[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO]

Bridged Polycyclic Compounds. III. Addition of *p*-Toluenesulfenyl Chloride to Norbornene, Norbornadiene, Aldrin and 9,10-Dihydro-9,10-ethenoanthracene[1,2]

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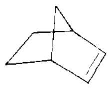
p-Toluenesulfenyl chloride has been allowed to react with four olefins, norbornene, norbornadiene, aldrin and 9,10-dihydro-9,10-ethenoanthracene. In each case the resulting β-chlorothioether was the *trans*-addition product; no evidence for either Wagner–Meerwein rearrangements or conjugate addition was observed. Proof of the structure of each of the products is given.

In the course of another study,[3,4] we undertook the preparation of various β-chlorosulfones and thus had opportunity to study the stereochemistry of the addition of *p*-toluenesulfenyl chloride to several bridged polycyclic olefins, including norbornene, norbornadiene, aldrin and 9,10-dihydro-9,10-ethenoanthracene. Although it has been demonstrated that sulfenyl halides add to olefins stereospecifically to give *trans*-addition products, presumably *via* cyclic sulfonium-ion intermediates[5–7] and although other mechanistic details have been thoroughly studied,[8,9] ionic electrophilic addition reactions to bridged bicyclic olefins such as those we have investigated are particularly prone to rearrangement[10–14] or to homoconjugate addition.[11,12,15,16]

Thus it seemed likely that the product of addition of *p*-toluenesulfenyl chloride to norbornene (I) might be *endo*-3-chloro-*exo*-2-norbornyl *p*-tolyl thioether (II) by *trans* addition (assuming the cyclic sulfonium-ion intermediate III) or the *cis*-*exo*-3-chloro-2-norbornyl *p*-tolyl thioether (IV) and/or Wagner–Meerwein rearrangement product *exo*-2-chloro-*syn*-7-norbornyl *p*-tolyl thioether (V) assuming the carbon-bridged intermediate VI.[10]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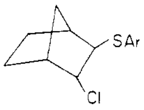
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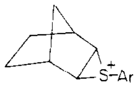
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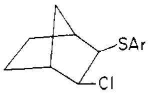
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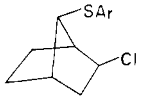
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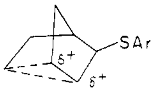
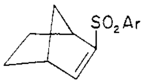

VI

Ar = *p*-tolyl.

When norbornene was treated with *p*-toluenesulfenyl chloride and pyridine in carbon tetrachloride, it was converted to a liquid chlorothioether in 85% yield. This material was relatively inert to silver nitrate and solvolyzed very slowly in 85% ethanol.[4] Oxidation with hydrogen peroxide led to a sulfone (99% yield) whose m.p. could not be increased markedly by recrystallization. Hence, it appeared to be a pure isomer. The chlorosulfone had a dipole moment $\mu = 4.32\ D.$[17] This value excludes structures IV and V for the parent thioether, as the related sulfones would be anticipated to have higher dipole moments and excludes as well the *cis-endo*-isomer of IV. It does not exclude the two anti-7-thioethers (with either *endo* or *exo*-2-chloro substituents) nor the *exo-endo* isomer of II. It was found, however, that the chlorosulfone was dehydrochlorinated with great ease with alkali[3] to give 2-norbornen-2-yl *p*-tolyl sulfone (VII) whose structure was demonstrated by catalytic hydrogenation to the known[1b] *endo*-2-norbornyl *p*-tolyl sulfone (VIII). When the dehydrochlorination was conducted in ethanol, a compound analyzing as an ether sulfone IX was obtained, presumably by base-catalyzed addition of ethanol to VII. The stereochemistry of IX is unknown. These facts are well accommodated by the structure X for the chlorosulfone and II for the chlorothioether, although the *endo-exo* isomer is not excluded. The ready ease of elimination seems to exclude structures such as XI which would have to eliminate *via* an unusual process, say, as shown in XII, to give the unsaturated sulfone VII, although a comparable process recently has been described in the reaction of certain 1,3-dihalides with iodide ion.[18] The structures II and X seem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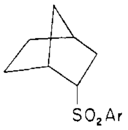
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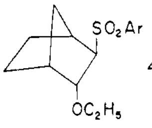
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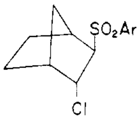
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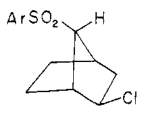
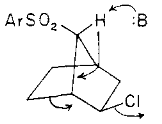

