# Bridged Polycyclic Compounds. XXXVII. Addition of Benzenesulfenyl Chloride and Bromine to 7-Chlorodibenzobicyclo[2.2.2]octatriene[1]

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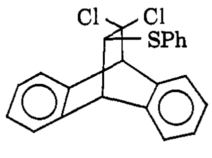
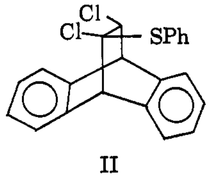
**Abstract:** Addition of benzenesulfenyl chloride to 7-chlorodibenzobicyclo[2.2.2]octatriene (III) proceeds with complete Wagner–Meerwein rearrangement to give *endo*-4,5-dichloro-*syn*-8-thiophenoxydibenzobicyclo[3.2.1]-octadiene (IX). This result may be contrasted with similar additions to dibenzobicyclo[2.2.2]octatriene (IV) itself, which under similar conditions gives simple 1,2-*trans* addition. Mechanisms for the addition reactions are discussed in terms of the geometry and the relative stability of each of the plausible intermediates. Addition of bromine to III, like that to IV, goes with complete Wagner–Meerwein rearrangement.

In connection with studies[2,3] on eliminations in dibenzobicyclo[2.2.2]octadiene compounds, we wished to synthesize 7,7-dichloro-8-thiophenoxydibenzobicyclo[2.2.2]octadiene (I) by addition of benzenesulfenyl chloride to 7-chlorodibenzobicyclo-[2.2.2]octatriene (III). We expected to obtain I, corresponding to Markovnikov addition, possibly mixed with a lesser amount of 7,8-dichloro-7-thiophenoxydibenzobicyclo[2.2.2]octadiene (II).[4] Previous work with arenesulfenyl chlorides indicated that these expectations were reasonable.[5] It has been demonstrated that sulfenyl halides add to olefins stereospecifically to give *trans*-addition products, presumably *via* cyclic sulfonium ion intermediates.[6–8] Furthermore, these intermediate sulfonium ions are not prone to rearrange, probably due to their greater stability in comparison with the carbonium ions resulting from rearrangement.[5]


I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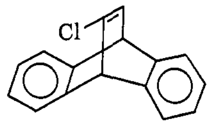
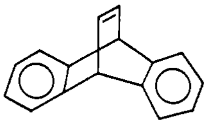
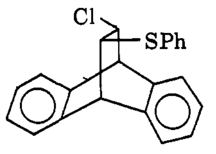
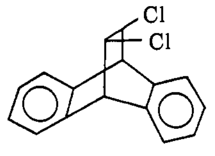
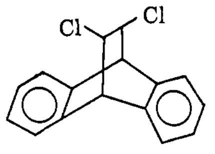

III

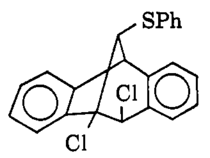

IV

Since the addition of benzenesulfenyl chloride in carbon tetrachloride to dibenzobicyclo[2.2.2]octatriene (IV) led to the chloro thioether V as the sole product, we anticipated similar results with the chloro olefin III. When we attempted the reaction, we observed that III reacted with benzenesulfenyl chloride in carbon tetrachloride only very slowly even at reflux, while the unchlorinated olefin IV reacted almost instantaneously at room temperature to give V. When ethyl acetate was used as solvent, the reaction with 0.02 mole of III was substantially complete in 8 hr at reflux. Only one compound, A, was found in the reaction mixture. The pattern of its pmr spectrum appeared to be almost consistent with either I or II, but there appeared to be no way to distinguish *a priori* between these structures.


V


VI


VII


VIII

Treatment of A with sodium methoxide in dimethyl sulfoxide at 100° did not result in elimination of hydrogen chloride, although it was known[9] that the corresponding dichlorides VI and VII are readily dehydrochlorinated under these conditions. Furthermore, the sulfone prepared by oxidation of A lost hydrogen chloride to a solution of sodium ethoxide in ethanol–dioxane at a measureable rate at 25°,[10] while those from the chloro thioether V and its *cis* isomer are known to eliminate under these conditions at 25° too rapidly to measure conveniently.[3] These observations seem to preclude both I and II as structures for A, and to focus attention on the rearranged structures, *exo*-4,5-dichloro-*syn*-8-thiophenoxydibenzobicyclo[3.2.1]octadiene (VIII) and its *endo*-4-chloro epimer IX.

