Bridged Polycyclic Compounds. XXXIV. Acetolysis of *cis*- and *trans*-β-Chlorodibenzobicyclo[2.2.2]octadienyl Thioethers[1]

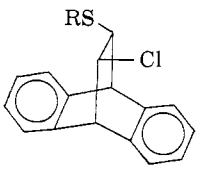
Stanley J. Cristol, Ronald Caple,[2] R. M. Sequeira, and L. Oliver Smith, Jr.[3]

Contribution from the Department of Chemistry, University of Colorado, Boulder, Colorado. *Received August 23, 1965*

Free-radical addition of methanethiol and benzenethiol to 7-chlorodibenzobicyclo[2.2.2]octatriene (III) gave mixtures of the trans- (I) and cis-β-chloro thioethers (II). Solvolysis of these substances in acetic acid led to exo-8-alkylthiodibenzobicyclo[3.2.1]octadien-4-ol acetates V and VII which could be isomerized to the corresponding endo acetates VI and VIII. While the acetolyses of the cis compounds II proceeded with the normal stereospecificity anticipated for Wagner–Meerwein rearrangements to yield syn-8 epimers V, the trans isomers did not react stereospecifically, but gave mixtures of the anticipated anti-8 compounds VII with the epimeric syn-8 acetates V. Attempts to study the reverse [3.2.1] to [2.2.2] isomerizations were unsuccessful due to side reactions. Comparative ratios of system interconversion for the two sets of thioethers suggest that the results for the trans isomers may be rationalized on the basis that two types of intermediates are formed competitively, one the [3.2.1] cation suggested by other work in similar systems, and the other a bridged sulfonium ion. This suggestion for these two competitive processes is supported by rate data for ethanolysis of the p-tolyl analogs of I and II as reported earlier; thus both isomers reacted slowly and with only slightly differing reactivities. Proton magnetic resonance data are reported for new compounds.

Solvolysis reactions on 7-substituted dibenzobicyclo[2.2.2]octadienes are known to proceed with a high degree of stereoselectivity to yield, by a Wagner–Meerwein rearrangement, an *exo*-4 derivative of dibenzobicyclo[3.2.1]octadiene.[4–8] From studies on 7,8-disubstituted dibenzobicyclo[2.2.2]octadienes, the carbon–carbon bond migration was shown to occur with inversion at the bond migration terminus in the normal Wagner–Meerwein fashion. It is the purpose of the present paper to report the results of an examination of the solvolysis of suitable 7,8-disubstituted dibenzobicyclo[2.2.2]octadienes where one of the groups could give rise to a bridged onium ion intermediate. This is of particular interest here as the geometry of the system (gunwale of a boat-form cyclohexene ring) is such that the preferred *trans–diaxial* relationship of the neighboring and leaving groups cannot be attained without serious strain. It already has been shown that there is very little anchimeric assistance to solvolysis in such systems.[9] It was thought that any neighboring-group interaction would either: (1) prevent rearrangement to the [3.2.1] system by stabilizing the [2.2.2] cation, or (2) cause the rearrangement to the [3.2.1] system to proceed with net retention. Since an adjacent thioether can form a sulfonium ion intermediate,[10–13] it was decided that an investigation of the *cis*- and *trans*-β-chloro thioethers I and II would be appropriate. Furthermore, a comparison of the thiophenoxy and thiomethoxy groups should give an indication of the relative importance of the sulfonium ion intermediate, the thiomethoxy group being more nucleophilic.[14]

The β-chloro thioethers I and II were synthesized by free-radical addition of the corresponding mercaptan to 7-chlorodibenzobicyclo[2.2.2]octatriene (III).[9] Methanethiol added to the chloroolefin III to give the *trans*-β-chloro thioether Ib and the *cis* isomer IIb in a ratio of 94:6. Thiophenol added to III to give the corresponding isomeric adducts Ia and IIa in a ratio of about 87:13. The *cis*- and *trans*-β-chloro thioethers were separated by column chromatography and/or a fractional recrystallization. The *trans* isomer Ia was also prepared stereospecifically by the polar addition of benzenesulfenyl chloride to dibenzobicyclo[2.2.2]octatriene (IV). Configurational assignments were confirmed by nuclear magnetic resonance spectroscopy.[15]



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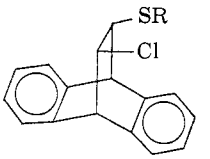
b, R = CH_3



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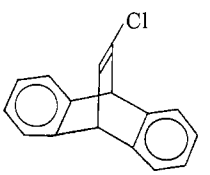
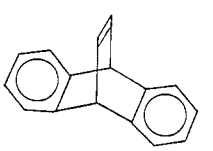