XI


XII

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(1) Previous papers in series: (a) S. J. Cristol and R. L. Snell, THIS JOURNAL, **76**, 5000 (1954); (b) S. J. Cristol and G. D. Brindell, *ibid.*, **76**, 5699 (1954).

(2) A portion of this work was reported at the 127th National Meeting of the American Chemical Society in Cincinnati, Ohio, April 1, 1955.

(3) S. J. Cristol and E. G. Hoegger, THIS JOURNAL, **79**, 3438 (1957).

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

(5) N. Kharasch and C. M. Buess, *ibid.*, **69**, 1612 (1947).

(6) D. J. Cram, *ibid.*, **71**, 3883 (1949).

(7) N. Kharasch and A. J. Havlik, *ibid.*, **75**, 3734 (1953).

(8) W. L. Orr and N. Kharasch, *ibid.*, **75**, 6030 (1953).

(9) N. Kharasch, C. M. Buess and W. King, *ibid.*, **75**, 6035 (1953).

(10) H. Kwart and L. Kaplan, *ibid.*, **76**, 4072 (1954).

(11) S. Winstein and M. Shatavsky, *Chem. and Ind.*, 56 (1956); THIS JOURNAL, **78**, 592 (1956).

(12) R. E. Lidov, S. B. Soloway, H. Bluestone and co-workers, private communication.

(13) R. P. Arganbright, Ph.D. thesis, University of Colorado, 1956.

(14) S. J. Cristol and R. K. Bly, unpublished work.

(15) G. D. Brindell, Ph.D. thesis, University of Colorado, 1954; S. J. Cristol and J. A. Reeder, unpublished work.

(16) L. Schmerling, J. P. Luvisi and R. W. Welch, THIS JOURNAL, **78**, 2819 (1956).

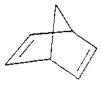
(17) M. T. Rogers, private communication.

(18) W. M. Schubert and S. M. Leahy, Jr., THIS JOURNAL, **79**, 381 (1957).

preferable to those in which the carbon–sulfur bonds are *endo*, as it may be assumed that the addition involves a sulfur-bridged (sulfonium-ion) intermediate,[5,9] such as III, and that addition of the arenesulfenium group to the olefinic bond occurs from the *exo* side, in analogy with other additions to norbornene and analogous compounds.[1b,10,11,19–24] Structure II is also consistent with the analogous structures reported by Kwart and Miller[24] for the addition products of 2,4-dinitrobenzenesulfenyl chloride to norbornene.

When the addition reaction was carried out in glacial acetic acid, a substantial amount of hydrogen chloride was evolved. Oxidation of this mixture gave a mixture of sulfones, from which 75% of chlorosulfone X and 18% of unsaturated sulfone VII were isolated. No other material was recovered from a chromatogram.