We now believe A to be the rearranged dichloro thioether IX and its related sulfone to be X for the following reasons. The pmr spectrum of A shows a complex multiplet for the aromatic protons (integration for 13), a singlet (integration for 1 proton) at

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[1] Previous paper in series: S. J. Cristol, T. C. Morrill, and R. A. Sanchez, *J. Am. Chem. Soc.*, **88**, 3087 (1966).

[2] S. J. Cristol and N. L. Hause, *ibid.*, **74**, 2193 (1952).

[3] S. J. Cristol and R. P. Arganbright, *ibid.*, **79**, 3441 (1957).

[4] N. Kharasch and C. M. Buess, *ibid.*, **71**, 2724 (1949).

[5] S. J. Cristol, R. P. Arganbright, G. D. Brindell, and R. M. Heitz, *ibid.*, **79**, 6035 (1957).

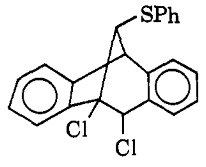
[6] N. Kharasch, H. L. Wehrmeister, and H. Tigerman, *ibid.*, **69**, 1612 (1947).

[7] D. J. Cram, *ibid.*, **71**, 3883 (1949).

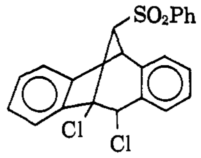
[8] N. Kharasch and A. J. Havlik, *ibid.*, **75**, 3734 (1953).

[9] D. C. Lewis, private communication.

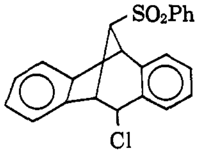
[10] S. J. Cristol and B. B. Jarvis, *J. Am. Chem. Soc.*, **88**, 3095 (1966) (paper XXXVIII).



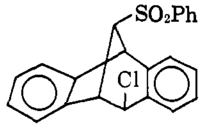
IX



X



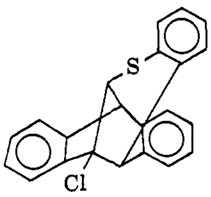
XI



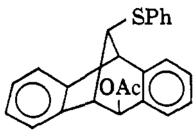
XII

$\tau$ 4.16, and two doublets (integration for one proton each) at 5.55 and 5.87. The coupling constant for the doublets is 4.6 cps which is typical for that between bridgehead and *anti*-8 protons in the dibenzobicyclo-[3.2.1]octadiene system.[11] The coupling constant is not consistent with that for *syn*-8 and bridgehead protons, which have coupling constants of less than 1 cps, and is rather high for that between bridgehead and bridge protons in the [2.2.2] system, which ordinarily have values of 3.0 cps or less.[12] Oxidation of A gave a sulfone with (considering aliphatic protons solely) a singlet (one proton) at $\tau$ 3.67 and two doublets ($J$ = 4.5 cps) (one proton each) at 5.42 and 5.67. As the singlet must be assigned to the proton at C-4 in the thioether and in the sulfone, the large change in chemical shift (0.5 ppm) downfield caused by change from thioether to sulfone is consistent only with assignment of the proton at C-4 as *exo*,[11] and thus the chlorine is *endo* (IX and X). Confidence in the assignment of the *endo* position of the chlorine in X is strengthened by a comparison of its reactivity with base with the *endo* and *exo* chlorides XI and XII.[10] Both X and XI react with sodium ethoxide in ethanol–dioxane to form a tricyclooctane, while XII, which has an *exo* chlorine, does not react under these conditions. This work is discussed in detail in the following paper.[10]

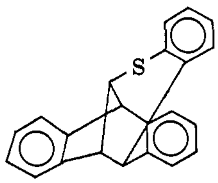
When the dichloro thioether IX was passed through Woelm grade I alumina, it suffered a self-alkylation giving XIII. Such an alkylation had been previously observed[13] when the acetate XIV was treated with acid, and XV was produced. The relationship of XIII and XV was demonstrated by conversion of XIII to XV by treatment with sodium in *t*-amyl alcohol.



