Bridged Polycyclic Compounds. XLIV. Stereochemistry of Cyclopropane Ring Formation from Substituted Dibenzobicyclo[3.2.1]octadienes[1]

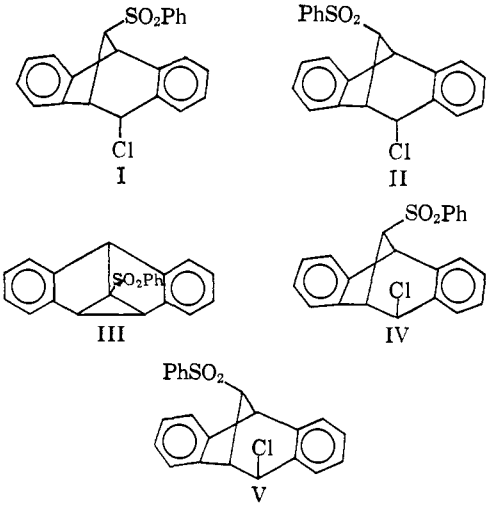
Stanley J. Cristol and Bruce B. Jarvis

Contribution from the Department of Chemistry, University of Colorado, Boulder, Colorado 80302. *Received June 20, 1966*

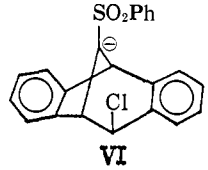
Abstract: 1,3 eliminations from the dibenzobicyclo[3.2.1]octadiene system to form derivatives of dibenzotricyclo-[3.3.0.0^{2,8}]-3,6-octadiene have been scrutinized with respect to the stereochemical requirements in the closure of the cyclopropane ring. Thus, when a carbanion is generated at the C-4 carbon, in order for ring closure to follow, the leaving group (chloride ion) on the C-8 bridge must be in the *anti* configuration. If the chlorine is in the *syn* configuration, the carbanionic carbon at C-4 is unable to displace the C-8 chlorine. Previously, it was shown that the *exo*-4-chloro-8-phenyl sulfones (IV and V) did not lose hydrogen chloride under moderately basic conditions (the *endo*-4-chloro-8-phenyl sulfones (I and II) readily lost hydrogen chloride under these conditions), but did lose hydrogen chloride with potassium *t*-butoxide in dimethyl sulfoxide (DMSO). Here, it is shown that with potassium *t*-butoxide in DMSO the C-4 benzylic proton is removed reversibly allowing epimerization of the C-4 chlorine to take place. Therefore, it seems likely that the chlorine must be *endo* at the C-4 position in order to be displaced by the C-8 carbanion. Stereochemical requirements appear to be identical for 1,3 eliminations of hydrogen chloride from chloro sulfones with base, from dichlorides with potassium *t*-butoxide, and from monochlorides with *n*-butyllithium and of chlorine from dichlorides with magnesium.

A study[2] of 1,3 eliminations in the dibenzobicyclo-[3.2.1]octadiene system has shown the strong preference for inversion in the formation of the cyclopropane ring. For example, whereas the *endo*-chloro sulfones I and II readily lost hydrogen chloride to give 1-phenylsulfonyldibenzotricyclo[3.3.0.0^{2,8}]-3,6-octadiene[3] (III) with sodium ethoxide in ethanol–dioxane, the *exo*-chloro sulfones IV and V would not undergo elimination under these conditions.

However, with potassium *t*-butoxide in dimethyl sulfoxide (DMSO) both IV and V gave the cyclopropyl sulfone III. Two plausible reaction pathways may be visualized to explain the elimination of hydrogen chloride from IV and V with potassium *t*-butoxide in DMSO. One may assume that with the strong base system[11] of potassium *t*-butoxide in DMSO the substrate (IV or V) does in fact undergo a frontside displacement of the C-4 chloride by the C-8 carbanion



(VI → III). That this process does not take place in the weaker base system, sodium ethoxide in ethanol–dioxane, may be rationalized as being due to the higher solvation of the C-8 carbanion VI by the protic solvent ethanol in comparison to solvation by the aprotic solvent DMSO.[12] This lack of solvation of VI in DMSO may have raised the ground-state energy sufficiently to allow elimination of the chlorine by way of a frontside displacement. A second possible mechanism would involve base-catalyzed epimerization of the C-4 chlorine in IV or V to give the *endo* epimer I or II followed by elimination of hydrogen chloride to give the cyclopropyl sulfone III.

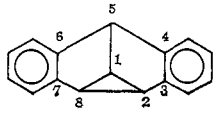


VI

(1) Previous paper in series: S. J. Cristol and R. Caple, *J. Org. Chem.*, 31, 2741 (1966).

(2) S. J. Cristol and B. Jarvis, *J. Am. Chem. Soc.*, **88**, 3091, 3095 (1966).

(3) Recently, Meinwald and Crandall[4] pointed out common errors in nomenclature found in the literature associated with bridged polycyclic compounds. We,[2] as well as other workers,[5–9] have incorrectly named this system.[10] Thus the numbering system for the tricyclo-[3.3.0.0^{2,8}]octane is shown below.



(4) J. Meinwald and J. K. Crandall, *ibid.*, **88**, 1292 (1966).

(5) O. L. Chapman, G. W. Borden, R. W. King, and B. Winkler, *ibid.*, **86**, 2660 (1964).

(6) J. Zirner and S. Winstein, *Proc. Chem. Soc.*, 235 (1964).

(7) W. R. Roth and B. Peltzer, *Angew. Chem. Intern. Ed. Engl.*, **3**, 440 (1964).

(8) M. Schwarz, A. Besold, and E. R. Nelson, *J. Org. Chem.*, **30**, 2425 (1965).

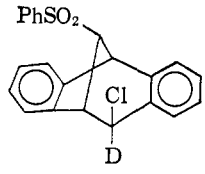
(9) H. E. Zimmerman and G. L. Grunwald, *J. Am. Chem. Soc.*, **88**, 183 (1966).