III



IV

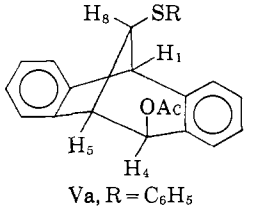
(1) Previous paper in series: S. J. Cristol and R. Caple, *J. Org. Chem.*, in press.
(2) National Science Foundation Postdoctoral Fellow, 1964–1965.
(3) National Science Foundation Summer Research Participation for College Teachers Program at the University of Colorado, 1962 and 1963.
(4) W. R. Vaughan and A. C. Schoenthaler, *J. Am. Chem. Soc.*, **80**, 1956 (1958).
(5) S. J. Cristol and R. K. Bly, *ibid.*, **82**, 6155 (1960).
(6) S. J. Cristol, R. P. Arganbright, and D. D. Tanner, *J. Org. Chem.*, **28**, 1374 (1963).
(7) S. J. Cristol and D. D. Tanner, *J. Am. Chem. Soc.*, **86**, 3122 (1964).
(8) S. J. Cristol, F. P. Parungo, and D. E. Plorde, *ibid.*, **87**, 2870 (1965).
(9) S. J. Cristol and R. P. Arganbright, *ibid.*, **79**, 3441 (1957).
(10) S. Winstein and E. Grunwald, *ibid.*, **70**, 828 (1948).
(11) P. D. Bartlett and C. G. Swain, *ibid.*, **71**, 1406 (1949).
(12) H. L. Goering and K. L. Howe, *ibid.*, **79**, 6542 (1957).
(13) K. D. Gundermann, *Angew. Chem. Intern. Ed. Engl.*, **2**, 599 (1963).
(14) H. Böhme and K. Sell, *Chem. Ber.*, **81**, 123 (1949).
(15) S. J. Cristol, T. W. Russell, J. R. Mohrig, and D. E. Plorde, *J. Org. Chem.*, in press.

Table I. Proton Assignments in the Dibenzobicyclo[3.2.1]octadiene System[a]

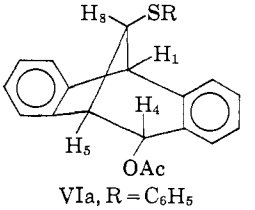
Compd.	Chemical shift, τ: *exo*-4-H	*endo*-4-H	*syn*-8-H	*anti*-8-H	5-H	1-H	Other	*J*, c.p.s.
Va		4.37		5.80	6.33	6.17	7.97 (acetate)	J_{45} = 1.5 J_{18} = J_{58} = 4.5
Vb		4.42		6.42	6.06	6.19	7.90 (acetate)[b] 7.98 (thioether)	J_{45} = 1.5 J_{58} = 3.8 J_{18} = 4.3
VIa[c]	3.60			*c*	*c*	*c*	8.02 (acetate)	J_{45} = 6.0
VIb	3.68			~6.1	~6.1	~6.1	7.80 (acetate)[b] 7.94 (thioether)	J_{45} = 4.5
VIIa		4.18	5.74		6.53	6.12	7.94 (acetate)	J_{45} = 2.1 J_{18} = J_{58} < 1
VIIb		4.17	6.52		6.28	6.07	7.93 (acetate) 7.93 (thioether)	J_{45} = 2.5 J_{18} = J_{58} < 1
VIIIa	3.80		6.12		6.16	5.95	7.97 (acetate)	J_{45} = 5.1 J_{18} < 0.5
VIIIb[d]	3.79		*d*		*d*	*d*	7.93 (acetate) 7.93 (thioether)	J_{45} = 5.3
X	*e*							
XI		5.86	7.69	7.75	6.68	6.12		J_{45} = 1 J_{18} = J_{58} = 4.0

[a] All spectra were obtained in CCl_4 except VIb and VIIIb where $CDCl_3$ was the solvent. [b] Assignment of methyl resonance signals equivocal. [c] Obtained as a mixture with Va, and the absorptions of the C-1, C-5, and C-8 protons overlapped with the corresponding absorptions of Va. [d] Obtained as a mixture with VIIb, and the absorptions of the C-1, C-5, and C-8 protons overlapped with the corresponding absorptions of VIIb. [e] See the Experimental Section.

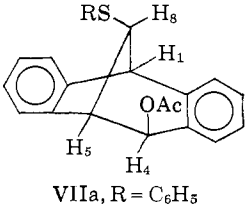
Acetolysis, assisted by silver acetate, of the *cis*-β-chloro thioethers IIa and IIb were stereospecific and produced, as expected, the *syn–exo* [3.2.1] acetates Va and Vb, respectively, along with small amounts (see the Experimental Section) of the corresponding *endo*-4 isomers VIa and VIb. The *exo*-4 acetates are the result of the normal inversion and rearrangement sequence.[4–8] The *endo*-4 acetates apparently arise from a subsequent epimerization of the *exo* isomer. All configurational assignments of the [3.2.1] acetates in this work were made by correlation of the n.m.r. spectra with the reported parameters for dibenzobicyclo[3.2.1]octadiene derivatives.[16] All n.m.r. data for compounds not reported in ref. 16 are given in Table I.