XIII



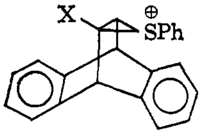
XIV



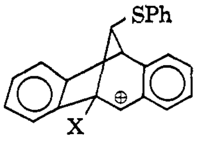
XV

We thought at first that the rearrangement accompanying the addition of benzenesulfenyl chloride to III was the result of the use of ethyl acetate rather than carbon tetrachloride, as one might anticipate that polar solvents could facilitate rearrangements.[14] This idea appeared consistent with the observation[13] that addition of benzenesulfenyl chloride to the olefin IV in carbon tetrachloride gives the unrearranged chloro thioether V, while addition in the polar (and protic) solvent acetic acid gave the rearranged acetate XIV. However, IV gave unrearranged V in ethyl acetate, and the chloro olefin III gave rearranged VIII in carbon tetrachloride, so one must conclude that the extra chlorine atom in III disposes the system toward rearrangement.

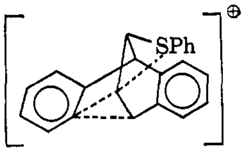
We have previously[13] discussed addition, displacements, and rearrangements in related systems as involving transformation *via* ions XVI and XVII. Thus, silver acetate assisted solvolysis of V, for example, has been considered to involve (in part) first the formation of the sulfonium ion XVIa which rearranges to the carbonium ion XVIIa before coordination with acetic acid or acetate to give XIV. In the addition of benzenesulfenyl chloride to the olefin IV, it is assumed that XVIa is also involved,[13] and that it reacts (in carbon tetrachloride) with the chloride gegenion of its ion pair before it has time to rearrange to XVIIa. If one considers a model of the sulfonium ion XVI, one notes that the groups present at C-7 and C-8 are on the gunwale positions of a boat-form cyclohexene ring, and that nucleophilic ring opening of the ring may occur only with difficulty, for, because of the rigidity of the system, C-8 cannot be truly inverted by the entering nucleophile.[15] Thus the nucleophilic displacement reaction must have a transition state with a 120° angle, or else must have a badly distorted ring system, either of which will, of course, raise the activation energy for the displacement process. On the other hand, migration of the C-3–C-4 bond has exactly the appropriate geometry for the direct formation of XVII from XVI (see *transition state* XVIII). This sulfonium ion system, then, is one in which the ordinary[6–8] ring opening leading to *trans* addition is more difficult than usual, and the ring opening Wagner–Meerwein rearrangement has (a) a relatively easy path and (b) proceeds to give a relatively stable benzylic cation. The combination *does not* result in rearrangement with XVIa with the chloride gegenion in carbon tetrachloride, but *does* result in rearrangement in this system when the nucleophilicity of chloride ion is reduced[19] by solvation with acetic acid.



XVIa, X = H
b, X = Cl



XVIIa, X = H
b, X = Cl



XVIII

The sulfonium ion XVIb may be anticipated to be substantially less stable than its chlorine-free analog

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(11) S. J. Cristol, J. R. Mohrig, and D. E. Plorde, *J. Org. Chem.*, **30**, 1956 (1965).

(12) S. J. Cristol, T. W. Russell, J. R. Mohrig, and D. E. Plorde, *ibid.*, **31**, 581 (1966).

(13) S. J. Cristol, R. Caple, R. M. Sequeira, and L. O. Smith, Jr., *J. Am. Chem. Soc.*, **87**, 5679 (1965).

(14) H. Kwart and R. K. Miller, *ibid.*, **78**, 5678 (1956).

(15) This lack of reactivity has been observed with bimolecular ring openings of similar epoxides,[16,17] as well as in ordinary bimolecular displacements at the gunwale positions of bicyclic compounds.[18]

(16) S. J. Cristol and R. K. Bly, *J. Am. Chem. Soc.*, **82**, 6155 (1960).