(10) A. M. Patterson, L. T. Capell, and D. F. Walker, "The Ring Index," 2nd ed, American Chemical Society, Washington, D. C., 1960.

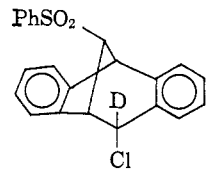
(11) D. J. Cram, B. Rickborn, C. A. Kingsbury, and P. Haberfield, *J. Am. Chem. Soc.*, **83**, 3678 (1961).

(12) A. J. Parker, *Quart. Rev. (Loudon)*, **16**, 163 (1962).

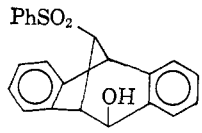
Consideration of the acidity of benzylic protons in this solvent–base system[13] made it seem reasonable that in fact the C-4 proton was being removed reversibly by potassium *t*-butoxide in DMSO, allowing epimerization of the C-4 chlorine to take place. To test this, the deuterated *exo*-chloro sulfone VII and the deuterated *endo*-chloro sulfone VIII were synthesized. Oxidation of the known[2] alcohol IX with Jones reagent gave the ketone X. Reduction of X with lithium aluminum deuteride gave the *endo* alcohol XI. Treatment of XI with thionyl chloride in dioxane gave a mixture of the chlorides VII and VIII with the *endo* chloride VIII predominanting slightly.



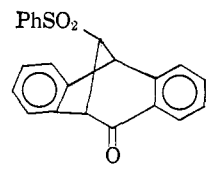
VII



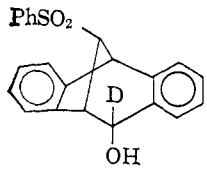
VIII



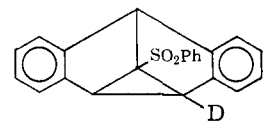
IX



X



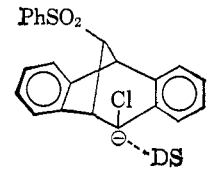
XI



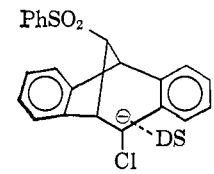
XII

As expected, the *endo*-chloro sulfone VIII readily lost hydrogen chloride to give the deuteriocyclopropyl sulfone XII with sodium ethoxide in ethanol–dioxane while the *exo* epimer VII was unreactive under these conditions. However, VII did lose hydrogen chloride with potassium *t*-butoxide in DMSO containing varying amounts of *t*-butyl alcohol. Thus in 75% *t*-butyl alcohol–25% DMSO with potassium *t*-butoxide, VII gave III with no observable (proton magnetic resonance (pmr) spectra) amount of deuterium left at C-2 (*i.e.*, no XII); in a 50:50 mixture of *t*-butyl alcohol and DMSO containing potassium *t*-butoxide, VII gave III with about 10% of the deuterium left at C-2; with potassium *t*-butoxide in 90% DMSO–10% *t*-butyl alcohol, VII gave III which retained 25–30% of the deuterium at C-2 (*i.e.*, about 25–30% XII). Furthermore, the deuterated cyclopropyl sulfone XII gave no exchange of the C-2 deuterium atom under any of the above reaction conditions. These data support the second proposed pathway involving base-catalyzed epimerization of the C-4 chlorine in IV and V prior to the loss of the chloride ion to give III.

The increasing amount of retention of the deuterium atom in the elimination of hydrogen chloride from VII with decreasing concentrations of *t*-butyl alcohol in DMSO is in accord with the idea that removal of the deuteron by S^- at C-4 results in a carbanion–SD pair XIII which does not become completely solvent separated[14] before carbanion inversion to give the *endo*-chloro carbanion XIV. Thus, increasing the concentration of *t*-butyl alcohol results in an increased probability that the carbanion–SD pair XIII will undergo exchange with the solvent, resulting in the observed loss of the deuterium atom in the product XII.



XIII



XIV

The question of whether a frontside displacement can or cannot take place directly in this system appeared to be confused by this possibility of base-catalyzed epimerization of the leaving group prior to the elimination process itself. Since benzylic protons are acidic enough under strongly basic conditions such as potassium *t*-butoxide in DMSO[13] to be removed reversibly, the leaving group should not have any benzylic protons α to it in order to avoid epimerization of the leaving group. A system such as this then would provide evidence for or against the possibility of direct displacement of a leaving group with retention to form a cyclopropane ring.

A system in which the carbanion is generated at the C-4 position and the leaving group is situated on the C-8 bridge might seem to fit into this scheme, for the C-8 bridge proton presumably would not be acidic enough to be readily removed by a strong base system.

The first of this type of system which we have studied was one in which the phenylsulfonyl group was on the C-4 carbon while the leaving group (chlorine) was located on the C-8 bridge (XV, XVI, and XVII). Treatment of the *anti-exo*-dichloride XVIII with potassium thiophenoxide in DMSO gave the *anti*-chloro-*endo* thioether XIX which upon oxidation gave the *endo* sulfone XV. Treatment of the *endo* sulfone XV with sodium ethoxide in ethanol–dioxane at room temperature readily gave the *exo* sulfone XVI with no observable (pmr analysis) amount of the *endo* epimer XV left.

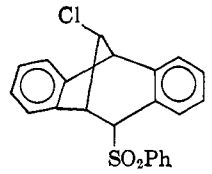
This result is rather surprising in view of previous results in this laboratory[15] which have shown that with no *syn*-8 substituent, an acetoxy group at C-4 gives an approximately 60:40 mixture of *exo* to *endo* acetates, respectively, under equilibrium conditions. This tremendous preference for the phenylsulfonyl group being *exo* in this system may be due at least in part to the greater steric requirement of the phenylsulfonyl group in comparison to the acetoxy group. As models show, the acetoxy group can easily avoid interference with the benzene rings, whereas the phenylsulfonyl group can not turn in any direction so as to avoid interaction between either the oxygens or the phenyl of the sulfone group and the benzene rings of the dibenzobicyclo[3.2.1]octadiene system.