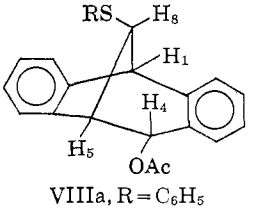
Va, R = C_6H_5
b, R = CH_3



VIa, R = C_6H_5
b, R = CH_3



VIIa, R = C_6H_5
b, R = CH_3



VIIIa, R = C_6H_5
b, R = CH_3

In contrast, however, acetolyses of the *trans*-β-chloro thioethers Ia and Ib were not stereospecific and produced mixtures of the *anti–exo* acetate, VIIa and VIIb, respectively, and the *syn–exo* acetate, Va and Vb, respectively. Again smaller amounts of the *anti–endo*, VIIIa and VIIIb, and *syn–endo*, VIa and VIb, acetates were formed, presumably by subsequent epimerization of the *exo* isomers. Although the *anti–exo* acetates arise from the normal Wagner–Meerwein inversion–rearrangement sequence,[4–8] the formation of the *syn–exo* acetates from the *trans*-β-chloro thioethers Ia and Ib is best rationalized as arising from the sulfonium ion intermediate IX yielding net retention of configuration in the migration (Figure 1).

Whereas the *exo*-4 acetates from the *trans*-phenyl thioether Ia were formed in *syn*/*anti* ratio of 1:1, the *syn*/*anti* ratio from the *trans*-methyl thioether IIb was greater than 2:1. This is clearly in line with the expected greater nucleophilicity of the methylthio over the phenylthio group,[14] and hence the greater importance of the intervention of the sulfonium ion IXb as opposed to IXa. Derivatives of dibenzobicyclo[2.2.2]octadiene were not observed upon acetolysis of either the *cis*- or *trans*-β-chloro thioethers in spite of the presumed intervention of the sulfonium ion intermediate IX.

The addition of benzenesulfenyl chloride to the olefin IV leading to the unrearranged *trans* adduct Ia has been rationalized previously in terms of the sulfonium ion intermediate IXa.[17] In the present acetolysis study, however, the sulfonium ion intermediate IXa is also postulated to account for the retention observed in the rearrangement to the *syn–exo* acetate Va from the *trans*-phenyl thioether Ia in contrast to the normal inversion–rearrangement pattern. Possibly the failure of the sulfonium ion intermediate to rearrange in the addition arises from the rapid collapse of a tight ion pair in the nonpolar carbon tetrachloride solvent. This is consistent with the observation that treatment of III with benzenesulfenyl chloride in acetic acid also leads to rearranged acetate.

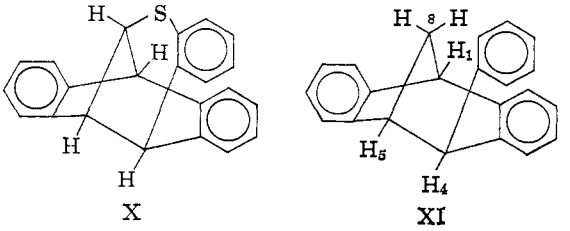
It has been previously observed that *exo*-4 isomers of various substituted dibenzobicyclo[3.2.1]octadiene de-

(16) S. J. Cristol, J. R. Mohrig, and D. E. Plorde, *J. Org. Chem.*, **30**, 1956 (1965). In this reference all of the [3.2.1] compounds are considered, numbered, and named as derivatives of the parent hydrocarbons. We have chosen to continue that numbering system to avoid confusion.

(17) S. J. Cristol, R. P. Arganbright, G. D. Brindell, and R. M. Heitz, *J. Am. Chem. Soc.*, **79**, 6035 (1957).

rivatives are readily epimerized by acid catalysis to the more stable *endo* epimers.[7,8,18] It has also been observed that more severe conditions often lead to rearrangements from dibenzobicyclo[3.2.1]octadienes to [2.2.2] isomers.[18] In view of these results, a similar study was made with the *syn–exo* acetates Va and Vb. Whereas the *exo*-4 acetate Vb epimerized readily at room temperature in dilute perchloric acid in acetic acid to the corresponding *endo* acetate VIb, under similar conditions the *exo*-2 acetate Va led to the very interesting alkylation product 4-thiatribenzotricyclo-[4.3.2.0^{5,9}]undeca-2,7,10-triene (X). The structure of the alkylation product X was readily determined by a Raney nickel desulfurization which gave *exo*-2-phenyldibenzobicyclo[3.2.1]octadiene (XI), which exhibited the expected n.m.r. spectrum.[16] However, treatment of Va with boiling acetic acid produced a mixture whose n.m.r. spectrum was consistent with that of a mixture of Va and VIa. Heating Va for longer periods of time gave X as the sole product. Attempts to convert the *syn–endo* acetate VIb to a dibenzobicyclo[2.2.2]-octadiene derivative led only to decomposition.

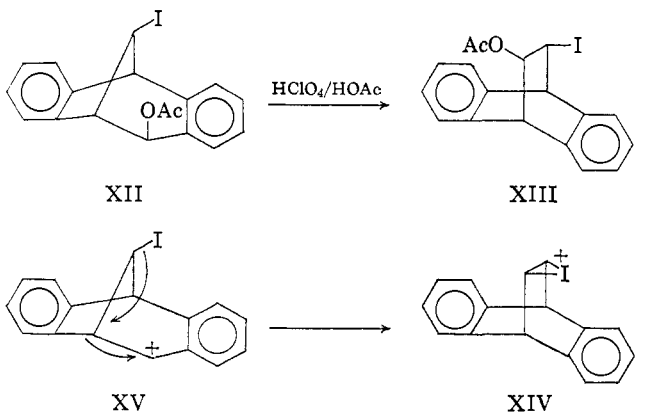
Although less extensively studied, the *anti–exo* acetate VIIb epimerized to a 60:40 *exo–endo* equilibrium mixture in dilute perchloric acid in acetic acid at room temperature. Prolonged treatment also led to decomposition, and no bicyclo[2.2.2] derivative was found. Similar results were observed with the *anti–exo* acetate VIIa.