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

(18) S. J. Cristol and G. D. Brindell, *J. Am. Chem. Soc.*, **76**, 5699 (1954).

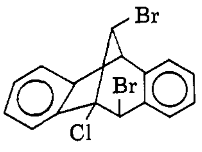
(19) A. J. Parker, *Quart. Rev.* (London), 16, 163 (1962).

XVIa, as the carbon–chlorine dipole will be a large destabilizing factor. This destabilization appears to be reflected in (a) the significant rate retardation in the addition to III compared with IV and (b) the much greater facility of XVIb to undergo rearrangement. Thus, no unrearranged addition product is observed from III, even in carbon tetrachloride solution.

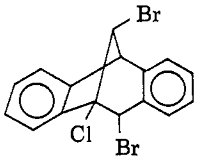
The last observation to account for in the addition of benzenesulfenyl chloride to the chloro olefin III is the *endo* configuration of the chlorine at C-4 in the product. Electrophilic additions to dibenzobicyclo[2.2.2]octatriene invariably have given largely *exo* substituents at C-4 as the kinetically controlled rearrangement products.[16,20–22] However, these compounds have been noted to epimerize in the presence of acids to the corresponding *endo* compounds.[21,23] For this reason and for the reason that the addition to III is so slow, it cannot be determined whether IX is in fact the kinetically determined product or whether it results from epimerization of the *exo* isomer VIII. It seemed possible that IX was the initial product, as evidence is strong that ions of type XVII are classical in nature, and the chlorine at C-5 may shield the *exo* side of C-4 more than the *endo* side, as its dihedral angle with the *exo* bond is substantially less than that with the *endo* bond.[11,24]

To test this, we decided to add bromine to III. In ethyl acetate, the addition proceeds rapidly to give a 50:50 mixture of the *syn–exo* dibromide XIX and the *syn–endo* product XX. XIX isomerizes very rapidly to XX in the presence of excess bromine, so that it is possible that little or no XX is formed directly.

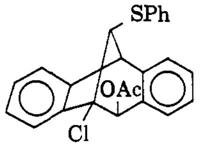
However, solvolysis of the *endo*-chloro thioether IX with silver acetate in acetic acid gave a 50:50 mixture of the *exo* and *endo* acetates XXI and XXII, while solvolysis of the chloro thioether XXIII under the same conditions has been reported to give exclusively the *exo* acetate XIV.[13] These results probably represent kinetic control and support the idea that the formation of IX in the benzenesulfenyl halide addition is not entirely the result of epimerization.



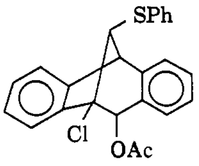
XIX



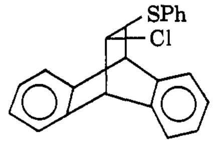
XX



XXI



XXII



XXIII

## Experimental Section

All pmr data were measured on a Varian A-60 spectrometer and are reported in τ units, where τ = 10.00 for the internal standard of tetramethylsilane. *J* values reported are "observed" ones.

**Preparation of *endo*-4,5-Dichloro-*syn*-8-thiophenoxydibenzobicyclo[3.2.1]octadiene (IX).** To a boiling solution of 3.84 g (16.1 mmoles) of 7-chlorodibenzobicyclo[2.2.2]octatriene (III)[13] dissolved in 100 ml of ethyl acetate was added dropwise 2.34 g (16.2 mmoles) of benzenesulfenyl chloride[25] dissolved in 25 ml of ethyl acetate. This mixture was heated at reflux in the dark. After 8 hr, the ethyl acetate was removed by rotary evaporation. The resulting yellow oil was dissolved in 100 ml of diethyl ether. The ether was washed with 10% sodium carbonate and then dried over anhydrous magnesium sulfate. The ether was removed by rotary evaporation, and the resulting yellow oil was chromatographed on Merck 71707 neutral alumina. After III and phenyl disulfide were eluted with petroleum ether (bp 60–70°), 4.70 g (76%) of IX was collected from the column with 20% benzene in petroleum ether as an uncrystallizable clear glass.