The *anti*-8-chloro *endo*-4-sulfone XV, which is presumably first converted to its *exo* epimer XVI before elimination takes place and the *anti*-8-chloro *exo*-4-sulfone XVI both readily lose hydrogen chloride with

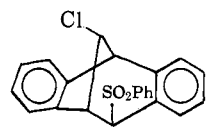
(13) J. E. Hofmann, R. J. Muller, and A. Schriesheim, *J. Am. Chem. Soc.*, **85**, 3000, 3002 (1963).

(14) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965, Chapter III.

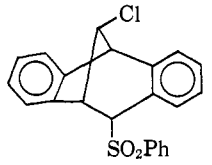
(15) S. J. Cristol and R. Kellman, unpublished results.



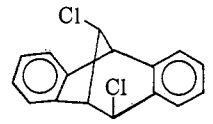
XV



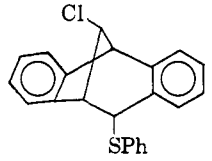
XVI



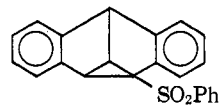
XVII



XVIII



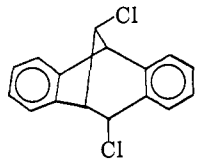
XIX



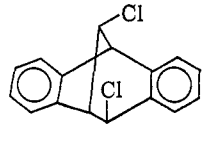
XX

sodium ethoxide in refluxing ethanol–dioxane to give the cyclopropyl sulfone XX.

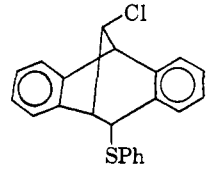
The *syn-endo*-dichloride XXI did not react with potassium thiophenoxide in DMSO, possibly because of the steric hindrance to attack from the *exo* side of C-4 provided by the *syn*-8-chloro substituent. The *syn-exo*-dichloride XXII did, however, react with potassium thiophenoxide in DMSO to give the *syn*-8-chloro *endo*-4-thioether XXIII though not as readily as the *anti-exo*-dichloride XVIII had reacted with potassium thiophenoxide in DMSO. When the reaction with XXII was run in absolute ethanol, the *syn*-chloro *endo*-thioether XXIII was obtained only in poor yields. Some *syn-endo*-dichloride XXI, presumably resulting from internal return of chloride ion was obtained, but the *exo*-ethyl ether XXIV was the major product. Oxidation of the thioether XXIII gave the corresponding *syn*-chloro *endo*-sulfone XVII. This was recovered unchanged from treatment with sodium ethoxide in refluxing ethanol–dioxane or with potassium *t*-butoxide in DMSO. Thus, no ring closure to the cyclopropyl sulfone XX or epimerization to the *syn*-chloro *exo*-sulfone XXV was observed, and it would appear that displacement with retention was proscribed in this system. Lack of epimerization of the *endo* sulfone XVII to the *exo* sulfone XXV is no doubt due to the steric effects of the *syn*-8-chlorine.



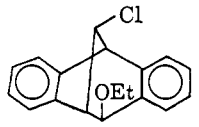
XXI



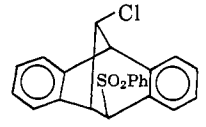
XXII



XXIII

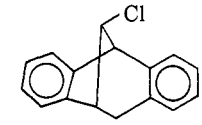


XXIV

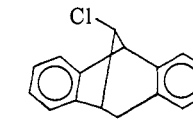


XXV

Attempted elimination of chlorine from the *anti-exo*- and *syn-endo*-dichlorides XVIII and XXI with zinc–copper couple in ethanol gave only the monochlorides XXVI and XXVII, respectively, which are the result of reduction of the benzylic chlorine. A similar reduction had been noted earlier[16] with XXI upon catalytic hydrogenation. Although the *syn-exo*-dichloride XXII was also catalytically hydrogenolyzed[16] to give XXVII, *syn-exo*-dichloride XXII was recovered unreacted when treated with the zinc–copper couple in ethanol. Again, this probably reflects the steric effect of the *syn*-8-chlorine on reactions at the C-4 *exo* position. All of the dichlorides XVIII, XXI, and XXII were recovered unreacted from treatment with zinc powder in benzene.

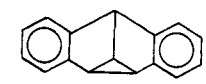


XXVII

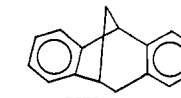


XXVI

When the *anti*-chloride XXVI was treated with excess *n*-butyllithium in tetrahydrofuran (THF) at room temperature, ring closure to the cyclopropane hydrocarbon XXVIII was observed. On the other hand, treatment of *syn*-chloride XXVII with excesss *n*-butyllithium in THF at room temperature gave no reaction, and, when this reaction was carried out in refluxing THF, only halogen–metal exchange occurred to give the hydrocarbon XXIX upon addition of water.