When *p*-toluenesulfenyl chloride was added to norbornadiene (XIII), a liquid chlorothioether was obtained which appeared to be *endo*-3-chloro-*exo*-5-norbornen-2-yl *p*-tolyl thioether (XIV). It absorbed one mole of hydrogen per mole of compound to give II which on oxidation gave X. Compound X also was obtained by oxidation of XIV with hydrogen peroxide in acetic acid to the corresponding sulfone XV, which gave X on catalytic hydrogenation. The oxidation of XIV also led to the formation of a compound analyzing for the epoxide XVI and with an infrared spectrum with peaks characteristic of epoxides. The *exo* structure for the epoxy group is based upon analogy to other addition reactions (see above). It is of interest to note that no nortricyclene products derived from homoconjugative addition, such as stereoisomers of XVII, nor from Wagner–Meerwein shifts, such as stereoisomers of XVIII, were observed, although trace amounts could have been present. The thioether XIV and sulfone XV were also characterized by their Diels–Alder addition products with 5,5-diethoxy-1,2,3,4-tetrachlorocyclopentadiene and with hexachlorocyclopentadiene.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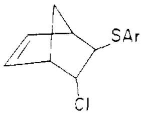

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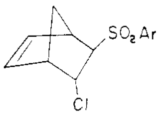

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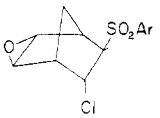

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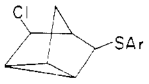

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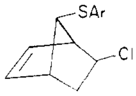
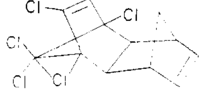


XVIII

Addition of *p*-toluenesulfenyl chloride to *endo-exo* - 1,2,3,4,10,10 - hexachloro - 1,4,4a,5,8,8a - hexahydro-1,4,5,8-dimethanonaphthalene (the insecticide "aldrin") (XIX) gave the chlorosulfide XX (*trans* addition). This compound and the corresponding sulfone were identical with the Diels–Alder addition products of XIV and XV with hexachlorocyclopentadiene. These identities also prove the non-rearrangements to compounds analogous to XI, as such rearrangements would lead to variations in the *exo-endo* stereochemistry at the fusion of the two norbornene rings.



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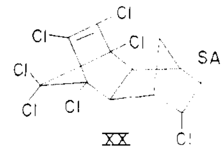

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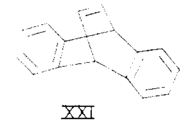
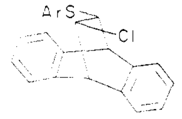
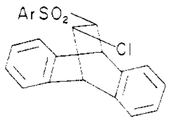

XXI

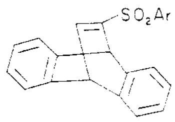


XXII

Reaction of the sulfenyl chloride with 9,10-dihydro-9,10-ethenoanthracene (XXI) led to only a single product which has been assigned the structure *trans*-12-chloro-11-thiocresoxy-9,10-dihydro-9,10-ethanoanthracene (XXII). This compound was oxidized to the chlorosulfone XXIII in good yield with peroxide and that sulfone reacted rapidly with alkali[25] at 0° to give unsaturated sulfone XXIV. The dipole moment $\mu = 4.30\ D$ reported[17] for XXIII is consistent with the *trans* structure and inconsistent with the *cis* structure, and the ready dehydrochlorination indicates an unrearranged β-chlorosulfone structure for XXIII.



XXIII



XXIV

Hence the bicycloöctene XXI, like the bicycloheptenes I, XIII and XIX, adds the *p*-thiocresoxy and chlorine fragments of *p*-toluenesulfenyl chloride in a *trans* fashion and without rearrangements. It is of interest to compare the lack of rearrangement in these additions with other ionic addition reactions reported with similar compounds. For example, Kwart and Kaplan[10] found that addition of bromine to norbornene (I) gives substantial amounts of 2,7-dibromonorbornane, and rearrangement occurs as well in the addition of strong acids to *endo*-dicyclopentadiene (cyclopentenonorbornene).[26] It has been reported[11,12,16] that addition of bromine to norbornadiene (XIII) gives largely 3,5-dibromonortricyclenes and *exo*-5-*anti*-7-dibromonorbornene and that other addition reactions also give substantial homoconjugative addition and/or Wagner–Meerwein rearrangements. Similarly additions to dihydroethenoanthracene XXI appear to lead from the bicyclo[2,2,2]octane system to a bicyclo[3,2,1]octane system.[13,14]

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(19) K. Alder and G. Stein, *Ann.*, **504**, 216 (1933); **515**, 185 (1935).