X XI

Discussion of Results

Our interest in the intervention of sulfonium ion intermediates stems primarily from two previous observations in this laboratory. First, it was noticed that the *syn*-8-iodo[3.2.1]-4-acetate XII rearranged rapidly under equilibrating conditions to the *trans*-iodo[2.2.2] acetate XIII,[18] whereas the *cis* acetate would be anticipated by *anti*-migration rules.[19] To account



XII XIII XV XIV

(18) S. J. Cristol, F. P. Parungo, D. E. Plorde, and K. Schwarzenbach, *J. Am. Chem. Soc.*, 87, 2879 (1965).

(19) For a discussion of this, see D. J. Cram in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 5.

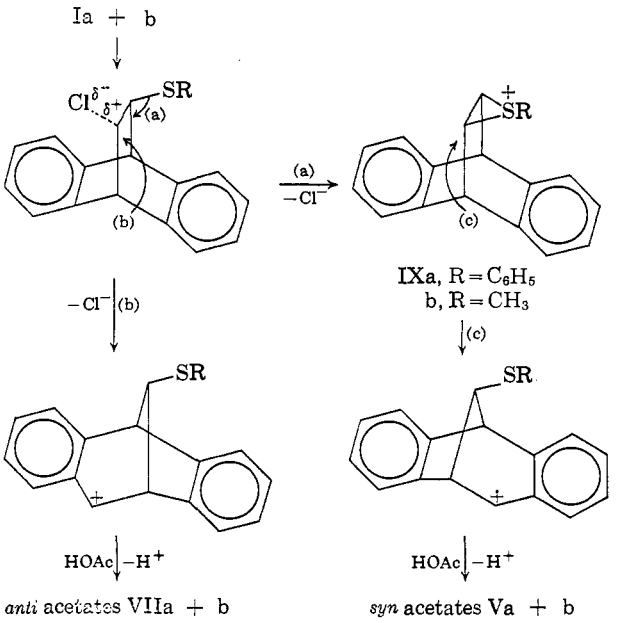
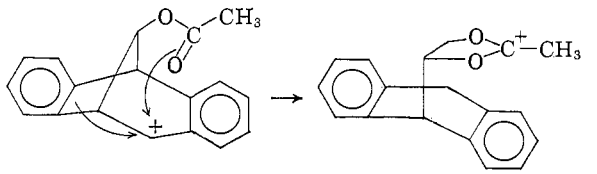


Figure 1.

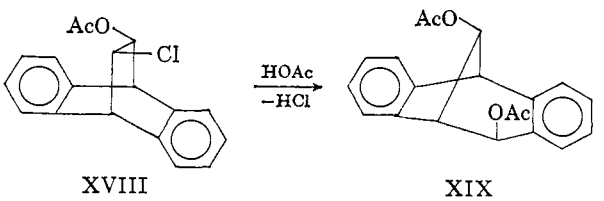
for this stereospecificity, the [2.2.2] iodonium ion XIV was postulated to intervene along the reaction path.[18] The ease of rearrangement was interpreted as evidence for neighboring-group participation by iodine in the *syn* [3.2.1] cation XV, which also explained the lack of any rearrangement with the corresponding chloro analog.[18]

Second, the greater ease of the rearrangement of the *syn*-8-[3.2.1]-4-diacetate compared with its *anti*-8 epimer was interpreted as acetoxy participation in the *syn* [3.2.1] cation XVI.[18] Again, the resulting acetoxonium ion intermediate XVII accounted for the observed products.[18]



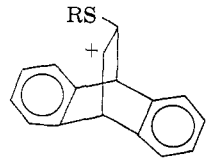
XVI XVII

These two cases of onium ion intermediates represent rearrangements from dibenzobicyclo[3.2.1]octadiene derivatives to the more stable [2.2.2] system.[18] In the other direction, however, the silver ion assisted acetolysis of the *trans*-acetoxy chloride XVIII gave the *anti–exo* diacetate XIX. This result is incompatible with an acetoxonium ion intermediate such as XVII and apparently the *trans*-chloro acetate XVIII underwent acetolysis according to the normal inversion scheme.[4–8] In fact, prior to the present study, no evidence existed for onium ion intervention in the kinetically controlled rearrangements of dibenzobicyclo-[2.2.2]octadiene derivatives to the [3.2.1] system.