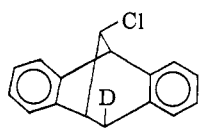
XXVIII



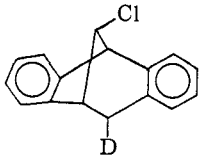
XXIX

Treatment of the *anti-exo*-dichloride XVIII with magnesium in refluxing THF gave the cyclopropane hydrocarbon XXVIII. However, treatment of the *syn-exo*- and *endo*-dichlorides XXI and XXII with magnesium in refluxing THF followed by addition of water gave only the *syn*-monochloride XXVII with no observable (by pmr analysis) amount of the cyclopropane hydrocarbon XXVIII. When deuterium oxide was used in place of water, approximately 67% of the product was XXX (*exo* deuteration) and approximately 33% of the product was XXXI (*endo* deuteration). Two interpretations of these data seem reasonable. First, since Grignard reagents are known to be destroyed with retention of configuration,[17] one may assume that the ratio of *exo* to *endo* carbon–magnesium bond is 2:1. Although C-4 substituents tend to be *endo* when a C-8 *syn*-chlorine is present,[15,18] in the above case the C-8 chlorine may in fact be complexed with the magnesium moiety and hold it in the *exo* position. A second explanation is that the carbanion at C-4 is rapidly inverting and, in fact, may spend most of the time in the *endo* position, but that protonation (deuteration) preferentially occurs at the *exo* bond. The fact that reactions in this system tend to occur *exo* has been substantiated in other types of reactions.[2,18–20]

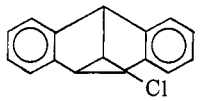
(16) S. J. Cristol, R. P. Arganbright, and D. D. Tanner, *J. Org. Chem.*, **28**, 1374 (1963).
(17) D. J. Cram, ref 14, pp 126–129.
(18) S. J. Cristol, F. P. Parungo, D. E. Plorde, and K. Schwarzenbach, *J. Am. Chem. Soc.*, **87**, 2879 (1965).
(19) S. J. Cristol, F. P. Parungo, and D. E. Plorde, *ibid.*, **87**, 2870 (1965).
(20) S. J. Cristol, R. Caple, R. M. Sequeira, and L. O. Smith, Jr., *ibid.*, **87**, 5679 (1965).



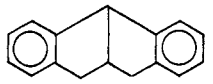
XXX



XXXI



XXXII



XXXIII

When the *syn-endo-* and *syn-exo*-dichlorides XXI and XXII were treated with potassium *t*-butoxide in DMSO, the only material isolated was the *syn-endo*-dichloride XXI. Again, it would appear that epimerization occurs readily at the C-4 benzylic position, that frontside displacement does not occur at C-8, and that the C-8 proton is not acidic enough to be removed by the base. Under the same conditions the *anti-exo*-dichloride XVIII gave the chlorocyclopropane XXXII. Treatment of the chlorocyclopropane XXXII with triphenyltin hydride gave the cyclopropane hydrocarbon XXVIII.

When treated with hydrogen in the presence of a palladium on charcoal catalyst, the cyclopropane XXVIII gave XXXIII, the result of hydrogenolysis of the 2,8 bond. The tricyclohydrocarbon itself, without the benzene rings, gives hydrogenation of the 1,2 bond[8] presumably because this results in a less strained system. However, with XXXIII, the 2,8 bond is now benzylic to two rings, thus making it more susceptible to hydrogenation.

Experimental Section

Spectra. The pmr spectra were determined as saturated solutions in either carbon tetrachloride or deuteriochloroform on a Varian A-60 instrument, and results are expressed in τ units, where τ is 10.00 for the internal standard tetramethylsilane. *J* values reported are "observed" ones.

Preparation of *anti*-8-Phenylsulfonyldibenzobicyclo[3.2.1]octadien-4-one (X). The *exo* alcohol IX (2 g, 5.6 mmoles) was dissolved in 70 ml of reagent grade acetone. This mixture was kept between 0 and 10° with stirring while 5 ml of Jones reagent (9 g of chromium trioxide dissolved in 27 ml of water and 8 ml of concentrated sulfuric acid) was added dropwise over a period of about 5 min. This solution then stood for 10 min at room temperature and was then poured into 100 ml of water. The water solution was extracted with 100 ml of ether. The ether layer was washed with water and with 10% sodium carbonate and dried with magnesium sulfate. The ether was removed by rotary evaporation, and the resulting solid was recrystallized from 95% ethanol–chloroform to give 1.5 g (74%) of the ketone X, mp 209–210°.

The pmr spectrum of X in deuteriochloroform showed two singlets at τ 5.15 (one proton) and at τ 5.51 (two protons). The aromatic protons were located between τ 2.0 and 3.1 (13 protons).

Anal. Calcd for $C_{22}H_{16}O_3S$: C, 73.31; H, 4.48. Found: C, 73.50; H, 4.60.

Reduction of the Ketone X with Lithium Aluminum Deuteride. To a solution containing 1.2 g (3.3 mmoles) of ketone X dissolved in 30 ml of tetrahydrofuran, which was freshly distilled from lithium aluminum hydride, was added 0.14 g (3.3 mmoles) of lithium aluminum deuteride (Metal Hydrides Inc., Beverly, Mass.). This mixture was stirred at room temperature for 45 min. The excess lithium aluminum deuteride was destroyed by the dropwise addition of first 10 ml of ethyl acetate and then 5 ml of water. This mixture was poured into 100 ml of water. The water solution was extracted with 100 ml of ether. The ether was washed with water and with saturated salt solution and dried with anhydrous magnesium sulfate. The ether was removed by rotary evaporation, and the resulting oil was crystallized from absolute methanol–petroleum ether to give 1.1 g (91%) of *exo*-4-deuterio-*anti*-8-phenylsulfonyldibenzobicyclo[3.2.1]octadien-*endo*-4-ol (XI), mp 162–163°, depressed with a sample of the *exo* alcohol IX.

The pmr spectrum of XI in deuteriochloroform showed three singlets (one proton each) at τ 5.59, 6.01, and 6.11 ($J_{18} \sim J_{38} \sim 0$ cps) and a series of complex overlapping multiplets for the aromatic protons (13 protons) between τ 2.1 and 3.0.

Anal. Calcd for $C_{22}H_{17}DO_3S$: C, 72.70; H, 5.27. Found: C, 72.79; H+D, 5.31.