The pmr spectrum of a solution of IX in carbon tetrachloride showed two doublets (1 H each) at τ 5.55 and 5.87 (*J* = 4.6 cps), one singlet (1 H) at 4.16, and a complex multiplet (13 H) for the aromatic protons at 2.2–2.9.

*Anal.* Calcd for $C_{22}H_{16}Cl_2S$: C, 68.92; H, 4.20. Found: C, 69.13; H, 4.31.

**Oxidation of IX to *endo*-4,5-Dichloro-*syn*-8-phenylsulfonyldibenzobicyclo[3.2.1]octadiene (X).** Two grams (5.2 mmoles) of *endo*-4,5-dichloro-*syn*-8-thiophenoxydibenzobicyclo[3.2.1]octadiene (IX) was dissolved in 80 ml of glacial acetic acid on a steam bath. Twenty milliliters of 30% hydrogen peroxide was then added slowly, and the resulting solution was allowed to cool to room temperature and was then poured into 300 ml of water. The aqueous acetic acid was extracted twice with 300 ml of ether. The ether layers were combined, washed with 10% sodium carbonate, and dried over anhydrous magnesium sulfate. The ether was concentrated to 15 ml, and the resuting solid (the sulfone–ether complex, melting at 78° with evolution of the ether) was filtered. This solid was recrystallized from 95% ethanol yielding 1.8 g (83%) of X, mp 161–162°.

The pmr spectrum of X in deuteriochloroform showed two doublets (1 H each) at τ 5.42 and 5.67 (*J* = 4.5 cps), one singlet (1 H) at 3.67, and two distinct sets of aromatic protons (2 H and 11 H) at 2.1–2.3 and at 2.4–3.0.

*Anal.* Calcd for $C_{22}H_{16}Cl_2O_2S$: C, 63.62; H, 3.88. Found: C, 63.24; H, 4.06.

**Addition of Bromine to 7-Chlorodibenzobicyclo[2.2.2]octatriene (III).** 7-Chlorodibenzobicyclo[2.2.2]octatriene (III, 2.3 g, 9.6 mmoles) was dissolved in 30 ml of ethyl acetate and to this was added 2.1 g (13.1 mmoles) of bromine in 10 ml of ethyl acetate. When an aliquot was taken shortly after the addition of bromine, the pmr spectrum showed a 50:50 mixture of *exo*-4-*syn*-8-dibromo-5-chlorodibenzobicyclo[3.2.1]octadiene (XIX) and *endo*-4-*syn*-8-dibromo-5-chlorodibenzobicyclo[3.2.1]octadiene (XX). Fractional crystallization of the oil isolated from the aliquot gave colorless needles of the *exo*-bromide XIX, mp 116–117° from 95% ethanol.

The pmr spectrum of XIX in carbon tetrachloride showed two doublets (1 H each) at τ 5.16 and at 5.98 (*J* = 4.5 cps), one singlet (1 H) at 4.56, and aromatic protons (8 H) at 2.3–3.1.

*Anal.* Calcd for $C_{16}H_{11}Br_2Cl$: C, 48.22; H, 2.78. Found: C, 48.34; H, 2.92.

The remainder of the reaction mixture was left standing at room temperature for 4 hr. The excess bromine was destroyed with 10% sodium thiosulfate after the reaction mixture had been taken up in 100 ml of diethyl ether. The ether was then dried with anhydrous magnesium sulfate and concentrated to 5 ml, and 15 ml of 95% ethanol was added. Compound XX (3.4 g, 89%) crystallized from this solution, mp 139–140°.

The pmr spectrum of XX in carbon tetrachloride showed two doublets (1 H each) at τ 5.06 and 5.88 (*J* = 4.5 cps), singlet (1 H) at 4.12, and aromatic protons (8 H) at 2.3–3.1.

*Anal.* Calcd for $C_{16}H_{11}Br_2Cl$: C, 48.22; H, 2.78. Found: C, 48.06; H, 2.76.