(20) R. B. Woodward and H. Baer, This Journal, **70**, 1161 (1948).

(21) G. Stork, E. E. van Tamelen, L. J. Friedman and A. W. Burgstahler, *ibid.*, **75**, 384 (1953).

(22) J. D. Roberts, F. O. Johnson and R. A. Carboni, *ibid.*, **76**, 5692 (1954).

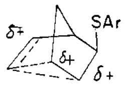
(23) (a) J. A. Berson and R. Swidler, *ibid.*, **76**, 4060 (1954); (b) J. A. Berson, *ibid.*, **76**, 5748 (1954).

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

(25) For rate data, see reference 4.

(26) H. A. Bruson and T. W. Riener, This Journal, **67**, 723, 1178 (1945); **68**, 8 (1946); P. D. Bartlett and A. Schneider, *ibid.*, **68**, 6 (1946); P. D. Bartlett and I. Goldstein, *ibid.*, **69**, 2553 (1947).

These observations appear to be consistent with considerations of the relative stabilities of the various possible mesomeric cations which might be intermediates in the reactions. Addition of the arenesulfenium cationic portion of the halide to norbornene (I) might lead either to the sulfur-bridged cation III or the carbon-bridged cation VI. The fact that the products obtained are derived from III implies that it is a lower energy intermediate than VI. This conclusion is consistent with solvolysis data where similar intermediates are postulated.[27-29] Solvolyses of β-chlorosulfides leading to a bridged sulfonium ion analogous to III (but *not* in this particular system, *cf.* reference 4) in the rate-determining step have been estimated to be 10^7 times more rapid than those of the corresponding simple alkyl halides due to neighboring-group participation of the β-sulfur atom.[27] On the other hand, solvolyses of *exo*-norbornyl derivatives leading to carbon-bridged mesomeric cations analogous to VI[28] or to homoallylic cations of type XXV[11,29] are less than 10^3 times as rapid as systems which do not lead to mesomeric intermediates in the rate-determining step. Thus the intermediate III must be substantially more stable than VI or XXV. The relative stabilities of cation III and VI should depend upon the electron-donating or electron-attracting properties of the aryl group attached to the sulfur atom. When the aryl group is *p*-tolyl, we have found and it has been reported elsewhere[24] as well that only the *trans*-chlorothioether is formed on addition of *p*-toluenesulfenyl chloride to norbornene. When 2,4-dinitrobenzenesulfenyl chloride is used, structure VI may be competitive in energy with III, because of the strong electron-attracting power of the nitro groups. Kwart and Miller[24] have indeed reported that this reagent gives about 10% of nortricyclyl 2,4-dinitrophenyl thioether (a product anticipated from an intermediate of type VI) along with 65% of the *trans* chloroethioether.



XXV

Acknowledgments.—The authors are grateful for the generous support of this research by grants from the Shell Development Company and the National Science Foundation and by a contract between the Office of Naval Research and the University of Colorado.

Experimental

endo-**3-Chloro-***exo***-2-norbornyl *p*-Tolyl Thioether (II).**—To a solution of 17.1 g. (0.182 mole) of norbornene,[30] m.p. 42–45°, in 15.3 ml. (0.19 mole) of dry pyridine was added 28.8 g. (0.182 mole) of *p*-toluenesulfenyl chloride[7,31] dissolved in 30 ml. of carbon tetrachloride. The solution was stirred during the addition, and the temperature was maintained at 20–25° by external cooling. The orange color of the sulfenyl chloride was discharged immediately upon addition. The small amount of deliquescent solid which was formed was removed by filtration and the filtrate was subjected to steam distillation until most of the solvent was removed. The residue was extracted with ether and the extract dried over calcium chloride. The ether and residual pyridine were removed, finally at reduced pressure. The chlorothioether II was distilled at 1.3 mm., b.p. 148–150° and weighed 38.8 g. (85% yield). It had n^{20}_D 1.5805, d^{20}_4 1.554. Calcd.[32] for $C_{14}H_{17}SCl$: M_D, 72.84. Found: M_D 72.87.