XVIII XIX

The present acetolysis study with the *cis* IIa and IIb and *trans* Ia and Ib, chloro thioethers produced the first evidence for an onium ion intermediate in the [2.2.2] to [3.2.1] rearrangement. It is very unlikely that the free [2.2.2] cation XX is an intermediate in this solvolysis rearrangement since the *cis*- and *trans*-β-chloro thioethers give a different product distribution. Furthermore, the stereospecificity of the rearrangement from the *cis*-β-chloro thioethers precludes an open ion. A



XX

sulfonium ion intermediate clearly accounts for the retention (double inversion) accompanying rearrangement of the *trans*-β-chloro thioethers (Figure 1). The sulfonium ion intermediate, on the other hand, clearly does not account for the formation of the *anti* acetates from the *trans*-β-chloro thioethers and, hence, must only be competitive with the normal inversion sequence. This is in agreement with the prior observation that there is little anchimeric assistance in the solvolysis of the *trans* relative to the *cis* isomers.[9]

Experimental Section

Preparation of 7-Chlorodibenzobicyclo[2.2.2]octatriene (III). The following procedure is an improved modification of the previously reported one.[20] *trans*-7,8-Dichlorodibenzobicyclo[2.2.2]octadiene[20] (13 g., 47 mmoles) and 7.0 g. (62 mmoles) of potassium *t*-butoxide were dissolved in 100 ml. of dimethyl sulfoxide (dried by standing over molecular sieves). The solution was stirred at room temperature for 10 min. and poured into 300 ml. of water, and the resulting suspension was extracted with two portions of ether. The ethereal extracts were combined and washed well with water and dried over anhydrous magnesium sulfate. The ether was removed by rotary evaporation, and the residue was crystallized from ethanol to yield 9.1 g. (80%) of III, m.p. 129–131° (cor.) (lit.[20] m.p. 127.5–128°).

Addition of Thiophenol to III. A solution of 32.1 g. (0.134 mole) of III in 400 ml. of petroleum ether (b.p. 85–95°) was heated to 50° on the steam bath. The flask was purged with nitrogen, and benzoyl peroxide (*ca.* 10 mg.) was added. The solution was irradiated with a 100-w. tungsten lamp while a solution of 43 g. (0.390 mole) of thiophenol in 100 ml. of petroleum ether was added dropwise. After the addition, the solution was heated at reflux for 2 hr. and then allowed to cool to room temperature. The solution was concentrated and was chromatographed over Merck 71707 neutral alumina. Elution with petroleum ether provided 19.3 g. (41%) of 7-chloro-8-thiophenoxydibenzobicyclo[2.2.2]octadiene (Ia), m.p. 142.5–143.5° (cor.) after recrystallization from carbon tetrachloride. Further elution with carbon tetrachloride gave a mixture of the *cis* IIa and *trans* Ia isomers. The *cis* IIa isomer, 2.9 g. (10%), m.p. 130.5–132° (cor.), was obtained from this mixture by fractional crystallization from a 1:3 carbon tetrachloride–ethanol mixture. *Anal.* Calcd. for $C_{22}H_{17}ClS$: C, 75.73; H, 4.91; Cl, 10.16; S, 9.19. Found: (for Ia) C, 75.92; H, 5.19, Cl, 10.03; S, 8.95; (for IIa) C, 75.54; H, 4.84; Cl, 10.45; S, 9.20.

Addition of Methyl Mercaptan to III. 7-Chlorodibenzobicyclo[2.2.2]octatriene (III)[20] (10.9 g., 0.046 mole) was dissolved in 300 ml. of petroleum ether (b.p. 60–70°) and 75 g. (1.6 moles) of methyl mercaptan (Eastman Kodak), and a trace (*ca.* 20 mg.) of benzoyl peroxide was added. The flask containing the solution was fitted with a Dry Ice–acetone condenser and irradiated with a G.E. sunlamp and heated at reflux for 2 hr. Irradiation was continued for 3 hr. at room temperature. The solvent and excess methyl mercaptan were removed under vacuum leaving 13.1 g. of a yellow oil. Thin layer chromatography (t.l.c.) indicated no starting olefin and predominantly one isomer with only a small amount of a second. Within the limits of error of t.l.c. and n.m.r., this ratio was invariable with reaction time. The isomeric adducts were separated in a ratio of 94:6 by column chromatography using ethyl acetate washed Merck 71707 neutral alumina, eluting with 10% benzene in petroleum ether (b.p. 60–70°), the major isomer having the shorter retention time. Both isomers were recrystallized from ethanol and characterized by n.m.r. analysis.[15] *trans*-7-Chloro-8-thiomethoxydibenzobicyclo[2.2.2]octadiene (Ib), had m.p. 92–93°. *Anal.* Calcd. for $C_{17}H_{15}ClS$: C, 71.18; H, 5.28; S, 11.18; Cl, 12.36. Found: C, 71.30; H, 5.17; S, 11.27; Cl, 12.49. *cis*-7-Chloro-8-thiomethoxydibenzobicyclo[2.2.2]octadiene (IIb) had m.p. 107–108°. *Anal.* Calcd. for $C_{17}H_{15}ClS$: C, 71.18; H, 5.28; S, 11.18; Cl, 12.36. Found: C, 71.18; H, 5.28; S, 10.93; Cl, 12.21.