**Preparation of 9-Chloro-4-thiatribenzotricyclo$[4.3.2.0^{5,9}]$undeca-2,7,10-triene (XIII).** Two grams (5.2 mmoles) of *endo*-4,5-dichloro-*syn*-8-thiophenoxydibenzobicyclo[3.2.1]octadiene (IX) was passed over 150 g of Woelm grade I alumina. XIII came off the

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(20) W. R. Vaughan and A. C. Schoenthaler, *J. Am. Chem. Soc.*, **80**, 1956 (1958).

(21) S. J. Cristol, R. P. Arganbright, and D. D. Tanner, *J. Org. Chem.*, **28**, 1374 (1963).

(22) S. J. Cristol, F. P. Parungo, and D. E. Plorde, *J. Am. Chem. Soc.*, **87**, 2870 (1965).

(23) S. J. Cristol, F. P. Parungo, D. E. Plorde, and K. Schwarzenbach, *ibid.*, **87**, 2879 (1965).

(24) A. R. Katritzky and B. Wallis, *Chem. Ind.* (London), 2025 (1964).

(25) H. Lecher, F. Holschneider, K. Köberle, W. Spear, and P. Stocklin, *Ber.*, **58**, 409 (1925).

column with 35% benzene in petroleum ether as a white solid and was recrystallized from acetone yielding 1.8 g (98%), mp 214–215°.

The pmr spectrum showed in deuteriochloroform two sharp singlets (2:1 H) outside the aromatic region at $\tau$ 5.70 and at 5.67, respectively. However, in benzene these peaks became two doublets (1 H each) at $\tau$ 5.95 and at 6.31 ($J$ = 5.0 cps) and a multiplet (1 H) at 5.73. The aromatic protons ($\tau$ 2.2–3.1) in deuteriochloroform gave the correct integration (12 H).

*Anal.* Calcd for $C_{22}H_{15}ClS$: C, 76.17; H, 4.36. Found: C, 76.05; H, 4.41.

**Reaction of 9-Chloro-4-thiatribenzotricyclo[4.3.2.0$^{5,9}$]undeca-2,7,-10-triene (XIII) with Sodium in *t*-Amyl Alcohol.** One gram (2.9 mmoles) of XIII was dissolved in 15 ml of *t*-amyl alcohol. To this was added 100 mg (4.3 mg-atoms) of sodium metal cut into small pieces. When the sodium metal had been completely destroyed, the alcohol was washed with water and was then removed by rotary evaporation. The resulting solid was recrystallized from 95% ethanol–acetone mixture to give 510 mg (56%) of 4-thiatribenzotricyclo[4.3.2.0$^{5,9}$]undeca-2,7,10-triene, mp 164–165°. The melting point of XV was not depressed when it was admixed with an authentic sample.[14]

**Addition of Benzenesulfenyl Chloride to Dibenzobicyclo[2.2.2]-octatriene (IV) in Ethyl Acetate.** Two grams (9.8 mmoles) of dibenzobicyclo[2.2.2]octatriene[2] (IV) was dissolved in 25 ml of ethyl acetate. This mixture was heated to reflux, and 1.5 g (10.4 mmoles of benzenesulfenyl chloride in 10 ml of ethyl acetate was slowly added until the red-orange color of benzenesulfenyl chloride persisted. The ethyl acetate was removed by rotary evaporation and a pmr spectrum was taken of the reaction mixture; the spectrum that was observed was that of *trans*-7-chloro-8-thiophenoxydibenzobicyclo[2.2.2]octadiene (V).[13]

**Addition of Benzenesulfenyl Chloride to III in Carbon Tetrachloride.** A solution of 50 ml of carbon tetrachloride containing 1.0 g (4.2 mmoles) of III and 1.0 g (6.9 mmoles) of benzenesulfenyl chloride was heated at reflux in the dark for 4 days. The carbon tetrachloride was removed on the rotary evaporator, and resulting orange oil was chromatographed on Merck 71707 alumina. The only addition product to come off the column was 610 mg (38%) of IX, and the remaining fractions were starting materials (benzenesulfenyl chloride isolated as phenyl disulfide).