Anal. Calcd. for $C_{14}H_{17}SCl$: C, 66.51; H, 6.78. Found: C, 66.59; H, 6.68.

endo-**3-Chloro-***exo***-2-norbornyl *p*-Tolyl Sulfone (X).**—A solution of 1.610 g. (6.38 moles) of the thioether II (prepared in pyridine–carbon tetrachloride) in 6 ml. of glacial acetic acid was mixed with 2.4 ml. of 30% hydrogen peroxide until a homogeneous solution resulted. This solution was heated 0.5 hr. on a steam-bath and then allowed to stand at room temperature for one day. Addition of water and cooling in an ice-bath produced a mass of white crystals which were washed with ice-water and dried. The crystals weighed 1.783 g. (98.5%) and melted at 114–115°. A sample recrystallized twice from methanol melted at 115–117°.

Anal. Calcd. for $C_{14}H_{17}SO_2Cl$: C, 59.04; H, 6.02. Found: C, 58.96; H, 5.98.

Oxidation of the crude chlorothioether prepared in acetic acid (545 mg.) was carried out with chromium trioxide (1.3 g.) in 15 ml. of glacial acetic acid.[33] A gummy product was isolated which gave 180 mg. (*ca.* 30% yield) of crude chlorosulfone, m.p. 105–111°. Chromatographic separation on alumina gave 135 mg. of chlorosulfone X, m.p. 113–114°, upon elution with benzene, and 32 mg. of an unsaturated sulfone, m.p. 85–87°, which did not depress the m.p. of pure 2-norbornen-2-yl *p*-tolyl sulfone (VII, see below).

Treatment of 123 mg. of chlorosulfone X with 50 ml. of 0.1 *N* ethanolic alkali at reflux for 1.5 hr. (many times longer than required for dehydrochlorination[3]) gave a solid which, after recrystallization from aqueous ethanol, melted at 79.9–80.2° and weighed 55 mg. It contained no chlorine, did not react with aqueous potassium permanganate or bromine in carbon tetrachloride but contained sulfur. Its properties are consistent with a stereoisomer of 2-ethoxy-3-norbornyl *p*-tolyl sulfone (IX).

Anal. Calcd. for $C_{16}H_{22}O_3S$: C, 65.27; H, 7.53. Found: C, 65.39; H, 7.64.

When the chlorosulfone was treated with sodium hydroxide in aqueous dioxane, there was obtained a poor yield of solid, m.p. 90.5–91°, which decolorized potassium permanganate and which is formulated as 2-norbornen-2-yl *p*-tolyl sulfone (VII).

Anal. Calcd. for $C_{14}H_{16}SO_2$: C, 67.71; H, 6.50. Found: C, 67.98; H, 6.43.

The structure of sulfone VII was demonstrated by catalytic hydrogenation over palladium-on-charcoal catalyst to *endo*-2-norbornyl *p*-tolyl sulfone (VIII). The product crystallized from petroleum ether to give an allotrope, m.p. 64–65°, which upon mixture with known *endo*-sulfone VIII,[1b] m.p. 84–85°, melted at 83–84°. When a supersaturated solution of the 65° allotrope was seeded with the 84° material, it crystallized in the higher melting form, m.p. 83–84.5°. The mixed m.p. with known *exo*-sulfone[1b] was depressed to 58–60°.

endo-**3-Chloro-***exo***-5-norbornen-2-yl *p*-Tolyl Thioether (XIV).**—Fifty-two and eight-tenths grams (0.333 mole) of *p*-toluenesulfenyl chloride was added dropwise to 30.7 g. (0.334 mole) of freshly distilled (under nitrogen) norbornadiene (XIII).[34] The reaction mixture was stirred during the addition (which required 1 hr.) and maintained at 10–20° by external cooling. The reaction product was distilled and a colorless oil, b.p. 127–129° (0.3 mm.), was obtained. The yield was 64 g. (77%).