Reaction of the Monodeuterated *endo* Alcohol XI with Thionyl Chloride in Dioxane. One gram (2.8 mmoles) of XI was dissolved in 15 ml of dry dioxane. To this solution was added 2 ml of thionyl chloride, and the mixture sat at room temperature for 8 hr. The excess thionyl chloride was destroyed by the dropwise addition of water, and the resulting solution was poured into 50 ml of water. The water solution was extracted with 75 ml of ether, but a precipitate appeared at the interphase and was removed by filtration. This precipitate amounted to 450 mg (42%) and was shown by melting point (244–245°), mixture melting point (undepressed with a sample of the nondeuterated *endo*-chloro sulfone II), and pmr and infrared spectra to be *exo*-4-deuterio-*endo*-4-chloro-*anti*-8-phenylsulfonyldibenzobicyclo[3.2.1]octadiene (VIII). The ether layer was washed with water and with 10% sodium carbonate and dried with anhydrous magnesium sulfate. The ether was removed by rotary evaporation, and the resulting solid was recrystallized from 95% ethanol to give 400 mg (37%) of *endo*-4-deuterio-*exo*-4-chloro-*anti*-8-phenylsulfonyldibenzobicyclo[3.2.1]octadiene (VII), mp 151–152°, undepressed with a sample of the nondeuterated *exo*-chloro sulfone V. A pmr spectrum of the resulting mother liquor showed a mixture of the *endo*- and *exo*-chlorides VIII and VII with the *endo*-chloride VIII slightly predominating.

A mass spectral analysis of these two deuterated chlorides VII and VIII gave identical patterns, and this same pattern was observed with the cyclopropyl sulfone XII. The compounds apparently decomposed in the instrument, for the highest peaks found were at *m/e* 203, 204, and 205. (A peak occurred at 218 but contained no deuterium. It seems likely that this peak was due to phenyl disulfide.) A sample of the nondeuterated chloro sulfones II and V gave the highest *m/e* peaks at 202, 203, and 204.

Preparation of 2-Deuterio-1-phenylsulfonyldibenzotricyclo[3.3.-0.0^{2,8}]-3,6-octadiene (XII). To a solution containing 195 mg (0.51 mmole) of the deuterated *endo* chloride VIII dissolved in 5 ml of dry dioxane was added 5 ml of absolute ethanol in which 100 mg (43 mg-atoms) of sodium metal had been dissolved. The mixture was held at reflux for 30 min and was worked up as usual. The resulting solid was recrystallized from 95% ethanol–chloroform to give 160 mg (90%) of XII, mp 179–180°, undepressed when admixed with a sample of III.

The mass spectral pattern of XII appeared to be identical with that of III except for the series of peaks which in III occurred at *m/e* 202, 203, and 204, whereas in XII these peaks appeared at *m/e* 203, 204, and 205.

The pmr spectrum of XII showed the same chemical shifts as III, but the integration for the two singlets was 1:1 rather than the 2:1 observed in III.

Elimination of Hydrogen Chloride from VIII with Various Concentrations of *t*-Butyl Alcohol in DMSO. In three separate experiments, 80 mg (0.21 mmole) of the *exo* chloride VII was treated with 114 mg (1.0 mmole) of potassium *t*-butoxide in (a) 4.5 ml of DMSO plus 0.5 ml of *t*-butyl alcohol for 10 min at room temperature, (b) 2.5 ml of DMSO plus 2.5 ml of *t*-butyl alcohol for 3 hr at 50°, and (c) 3 ml of *t*-butyi alcohol and 1 ml of DMSO at reflux for 8 hr. The pmr spectra showed no starting material left in any of the runs and the ratio of the benzhydryl to cyclopropyl proton in III to be (a) 1.0:1.7–1.75, (b) 1.0:1.9, (c) 1.0:2.0. The solids were isolated from each run, mp 179–180°, undepressed with a sample of III.

When the cyclopropyl sulfone containing a deuterium atom (XII) was treated under the above reaction conditions, no exchange of the deuterium was observed in the pmr spectrum.

Preparation of *anti*-8-*exo*-4-Dichlorodibenzobicyclo[3.2.1]octadiene (XVIII). To a solution of 5.0 g (19 mmoles) of *anti*-8-chlorodibenzobicyclo[3.2.1]octadien-*exo*-4-ol[19] in 50 ml of dry dioxane was added 5 ml of thionyl chloride. This mixture sat for 8 hr at room temperature and was then poured into 100 ml of water after the excess thionyl chloride had been carefully destroyed by the dropwise addition of water. The water solution was extracted with two 50-ml portions of ether. The ether extracts were combined, washed with water and with 10% sodium carbonate solution decolorized with activated charcoal, and dried with anhydrous magnesium sulfate. The ether was removed by rotary evaporation,

and the resulting solid was recrystallized from 95% ethanol to give 4.8 g (90%) of XVIII, mp 128–129°, undepressed with an authentic sample.[21]

Preparation of Potassium Thiophenoxide. A solution containing 25 g (0.45 mole) of potassium hydroxide, 50 ml (0.45 mole) of thiophenol, 75 ml of water, and 200 ml of benzene was held at reflux under a stream of nitrogen. The water (85 ml) was removed by azeotropic distillation with benzene. The resulting precipitate was filtered and washed several times with *n*-pentane. The potassium thiophenoxide, moist with pentane, was dried under aspirator pressure and then placed under vacuum (0.2 mm) for 12 hr. The dried potassium thiophenoxide was transferred to a tared, well-stopped bottle, 43 g (70%).

Preparation of *anti*-8-Chloro-*endo*-4-thiophenoxydibenzobicyclo-[3.2.1]octadiene (XIX). To 5.0 g (18.2 mmoles) of *anti*-8-*exo*-4-dichlorodibenzobicyclo[3.2.1]octadiene (XVIII) dissolved in 50 ml of dry DMSO was added 4.45 g of potassium thiophenoxide (30.0 mmoles). This mixture was stirred at room temperature under a nitrogen atmosphere for 6 hr and was then poured into 100 ml of water and extracted with 100 ml of ether. The ethereal solution was then washed with water and saturated salt solution and was then dried with anhydrous magnesium sulfate. After the solution had been decolorized with activated charcoal, the ether was removed by rotary evaporation, and the resulting solid was recrystallized from 95% ethanol to give 4.8 g (76%) of XIX, mp 143–144°.