**Silver Ion Assisted Acetolysis of the Dichloro Thioether IX.** One gram (2.6 mmoles) of IX was dissolved in 25 ml of glacial acetic acid, and 0.50 g (3.0 mmoles) of silver acetate was added. The solution was heated at reflux with stirring for 1 hr. After the silver chloride and unreacted silver acetate were removed by filtration, 100 ml of water was added. The aqueous mixture was extracted with two 100-ml portions of ether. The ether extracts were combined and washed successively with water and 10% aqueous sodium carbonate. The ether was dried over anhydrous magnesium sulfate, and the ether was removed under vacuum. A pmr spectrum of the residue indicated the presence of the two acetates, 5-chloro-*syn*-8-thiophenoxydibenzobicyclo[3.2.1]-octadien-*exo*-4-ol acetate (XXI) and 5-chloro-*syn*-8-thiophenoxydibenzobicyclo[3.2.1]octadien-*endo*-4-ol acetate (XXII), in a 1:1 ratio.

The resulting oil was passed over 80 g of Merck 71695 acid-washed alumina. The *exo* acetate XXI was eluted with 60% carbon tetrachloride in petroleum ether and recrystallized from petroleum ether to give 420 mg (40%) of XXI, mp 64–66°. The *endo* acetate XXII was eluted with 75% carbon tetrachloride in petroleum ether and recrystallized from petroleum ether to give 480 mg (46%) of XXII, mp 161–162°.

The pmr spectrum of a solution of the *exo* acetate XXI in carbon tetrachloride showed two singlets (one and three protons, respectively) at $\tau$ 3.99 and 7.82, two doublets ($J$ = 4.5 cps) at 5.73 and 6.05 (1 H each), and a complex multiplet (13 H) for the aromatic protons from 2.5 to 3.1.

*Anal.* Calcd for $C_{24}H_{19}ClO_2S$: C, 70.84; H, 4.71. Found, C, 70.70; H, 4.61.

The pmr spectrum of a solution of the *endo* acetate XXII in carbon tetrachloride showed two singlets (one and three protons, respectively) at $\tau$ 3.32 and 7.92, two doublets ($J$ = 4.5 cps) at 5.68 and 5.94 (1 H each), and a complex multiplet (13 H) for the aromatic protons from 2.4 to 3.0.

*Anal.* Calcd for $C_{24}H_{19}ClO_2S$: C, 70.84; H, 4.71. Found: C, 71.00; H, 4.56.

Oxidation of the thioether XXI was carried out in the same manner as IX was oxidized to X. The yield of 5-chloro-*syn*-8-phenylsulfonyldibenzobicyclo[3.2.1]octadien-*exo*-4-ol acetate was 75%. This was recrystallized from 95% ethanol–petroleum ether, mp 138–139°.

The pmr spectrum of the sulfone derived from XXI in a deuteriochloroform solution showed three singlets (1:2:3 H) at $\tau$ 3.77 5.62, and 7.68 ($H_1$ and $H_8$ having the same chemical shift) and a complex multiplet (13 H) for the aromatic protons from 2.0 to 3.0.

*Anal.* Calcd for $C_{24}H_{19}ClO_4S$: C, 65.67; H, 4.36. Found: C, 65.83; H, 4.62.

In the same manner, the thioether XXII gave 5-chloro-*syn*-8-phenylsulfonyldibenzobicyclo[3.2.1]octadien-*endo*-4-ol acetate in 85% yield. The sulfone was recrystallized from 95% ethanol, mp 229–230°.

The pmr spectrum of the sulfone derived from XXII in a deuteriochloroform solution showed a multiplet at $\tau$ 5.55 (2 H) and a singlet at 7.88 (3 H) and complex multiplet (14 H) for the aromatic protons (and the C-4 proton which is buried underneath them) from 2.0 to 3.0.

*Anal.* Calcd for $C_{24}H_{19}ClO_4S$: C, 65.67; H, 4.36. Found: C, 65.33; H, 4.66.

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