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[27] S. Winstein and E. Grunwald, THIS JOURNAL, **70**, 828 (1948).

[28] S. Winstein and D. Trifan, *ibid.*, **71**, 2953 (1949); **74**, 1154 (1952).

[29] S. Winstein, H. M. Walborsky and K. Schreiber, *ibid.*, **72**, 5795 (1950).

[30] L. M. Joshel and L. W. Butz, *ibid.*, **63**, 3350 (1941).

[31] H. Lecher, R. Holschneider, K. Koberle, W. Speer and P. Stocklin, *Ber.*, **58**, 423 (1925).

[32] A. I. Vogel, *J. Chem. Soc.*, 1820 (1948).

[33] Method of W. E. Truce, G. H. Birum and E. T. McBee, THIS JOURNAL, **74**, 3544 (1952).

[34] Obtained from Shell Development Company.

Anal. Calcd. for $C_{14}H_{15}SCl$: C, 67.05; H, 6.03. Found: C, 67.20; H, 6.02.

The compound XIV absorbed one mole of hydrogen per mole of compound over a palladium-on-charcoal catalyst to give II, which was not isolated but was oxidized directly (85% yield) to the chlorosulfone X, m.p. and mixed m.p. with an authentic sample 110–112°.

***endo*-3-Chloro-*exo*-5-norbornen-2-yl *p*-Tolyl Sulfone (XV) and *endo*-3-Chloro-*exo*-5,6-epoxy-2-norbornyl *p*-Tolyl Sulfone (XVI).**—One and eight-tenths milliliters (17.6 mmoles) of 30% hydrogen peroxide was added dropwise to a stirred solution of 1.79 g. (7.1 mmoles) of XIV in 20 ml. of glacial acetic acid at 15–20°. The solution was allowed to stand at room temperature for 2.5 hr. and then was heated on a steam-bath for 0.5 hr. Addition of 40 ml. of water gave a precipitate which could be fractionally recrystallized from ethanol, methanol, carbon tetrachloride and aqueous ethanol to give three compounds, XVI, m.p. 157–158° after recrystallization from ethanol, XV, m.p. 94° after recrystallization from ethanol, and an unknown compound, m.p. 219–220° after recrystallization from ethanol–acetone, in yields of about 30, 60 and 10%, respectively.

The unsaturated sulfone XV gave a positive Baeyer test for unsaturation and a positive Beilstein test for halogen.

Anal. Calcd. for $C_{14}H_{15}ClSO_2$: C, 59.45; H, 5.35. Found: C, 59.29; H, 5.41.

Upon hydrogenation over palladium-on-charcoal catalyst, it absorbed one mole of hydrogen per mole of compound to give X.

The compound, m.p. 157–158°, had a strong absorption peak in its infrared spectrum at 11.78 μ, which is characteristic of epoxides.[35,36] These facts, plus analytical data, indicate that this material is XVI.

Anal. Calcd. for $C_{14}H_{15}ClSO_3$: C, 56.33; H, 5.08; S, 10.74; Cl, 11.88. Found: C, 56.22; H, 5.27; S, 10.91; Cl, 11.61.

Compound XVI was obtained in excellent yield by oxidation of either XIV or XV with a large excess of hydrogen peroxide in glacial acetic acid.

