*-5-Chlorobicyclo[2.2.2]oct-2-ene (V).** Heating 5.7 g of bicyclo[2.2.2]oct-2-enyl-5-mercuric chloride to its melting point (150°) in air led to decomposition to metallic mercury and a yellow oil in a few minutes. The mixture was triturated with ether and filtered. Concentration of the filtrate and sublimation of the residue at 50° (14 mm) yielded 1.05 g (45%) of *exo*-5-chlorobicyclo[2.2.2]oct-2-ene, mp 39–40° with prior softening. Evidence for the unsaturated group appeared in the infrared at 3.27 and 6.20 μ (in CS_2) and in the nmr at τ 3.5–4.4, integral 2.0/11 of total. Infrared fingerprint bands appeared at 10.35, 10.93, 11.44, 12.20, 12.43, 13.93 (vs), and 14.81 μ.

Anal. Calcd for $C_8H_{11}Cl$: C, 67.36; H, 7.78; Cl, 24.86. Found: C, 67.13; H, 7.80; Cl, 24.88.

Heating tricyclooctylmercuric chloride on the steam bath led to rapid decomposition to *exo*-5-chlorobicyclo[2.2.2]oct-2-ene in similar yield, infrared spectrum identical, nmr integral at τ 3.5–4.4 was 1.8/11 of total. Storage of the mercury compound at room temperature under nitrogen for 5 days led to similar decomposition.

Solvolysis of *exo*-5-chlorobicyclo[2.2.2]oct-2-ene (V) was accomplished by refluxing 1.03 g of the compound in 60 ml of water and 4 ml of dioxane with 1.5 g of lithium carbonate under nitrogen for 3 days. Extraction with ether, concentration, and sublimation led to 0.76 g (85%) of tricyclo[2.2.2.$0^{2,6}$]octan-3-ol. Gas chromatography indicated this alcohol to be 95% pure with 1–2% each of compounds having identical retention times with *exo*- and *endo*-bicyclo[2.2.2]oct-2-en-5-ol plus a similar amount of an unidentified impurity, probably *exo*-bicyclo[3.2.1]oct-6-en-2-ol.[6]

Isomerization of Tricyclooctylmercuric Chloride (III). A solution of 1.0 g of tricyclo[2.2.2.0^{226}]octyl-3-mercuric chloride and 4.0 g of mercuric chloride in 80 ml of acetone was stirred with 1.5 g of calcium carbonate under nitrogen at room temperature for 26 hr. Filtration followed by addition of 300 ml of water precipitated 0.82 g of *exo*-bicyclo[2.2.2]oct-2-ene-5-mercuric chloride (IV), mp 148–149° dec, identity checked by infrared.

Isomerization of Tricyclooctanol (VI). A solution of 0.50 g of 95% tricyclo[2.2.2.$0^{2,6}$]octan-3-ol (VI) in 28 ml of water, 12 ml of acetone, and 0.023 ml of hydrochloric acid was refluxed 24 hr, then saturated with sodium chloride and extracted with ether. The ether extracts yielded 0.45 g (90%) of a sublimed mixture of alcohols, mainly *exo*-bicyclo[2.2.2]oct-2-en-5-ol according to the infrared and nmr spectra. Gas chromatography showed 76% *exo*-bicyclooctenol, 10.5% unchanged tricyclooctanol, less than 1% *endo*-bicyclooctanol, and 13% of an unidentified component presumed to be *exo*-bicyclo[3.2.1]oct-6-en-2-ol.[6] Similar treatment of tricyclooctanol under reflux for 7 days yielded 75% of a mixture of alcohols containing 86% *exo*-bicyclooctenol, 2% *endo*-bicyclooctanol, 0.15% tricyclooctanol, and 12% of the unidentified compound.

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[16] H. L. Goering and M. F. Sloan, *J. Am. Chem. Soc.*, **83**, 1397 (1961).

The Photochemistry of (+)-2-Carene-4α-methanol

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Contribution from The Procter & Gamble Company, Miami Valley Laboratories, Cincinnati, Ohio 45239. *Received October 13, 1966*

Abstract: In order to gain additional insight into the photochemical behavior of conjugated cyclopropyl systems, the light-induced behavior of the vinylcyclopropane **2**, a 2-carene derivative, was investigated. On irradiation in the presence of photosensitizers having $E_T \geq 74$ kcal/mole, **2** underwent selective isomerization involving the internal 1,6-cyclopropyl bond, to afford, as the only detectable photoproducts, a mixture of two bicyclo[3.2.0]hept-2-enes, to which are given the *cis,endo* and *cis,exo* assignments **3** and **4**, respectively. The behavior of **2** on direct irradiation was found to be more complex; the principal photoproducts were **3** and **4** and the menthene **24**, a product resulting from fission of the external 1,7-cyclopropyl bond. Thermal treatment of the photoproduct **4** did not effect any detectable reversion to **2**, but gave instead the bicyclo[2.2.1]heptane **20** by way of the endocyclic olefin **19**. Mechanistic implications of these results are discussed.

The cyclopropane ring has played an enigmatic role throughout the history of organic chemistry. Being labile and exhibiting many of the reactions characteristic of double bonds, it has, nevertheless, often displayed an ostensibly capricious behavior which has fostered long-standing controversies concerning, among other properties, its ability to transmit or extend conjugation[1] and its geometrical requirements, if any,