The pmr spectrum of XIX in deuteriochloroform showed two doublets (J_{45} = 5.0 cps) at τ 5.05 and 6.22, two singlets ($J_{18} \sim J_{58} \sim$ 0 cps) at τ 5.42 and 5.97 (1 H each), and aromatic protons (13 H) from τ 2.3 to 3.0.

Anal. Calcd for $C_{22}H_{17}ClS$: C, 75.73; H, 4.91. Found: C, 75.76; H, 4.82.

Preparation of *anti*-8-Chloro-*endo*-4-phenylsulfonyldibenzobicyclo-[3.2.1]octadiene (XV). Two grams (5.73 mmoles) of XIX was dissolved in 50 ml of glacial acetic acid, and to this was added 3.45 g (20.0 mmoles) of *m*-chloroperbenzoic acid (85% min assay—FMC Corp., Carteret, N. J.). This solution sat for 10 min at 70° and was then poured into 200 ml of ice water. The water was extracted with two 100-ml portions of ether. The ether extracts were combined, washed with 10% sodium carbonate until basic, dried with anhydrous magnesium sulfate, and decolorized with activated charcoal. The ether was removed by rotary evaporation, and the resulting solid was recrystallized from 95% ethanol–chloroform mixture to give 2.0 g (92%) of XV, mp 212–212.5°.

The pmr spectrum of XV in deuteriochloroform showed two doublets (J_{45} = 5.0 cps) at τ 4.80 and 5.68 (1 H each), two singlets ($J_{18} \sim J_{58} \sim$ 0 cps) at τ 5.39 and 5.94 (1 H each), and two distinct sets of aromatic protons (2 H, 11 H) from τ 1.9 to 2.1 and 2.2 to 3.0.

Anal. Calcd for $C_{22}H_{17}ClO_2S$: C, 69.37; H, 4.50. Found: C, 69.32; H, 4.60.

Preparation of *anti*-8-Chloro-*exo*-4-phenylsulfonyldibenzobicyclo-[3.2.1]octadiene (XVI). The *endo* sulfone XV (500 mg, 1.31 mmoles) was dissolved in 15 ml of dry dioxane and 10 ml of absolute ethanol, and to this was added a solution prepared by dissolving 30 mg (1.31 mg-atoms) of sodium metal in 5 ml of absolute ethanol. This mixture stood at room temperature, and 5-ml aliquots were taken from 5 min to 2 weeks of reaction time. These aliquots were worked up by quenching in water and extracting with ether. The solution was then dried with anhydrous magnesium sulfate. The ether was removed by rotary evaporation, and a pmr spectrum of each aliquot showed only the *exo* sulfone XVI present. All of the material was combined and recrystallized from 95% ethanol to give 420 mg (84%) of XVI, mp 203–204°.

The pmr spectrum of XVI in deuteriochloroform showed two doublets (J_{45} = 1.0 cps) at τ 5.49 and 5.97 (1 H each) and two singlets ($J_{18} \sim J_{58} \sim$ 0 cps) at τ 5.01 and 5.88 (1 H each), and three distinct sets of aromatic protons ranging from τ 1.9 to 2.8 (13 H).

Anal. Calcd for $C_{22}H_{17}ClO_2S$: C, 69.37; H, 4.50. Found: C, 69.63; H, 4.52.

Preparation of 2-Phenylsulfonyldibenzotricyclo[3.3.0.0^{2,8}]-3,6-octadiene (XX). To a solution containing 800 mg (2.10 mmoles) of XV or XVI dissolved in 15 ml of dry dioxane and 10 ml of absolute ethanol was added a solution prepared by dissolution of 184 mg (8.00 mg-atoms) of sodium metal in 5 ml of absolute ethanol. This mixture was brought to reflux whereupon a precipitate began to form. The solution was held at reflux for 10 min and was then poured into 100 ml of water which was then extracted with 100 ml of ether. The ether was washed with water and dried over anhydrous magnesium sulfate. The ether was removed by rotary evaporation, and the resulting solid was recrystallized from 95% ethanol to give 550 mg (76%) of XX, mp 209–209.5° dec.

The pmr spectrum of XX in deuteriochloroform showed two doublets (1 H each) at τ 5.46 (J_{15} = 7.1 cps) and τ 5.51 (J_{18} = 5.2 cps), a doublet of doublets centered at τ 6.05 (1 H), and three distinct sets of aromatic protons ranging from τ 2.0 to 3.1 (13 H).

Anal. Calcd for $C_{22}H_{16}O_2S$: C, 76.71; H, 4.68. Found: C, 76.58; H, 4.72.

Preparation of *syn*-8-Chloro-*endo*-4-thiophenoxydibenzobicyclo-[3.2.1]octadiene (XXIII). A solution containing 2.00 g (7.27 mmoles) of *syn*-8-*exo*-4-dichlorodibenzobicyclo[3.2.1]octadiene (XXII)[16] and 2.0 g (13.5 mmoles) of potassium thiophenoxide dissolved in 30 ml of dry DMSO was held at 70–80° for 6 hr. This mixture was then poured into 100 ml of water which was then extracted with two 100-ml portions of ether. The ether was washed with water and dried over anhydrous magnesium sulfate. The ether was removed by rotary evaporation, and the yellow oil was chromatographed on 200 g of Merck 71707 neutral alumina. Starting material was washed off with petroleum ether, and 900 mg of the thioether XXIII came off with 5% benzene in petroleum ether. This was recrystallized from 95% ethanol to give 850 mg (34%) of XXIII, mp 144–145°.