***exo*-2-*p*-Thiocresoxy-*endo*-3,5,6,7,8-pentachloro-9,9-diethoxy-1,2,3,4,4a,5,8,8a-octahydro-1,4,5,8-dimethanonaphthalene (XXVI).**—A mixture of 10.0 g. (0.04 mole) of the chlorothioether XIV and 11.8 g. (0.04 mole) of 1,2,3,4-tetrachloro-5,5-diethoxycyclopentadiene was heated at 80° for 40 hr. After this time the unreacted acetal was removed by distillation at 1 mm. pressure. The residual oil was triturated with cold methanol and 7.2 g. (33%) of white solid, m.p. 102–105° after recrystallization from methanol, was obtained. This solid gave a positive Beilstein test for halogen and was the Diels–Alder addition product XXVI.

Anal. Calcd. for $C_{23}H_{25}Cl_5O_2S$: C, 50.88; H, 4.64. Found: C, 50.98; H, 4.87.

Chromatographic analysis of the mother liquors on activated alumina led to the recovery of about 45% of starting material XIV by elution with petroleum ether, b.p. 60–70°, and carbon tetrachloride mixtures and an additional 10% of XXVI by elution with benzene.

To improve the yield of XXVI, it would seem advisable to increase the proportion of 1,2,3,4-tetrachloro-5,5-diethoxycyclopentadiene in the starting mixture and raise the reaction temperature slightly.

***exo*-2-*p*-Toluenesulfonyl-*endo*-3,5,6,7,8-pentachloro-9,9-diethoxy-1,2,3,4,4a,5,8,8a-octahydro-1,4,5,8-dimethanonaphthalene (XXVII).**—One and seventy-five hundredths milliliters (17.1 mmoles) of 30% hydrogen peroxide was added dropwise with stirring to a solution of 4.0 g. (7.2 mmoles) of the thioether XXVI in 60 ml. of glacial acetic acid maintained at 15–20°. The mixture was allowed to stand at room temperature for 2.5 hr. and was then heated on a steam-bath for 25 minutes. White crystals were formed on cooling, and addition of 40 ml. of water led to the precipitation of 4.0 g. (95%) of the slightly crude sulfone XXVII, m.p. 177–180°. Several recrystallizations from methanol gave a m.p. of 183–184°.

Anal. Calcd. for $C_{23}H_{25}Cl_5O_4S$: C, 48.05; H, 4.38. Found: C, 47.75; H, 4.29.

***exo*-2-*p*-Thiocresoxy-*endo*-3,5,6,7,8,9,9-heptachloro-*endo*-*exo*-1-2,3,4,4a,5,8,8a-octahydro-1,4,5,8-dimethanonaphthalene (XX).**—Four and seven-tenths grams (0.03 mole) of *p*-toluenesulfenyl chloride was added dropwise to a solution of 10.95 g. (0.03 mole) of aldrin (XIX)[34] in 30 ml. of carbon tetrachloride. The red color of the *p*-toluenesulfenyl chloride disappeared immediately upon addition until the last drop was added. About half of the solvent was removed by evaporation on a steam plate, and the product was crystallized by addition of *n*-hexane. The crystals were filtered and allowed to dry. The crude yield was 13.89 g. (89%), m.p. 114–120°. After several recrystallizations from acetone, the m.p. of XX was 128.8–129.6°.

Anal. Calcd. for $C_{19}H_{15}Cl_7S$: C, 43.58; H, 2.89. Found: C, 43.37; H, 2.76.

This product XX also was prepared *via* a Diels–Alder reaction between hexachlorocyclopentadiene and *endo*-3-chloro-*exo*-5-norbornen-2-yl *p*-tolyl thioether (XIV). A solution of 100 mg. (0.4 mmole) of XIV in excess hexachlorocyclopentadiene was heated on a steam-bath for 3 days. The excess hexachlorocyclopentadiene was then removed by evaporation in a stream of air, and the remaining material was recrystallized from ethanol. The white crystals weighed 115 mg. (55% yield) and melted at 128–130°. This product when mixed with product XX obtained from aldrin and *p*-toluenesulfenyl chloride showed no depression in its melting point.