Addition of Benzenesulfenyl Chloride to Dibenzobicyclo[2.2.2]octatriene (IV). A. In Carbon Tetrachloride. Dibenzobicyclo[2.2.2]octatriene (IV)[20] (4.56 g., 22.3 mmoles), was dissolved in 100 ml. of carbon tetrachloride. A solution of 6.0 g. (42 mmoles) of benzenesulfenyl chloride[21] in 100 ml. of carbon tetrachloride then was added dropwise with stirring at room temperature. The yellow color of the benzenesulfenyl chloride solution was discharged immediately, and the addition was continued until the color persisted. The solution was decolorized with activated charcoal and was concentrated to a volume of 30 ml., whereupon crystallization of 5.8 g. (73%) of *trans*-7-chloro-8-thiophenoxydibenzobicyclo[2.2.2]octadiene (Ia) occurred.

B. In Acetic Acid. Dibenzobicyclo[2.2.2]octatriene (IV) (2.0 g., 9.8 mmoles) was dissolved in 35 ml. of dry acetic acid. A solution of 1.5 g. (10.3 mmoles) of benzenesulfenyl chloride in 20 ml. of dry acetic acid was then added dropwise and with stirring. The temperature of the reaction mixture was kept below 20° with an ice bath. After the addition was complete, the solution was stirred for 5 additional min. and then was poured into 150 ml. of water. The resulting suspension was extracted twice with ether. The combined ethereal extracts were washed well with water and sodium carbonate solution and dried over anhydrous magnesium sulfate. The ether was removed by rotary

(20) S. J. Cristol and N. L. Hause, *J. Am. Chem. Soc.*, 74, 2193 (1952).

(21) H. Lecher, F. Holschneider, K. Köberle, W. Speer, and P. Stocklin, *Chem. Ber.*, 58, 409 (1925).

evaporation leaving 3.2 g. of a clear oil. Analysis of the oil by n.m.r. indicated that it consisted mainly of *syn*-8-thiophenoxydibenzobicyclo[3.2.1]octadiene-*exo*-4-ol acetate (Va) along with other substances, possibly *syn*-8-thiophenoxydibenzobicyclo[3.2.1]octadiene-*endo*-4-chloride.[22] No absorptions in the n.m.r. spectrum which could be attributed to the [2.2.2] ring system were observed.

Silver Ion Assisted Acetolysis of trans-7-Chloro-8-thiomethoxydibenzobicyclo[2.2.2]octadiene (Ib). Six grams (0.021 mole) of *trans* isomer Ib was dissolved in 180 ml. of glacial acetic acid, and 3.5 g. (0.021 mole) of silver acetate was added. The solution was heated at reflux with stirring for 15 hr. After cooling the solution to room temperature, 200 ml. of water was added, and the aqueous mixture was extracted with diethyl ether. The ether extracts were washed succesively with water and 10% aqueous sodium carbonate. The ether extracts were dried over anhydrous magnesium sulfate and the ether was removed under vacuum. An n.m.r. analysis on the residue indicated the presence of four acetates but no starting chloroolefin III. The acetates, 62% *syn–exo* Vb, 26% *anti–exo* VIIb, and 13% of a mixture of the corresponding *endo* isomers VIb and VIIIb, were separated by a combination of column chromatography over ethyl acetate washed Merck 71707 neutral alumina eluting with 10% benzene in petroleum ether (b.p. 60–70°), to remove the *endo* isomers, and a fractional recrystallization from ethanol. *syn*-8-Thiomethoxydibenzobicyclo[3.2.1]octadiene-*exo*-4-ol acetate (Vb) had m.p. 138–139°. *Anal.* Calcd. for $C_{19}H_{18}O_2S$: C, 73.52; H, 5.84; S, 10.33. Found: C, 73.62; H, 5.75; S, 10.50. *anti*-8-Thiomethoxydibenzobicyclo[3.2.1]octadiene-*exo*-4-ol acetate (VIIb) had m.p. 151.5–152°. *Anal.* Calcd. for $C_{19}H_{18}O_2S$: C, 73.52; H, 5.84; S, 10.33. Found: C, 73.57; H, 5.80; S, 10.48.

Silver Ion Assisted Acetolysis of Ia. The *trans* isomer Ia (5.5 g., 14 mmoles) and 3.0 g. (18 mmoles) of silver acetate were heated at reflux with stirring in 50 ml. of glacial acetic acid for 2 hr. The solution was allowed to cool to room temperature, and the silver chloride was filtered and washed well with ether. Work-up as described above produced an oil which was shown to be a 1:1 mixture of *syn*-8-thiophenoxydibenzobicyclo[3.2.1]octadiene-*exo*-4-ol acetate (Va) and *anti*-8-thiophenoxydibenzobicyclo[3.2.1]octadiene-*exo*-4-ol acetate (VIIa) upon n.m.r. analysis. Fractional crystallization of the mixture from ethanol gave 1200 mg. (23%) of VIIa, m.p. 178–179° (cor.), and 900 mg. (17%) of Va, m.p. 133–134.5° (cor.). In another run, the solvolysis was allowed to continue for 3 days. Product analysis indicated the presence of *anti*-8-thiophenoxydibenzobicyclo[3.2.1]octadiene-*endo*-4-ol acetate (VIIIa), m.p. 158.5–160° (cor.), which was subsequently isolated by chromatography on Merck 71707 neutral alumina and which accounted for about 2% of the total product yield of this latter run. Separation of the two major *exo* isomers Va and VIIa by chromatography was not clean and resulted in considerable decomposition on the column. Elemental analyses for VIIa were unsatisfactory. The n.m.r. spectrum of this substance provided an unequivocal structural assignment, however. *Anal.* Calcd. for $C_{24}H_{20}O_2S$: C, 77.39; H, 5.41; S, 8.61. Found: (for Va) C, 77.22; H, 5.34; S, 8.73; (for VIIa) C, 75.77; H, 4.96; S, 7.69; (for VIIIa) C, 77.17; H, 5.27; S, 8.55.