The pmr spectrum of XXIII in carbon tetrachloride showed two doublets at τ 4.84 (J_{45} = 4.6 cps) and τ 6.12 (1 H each), two doublet of doublets (J_{18} = 4.4 cps) (having the appearance of triplets) at τ 5.28 and 6.44 (1 H each), and aromatic protons from τ 2.3 to 3.0 (13 H).

Anal. Calcd for $C_{22}H_{17}ClS$: C, 75.73; H, 4.91. Found: C, 75.97; H, 4.73.

Similar treatment of the *syn-endo*-dichloride XXI[16] with potassium thiophenoxide in DMSO gave only recovered starting material.

Treatment of 3.0 g (11 mmoles) of the *syn-exo*-dichloride XXII with potassium thiophenoxide in absolute ethanol (made by adding 2.0 g (18 mmoles) of thiophenol to 60 ml of absolute ethanol in which 800 mg (21 mg-atoms) of potassium metal had been dissolved) at reflux for 45 hr, followed by quenching in water, extracting with ether, and chromatographing on 250 g of Merck 71707 neutral alumina, gave 0.3 g (10%) of *syn-endo*-dichloride XXI (eluted with petroleum ether), 500 mg (13%) of the thioether XXIII (eluted with 5% benzene in petroleum ether), and 2.1 g (67%) of *syn*-8-chloro-*exo*-4-ethoxydibenzobicyclo[3.2.1]octadiene (XXIV) (eluted with 20% benzene in petroleum ether). The ethyl ether XXIV was recrystallized from 95% ethanol, mp 87–88°.

The pmr spectrum of XXIV in carbon tetrachloride showed a triplet at τ 8.73 (3 H), a doublet of doublets (appearing like a triplet) at τ 5.37, a singlet at τ 5.88 ($J_{45} \sim$ 0 cps) (1 H), a series of complex overlapping multiplets from τ 6.1 to 6.6 (4 H), and aromatic protons from τ 2.7 to 3.1 (8 H).

Anal. Calcd for $C_{18}H_{17}ClO$: C, 75.91; H, 6.02. Found: C, 75.86; H, 5.97.

Preparation of *syn*-8-Chloro-*endo*-4-phenylsulfonyldibenzobicyclo-[3.2.1]octadiene (XVII). To a solution containing 360 mg (1.03 mmoles) of the thioether XIII dissolved in 25 ml of glacial acetic acid was added 600 mg (3.48 mmoles) of *m*-chloroperbenzoic acid. This mixture stood at 70° for 15 min and was then poured into 100 ml of water. The water was extracted with 100 ml of ether. The ether was washed with 10% sodium carbonate and dried with anhydrous magnesium sulfate. The ether was removed by rotary evaporation and the resulting solid was recrystallized from 95% ethanol to give 320 mg (82%) of XVII, mp 199–200°.

The pmr spectrum of XVII in deuteriochloroform showed two doublets at τ 4.70 (J_{45} = 4.6 cps) and τ 5.97 (J_{18} = 4.0 cps) (1 H each), two doublet of doublets (appearing like triplets) at τ 5.10 and 5.73 (1 H each), and aromatic protons from τ 1.8 to 2.9 (13 H).

Anal. Calcd for $C_{22}H_{17}ClO_2S$: C, 69.37; H, 4.50. Found: C, 69.47; H, 4.67.

Reaction of Zinc–Copper Couple with the Dichlorides XVIII, XXI, and XXII in 95% Ethanol. A solution containing 1.0 g (3.6 mmoles) of *anti-exo*-dichloride XVIII, 1.5 g (23 mg-atoms) of zinc powder (which had been treated with a 2% copper sulfate solution), and 35 ml of 95% ethanol was stirred at reflux for 10 hr. This solution was treated with activated charcoal, filtered, and evaporated to about 5 ml. Upon cooling, crystals of *anti*-8-chlorodibenzobicyclo[3.2.1]octadiene (XXVI) precipitated, weighing 750 mg (86%), mp 122–123°, undepressed with an authentic sample.[19]

This same procedure with *syn*-8-*endo*-4-dichlorodibenzobicyclo-[3.2.1]octadiene (XXI) gave *syn*-8-chlorodibenzobicyclo[3.2.1]-

(21) D. E. Plorde, Ph.D. Thesis, University of Colorado, 1963.

octadiene (XXVII)[16] in 80% yield, mp 142–143°, undepressed with an authentic sample.

This same procedure with the *syn-exo*-dichloride XXII gave only recovered starting material. Longer reaction time, up to 2 weeks, still gave no reduction product.

When a mixture of XXI and XXII was treated in this manner, XXII was recovered while XXI was dechlorinated to XXVII.

None of these dichlorides gave any reaction with zinc powder in refluxing benzene for extended periods of time.

Dehydrochlorination of *anti*-Chloride XXVI with *n*-Butyllithium. To a solution containing 600 mg (2.49 mmoles) of *anti*-chloride XXVI in 15 ml of tetrahydrofuran (freshly distilled from lithium aluminum hydride) under a nitrogen atmosphere was added 5 ml of 1 *M* *n*-butyllithium[22] in ethyl ether. The solution turned purple quickly and warmed slightly. This mixture stood for 2 hr at room temperature, and was then poured into 50 ml of water, whereupon the purple color disappeared. The solution was extracted with two 50-ml portions of ether. The ether extracts were combined, washed with water and saturated salt solution, dried with anhydrous magnesium sulfate, and decolorized with activated charcoal. The ether was removed by rotary evaporation, and a pmr spectrum of the resulting oil showed the product to be dibenzotricyclo-[3.3.0.0^{2,8}]-3,6-octadiene (XXVIII) in higher than 90% yield. Crystallization of the oil from petroleum ether gave 435 mg (86%) of XXVIII,[23] mp 104–105°.

Under these same conditions, *syn*-8-chloride XXVII gave no reaction.