Unassisted Acetolysis of Ia. The *trans* isomer Ia (3.5 g., 10 mmoles) and 30.9 g. (47 mmoles) of sodium acetate were heated at reflux in 250 ml. of glacial acetic acid for 298 hr. A gravimetric chloride determination indicated the reaction to be 97% complete at this time. The solution was allowed to cool overnight and then was poured into 200 ml. of water and was extracted twice with a total of 350 ml. of diisopropyl ether. The ether extracts were combined and worked up as usual, leaving an oil which was chromatographed on Merck 71707 neutral alumina. Elution with petroleum ether (b.p. 60–70°) provided 2.6 g. of an oil which appeared by n.m.r. analysis to be a mixture of 33% VIa, 22% VIIIa, 31% VIIa, and 14% Va.

Silver Ion Assisted Acetolysis of IIa. The *cis* isomer IIa (480 mg., 1.37 mmoles) and 253 mg. (1.51 mmoles) of silver acetate were heated at reflux with stirring in 20 ml. of glacial acetic acid for 1 hr. The solution was allowed to cool to room temperature, the solids filtered off and washed well with ether, and 100 ml. of water was added. Work-up gave an oil which was shown by n.m.r. analysis to consist of only Va. The oil was redissolved in 20 ml. of glacial acetic acid and silver acetate, 0.250 g. (1.50 mmoles), was added. The solution was allowed to react as before for 1 additional hr. Similar work-up and analysis indicated only Va as before. Further reaction for 3 days gave only the *syn–exo* isomer Va plus a few per cent of the *syn–endo* isomer VIa.

Silver Ion Assisted Acetolysis of cis-7-Chloro-8-thiomethoxydibenzobicyclo[2.2.2]octadiene (IIb). Acetolysis of the *cis* isomer IIb was carried out as in the case of the *trans* isomer Ib except refluxing was for 18 hr. An n.m.r. analysis indicated the major product, *ca.* 90%, to be the *syn–exo* acetate Vb, the remainder being largely the corresponding *endo* acetate VIb.

Epimerization of syn-8-Thiomethoxydibenzobicyclo-[3.2.1]octadiene-exo-4-ol acetate (Vb) to the endo Isomer VIb. The *syn–exo* acetate Vb (590 mg., 1.90 mmoles) was dissolved in 40 ml. of anhydrous 0.1 *M* perchloric acid in acetic acid and stirred at room temperature for 2 hr. The solution was then poured into water and worked up as in the acetolysis reactions. An n.m.r. analysis indicated predominantly the *syn–endo* acetate VIb, *ca.* 75%, a trace of the corresponding *exo* isomer Vb, and some unknown products. The *syn–endo* acetate VIb was purified by recrystallization from ethanol, m.p. 170.5–171.5°. A further attempt to rearrange the *syn–endo* acetate VIb to a bicyclo[2.2.2] derivative led to a variety of new products which were undecipherable by n.m.r., could not be recrystallized, and polymerized over alumina. *syn*-8-Thiomethoxydibenzobicyclo[3.2.1]octadiene-*endo*-4-ol acetate (VIb) had m.p. 170.5–171.5°. *Anal.* Calcd. for $C_{19}H_{18}O_2S$: C, 73.52; H, 5.84; S, 10.33. Found: C, 73.70; H, 5.87; S, 10.43.

Attempted Epimerization of syn-8-Thiophenoxydibenzobicyclo[3.2.1]octadiene-exo-4-ol Acetate (Va). Experi-

(22) The production of Va under these conditions must be a direct result of the reaction with benzenesulfenyl chloride and acetic acid and not a result of prior formation of either Ia or IIa with subsequent solvolysis. Unassisted solvolysis of either Ia or IIa, for example, proceeds quite slowly even in boiling acetic acid.

ment 1. Acetate Va (353 mg., 0.95 mmole), 720 mg. (10 mmoles) of sodium acetate, and 25 ml. of glacial acetic acid were heated at reflux for 1 month. Usual work-up provided 350 mg. of a clear, colorless oil. Analysis of the oil by n.m.r. indicated that it was a mixture of 73% VIa and 27% unchanged Va. This mixture was dissolved in 25 ml. of glacial acetic acid and allowed to react as before for 1 additional month. Work-up and n.m.r. analysis of the product showed a quantitative conversion to 4-thiatribenzotricyclo-[4.3.2.0^{5,9}]undeca-2,7,10-triene (X). Although VIa was produced in this and other experiments, it was not isolated.