Dechlorination of *syn*-8-Chloride XXVII with *n*-Butyllithium in Refluxing THF. Under a nitrogen atmosphere to a solution containing 500 mg (2.08 mmoles) of *syn*-8-chloride XXVII in 15 ml of tetrahydrofuran (freshly distilled from lithium aluminum hydride) was added 10 ml of 1 *M* *n*-butyllithium in ethyl ether. The ethyl ether was distilled from the reaction flask, and the tetrahydrofuran solution was held at reflux for 30 hr. The reaction was worked up as usual (the purple color which had developed upon addition of the *n*-butyllithium disappeared when water was added), and a pmr spectrum of the crude reaction mixture showed a trace of *syn*-8-chloride XXVII left and the major product to be dibenzobicyclo-[3.2.1]octadiene (XXIX). Crystallization from 95% ethanol gave 300 mg (72%) of XXIX, mp 36–37°, undepressed with an authentic sample.[19]

Elimination of Chlorine from *anti*-8-*exo*-4-Dichloride VI Using Magnesium. A solution of 100 ml of dry THF containing 3.00 g (10.9 mmoles) of *anti*-8-*exo*-4-dichloride XVIII and 400 mg (16.5 mg-atoms) of magnesium turnings was held at reflux with stirring for 10 hr. (Reaction was initiated with a crystal of iodine.) The solution was filtered into a flask containing 100 ml of 5% hydrogen chloride solution. This solution was extracted with two 100-ml portions of ether. The ether portions were combined, washed with water and 10% sodium carbonate, dried with anhydrous magnesium sulfate, and decolorized with activated charcoal. The ether was removed by rotary evaporation, and a pmr spectrum of the resulting oil showed no starting material left and only the cyclopropane hydrocarbon XXVIII with some trace impurities. Crystallization from petroleum ether gave 2.1 g (94%) of XXVIII, mp 104–105°.

Hydrogenation of Dibenzotricyclo[3.3.0.0^{2,8}]-3,6-octadiene (XXVIII). The cyclopropane hydrocarbon XXVIII (100 mg, 4.9 mmoles) was dissolved in 10 ml of 95% ethanol, and to this was added 80 mg of 10% palladium on charcoal catalyst. The system was flushed with hydrogen, and the solution was stirred at room temperature for 30 hr (flushing with hydrogen about every 10 hr). The catalyst was filtered, and the ethanol was evaporated down to about 5 ml whereupon 95 mg (94%) of *cis*-dibenzobicyclo[3.3.0]-3,6-octadiene (XXXIII) precipitated, mp 95.0–95.5° (lit.[24] 95°).

Deuteration of *syn*-8-*endo*- (or *exo*-) 4-Dichloride XXI (or XXII). A solution containing 2.00 g (7.27 mmoles) of XXI (or XXII), 200 mg (8.23 mg-atoms) of magnesium, and 100 ml of tetrahydrofuran (freshly distilled from lithium aluminum hydride) under a nitrogen atmosphere was stirred at reflux for 18 hr during which time the reaction mixture got progressively darker until it was nearly black. The solution was allowed to cool and 5 ml of deuterium oxide (99.5% min, Matheson Coleman and Bell) was slowly added (vigorous reaction). After all the deuterium oxide had been added, the solution was stirred for an additional 10 min, poured into 100 ml of 5% hydrogen chloride solution, and worked up as usual. The resulting oil was chromatographed on 200 g of Merck 71707 alumina and the deuterated *syn*-8-chlorides XXX and XXXI were eluted with 5% carbon tetrachloride in petroleum ether, yielding 1.68 g (95%) of XXX and XXXI, mp 143–144°, undepressed with an authentic sample of nondeuterated XXVII.[16]

The pmr spectrum of the mixture of XXX and XXXI in carbon tetrachloride gave a ratio of *endo* proton to *exo* proton at C-4 of 2:1, and, therefore, the ratio of *exo* deuteration (XXX) to *endo* deuteration (XXXI) was 2:1.

Preparation of 2-Chlorodibenzotricyclo[3.3.0.0^{2,8}]-3,6-octadiene (XXXII). *anti*-8-*exo*-4-Dichloride XVIII (2 g, 7.3 mmoles) was dissolved in 20 ml of dry DMSO, and to this was added 1.5 g (13 mmoles) of potassium *t*-butoxide dissolved in 10 ml of DMSO. This mixture sat at room temperature for 5 min and was then poured into 50 ml of water. The water was then extracted with 100 ml of ether. The ethereal solution was washed with water and with saturated salt solution. The ether was dried over anhydrous magnesium sulfate and was removed by rotary evaporation. The resulting oil was passed over 100 g of Merck 71707 neutral alumina. The chlorocyclopropane XXXII was eluted with petroleum ether, 1.6 g (92%) of XXXII, mp 127–128° (recrystallized from 95% ethanol) (mol wt 238.7, mass spectroscopy.)

Anal. Calcd for $C_{16}H_{11}Cl$: C, 80.50; H, 4.65. Found: C, 80.67; H, 4.79.

A pmr spectrum of XXXII in carbon tetrachloride showed a doublet ($J_{1,8}$ = 5.4 cps) at τ 5.65 (1 H), a series of complex overlapping multiplets from τ 6.27 to 6.71 (2 H), and aromatic protons (8 H) from τ 2.6 to 3.2.

Dechlorination of the Chlorocyclopropane XXXII to the Cyclopropane XXVIII. A solution containing 150 mg (0.63 mmole) of XXXII and 350 mg (1.0 mmole) of triphenyltin hydride[25] dissolved in 25 ml of benzene was held at reflux for 4 days. The benzene was removed by rotary evaporation, and the resulting oil was chromatographed on 50 g of Merck 71707 neutral alumina. The cyclopropane XXVIII (100 mg, 78%) was eluted with petroleum ether. The compound was recrystallized from petroleum ether, mp 104–105°.

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