Experiment 2. Acetate Va (460 mg., 1.2 mmoles) was warmed on the steam bath in 10 ml. of 0.01 *M* perchloric acid in glacial acetic acid for 20 min. Usual work-up and n.m.r. analysis showed X to be the only product.

Experiment 3. Acetate Va (894 mg., 2.4 mmoles) was dissolved in 35 ml. of 1 *M* perchloric acid in acetic acid. The solution was stirred at room temperature for 3 days and then poured into water. Usual work-up gave 1.2 g. of a clear oil. The oil was crystallized from ethanol yielding 547 mg. (73%) of pure X, m.p. 165–166.5° (cor.).[23] The n.m.r. spectrum of X had the usual complex aromatic absorptions at τ 2.9 (12 protons), an overlapping multiplet at 6.0 (three protons), and a multiplet at 6.9 (one proton). *Anal.* Calcd. for $C_{22}H_{16}S$: C, 84.57; H, 5.16; S, 10.26. Found: C, 84.43; H, 5.19; S, 10.16.

Desulfurization of 4-Thiatribenzotricyclo[4.3.2.0^{5,9}]-undeca-2,7,10-triene (X). The thioether X (0.400 g., 1.3 mmoles) was dissolved in 100 ml. of dioxane containing 20 ml. of water. Raney nickel W-2[25] (15 g.) was added, and the solution was heated at reflux for 23 hr. The nickel sludge was removed by filtration and the filtrate was evaporated with a stream of warm, dry air, leaving a clear oil. The oil was crystallized from ethanol to yield 0.280 g. (78%) of pure *exo*-4-phenyldibenzobicyclo[3.2.1]octadiene (XI), m.p. 112–114° (cor.). A mixture melting point of XI with 7-phenyldibenzobicyclo[2.2.2]octadiene[26] was depressed.

Epimerization of anti-8-Thiomethoxydibenzobicyclo-[3.2.1]octadiene exo-4-ol Acetate (VIIb) to the endo Isomer VIIIb. Treatment of the *anti–exo* acetate VIIb with 0.1 *M* anhydrous perchloric acid in acetic acid as in the case of the *syn–exo* acetate Va produced an *exo–endo* equilibrium ratio of 6:4. This mixture also did not rearrange back to a bicyclo[2.2.2] derivative on prolonged treatment with 0.1 *M* perchloric acid but decomposed instead. The *endo* isomer VIIIb was not isolated.

Analytical. Nuclear magnetic resonance spectra were obtained using a Varian Associates Model A-60 spectrometer. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Melting points are uncorrected, except where noted.

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(23) Although n.m.r. analysis clearly indicated the presence of X as a product in these reactions, an unequivocal proof of its structure was obtained only upon Raney nickel desulfurization (*vide infra*). Furthermore, the n.m.r. spectrum of X was different from that of another possible isomer, 3-thiatribenzotricyclo[5.2.2.0^{2,6}]undeca-4,8,10-triene,[24] which exhibited a complex multiplet at τ 5.8 and a doublet at 6.3 (J = 7 c.p.s.) which had additional fine splitting.

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Sulfenes in the Base-Induced Solvolysis of Alkanesulfonyl Chlorides[1,2]

J. F. King and T. Durst

Contribution from the Department of Chemistry, University of Western Ontario, London, Ontario, Canada. *Received July 22, 1965*

The solvolysis of alkanesulfonyl chlorides in various basic media is found to be accompanied by exchange of one and only one hydrogen atom α to the sulfonyl group. In nonbasic media the solvolysis proceeds without α-hydrogen exchange. From a detailed consideration of the possible mechanisms of reaction, it is inferred that the data show that the base-induced reaction takes place through the intermediacy of a sulfene.

In 1911 Wedekind and Schenk[3] suggested that the action of tertiary amines on an aliphatic sulfonyl halide may lead to a species $RR'C{=}SO_2$, which they named a "sulfene," by analogy with ketene which had been discovered only a short time before. Subsequent study has lent considerable support to the idea that sulfenes are intermediates in this and other transformations, though none of the work reported before the initiation of this study[4] could be said to have established the point rigorously. These earlier studies have, however, made it possible to describe in some detail the chemical properties which sulfenes must have if, in fact, they do play the role which has been ascribed to them. Of particular relevance to the present discussion is the

(1) Organic Sulfur Mechanisms. II. Reference 4a is to be considered as part 1 in the series.

(2) This work was supported *via* a grant-in-aid and a studentship by the National Research Council of Canada.

(3) E. Wedekind and D. Schenk, *Ber.*, **44**, 198 (1911).

(4) The earlier investigations are summarized elsewhere: (a) J. F. King, P. de Mayo, E. Morkved, A.B.M.A. Sattar, and A. Stoessl, *Can. J. Chem.*, **41**, 100 (1963); (b) W. E. Truce and J. R. Norell, *J. Am. Chem. Soc.*, 85, 3231 (1963).