***exo*-2-*p*-Toluenesulfonyl-*endo*-3,5,6,7,8,9,9-heptachloro-*endo*-*exo*-1,2,3,4,4a,5,8,8a-octahydro-1,4,5,8-dimethanonaphthalene (XXVIII).**—Sixteen milliliters of 30% hydrogen peroxide was added dropwise at room temperature to a solution of 4.19 g. (8 mmoles) of XX in 75 ml. of glacial acetic acid. The solution was then heated on a steam-bath for 0.5 hr. and was allowed to stand overnight. Addition of water caused the precipitation of crystals which were filtered and dried. The crude yield was 4.5 g., m.p. 216–245°. The product was recrystallized from carbon tetrachloride to give 4.0 g. (90%) of white crystals melting at 265–270°. Recrystallization again from acetic acid gave the sulfone XXVIII melting at 267–268° dec.

Anal. Calcd. for $C_{19}H_{15}Cl_7O_2S$: C, 41.07; H, 2.73. Found: C, 41.15; H, 2.73.

The sulfone samples were identical (m.p. and mixed m.p.) when prepared from the thioethers derived from both procedures described above.

***trans*-12-Chloro-11-*p*-thiocresoxy-9,10-dihydro-9,10-ethanoanthracene (XXII).**—9,10-Dihydro-9,10-ethanoanthracene (XXI) was prepared by the dehalogenation of *trans*-11,12-dichloro-9,10-dihydro-9,10-ethanoanthracene[37] by treating a solution in *n*-amyl alcohol at the reflux temperature with sodium. The olefin product was somewhat easier to work up than that prepared with sodium in isopropyl alcohol.[37]

One-hundred sixty-seven milligrams (1.05 mmoles) of *p*-toluenesulfenyl chloride was added dropwise to 204 mg. (1.00 mmole) of XXI dissolved in 10 ml. of carbon tetrachloride. The solution was heated at reflux for 1 hr. and was allowed to stand overnight. About half the solvent was removed by evaporation, and the product was crystallized from the remaining solvent. The yield was 279 mg. (77%) of white crystals which melted at 180–185°. The thioether XXII was recrystallized from acetone to give a m.p. of 193–195°.

Anal. Calcd. for $C_{23}H_{19}SCl$: C, 76.12; H, 5.28. Found: C, 75.95; H, 5.40.

***trans*-12-Chloro-11-*p*-toluenesulfonyl-9,10-dihydro-9,10-ethanoanthracene (XXIII).**—Eight-tenths of a milliliter of 30% hydrogen peroxide was added to a solution of 97 mg. (0.267 mmole) of XXII in 5 ml. of glacial acetic acid. The solution was heated on a steam-bath for 0.5 hr. and was then allowed to stand overnight. Addition of water caused crystals, m.p. 158–159°, to form. The yield was 98 mg. (71%). After recrystallization from ethanol the melting point was 160.5–161°.

Anal. Calcd. for $C_{23}H_{19}ClO_2S$: C, 69.95; H, 4.85. Found: C, 69.77; H, 4.93.

11-*p*-Toluenesulfonyl-9,10-dihydro-9,10-ethenoanthracene (XXIV).—The reaction products from kinetic studies[4] on the rate of dehydrochlorination of XXIII with sodium

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[35] G. M. Barrow and S. Searles, This Journal, **75**, 1175 (1953).

[36] S. J. Cristol and S. B. Soloway, unpublished work.

[37] S. J. Cristol and N. L. Hause, This Journal, **74**, 2193 (1952).

hydroxide in ethanolic dioxane were isolated by removal of solvent and recrystallization from ethanol, m.p. 176.5–177.5°. The unsaturated sulfone XXIV gave a positive Baeyer (potassium permanganate) test for unsaturation.

Anal. Calcd. for $C_{23}H_{18}O_2S$: C, 77.07; H, 5.06. Found: C, 77.02; H, 5.06.

BOULDER, COLORADO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO]

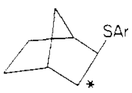
Bridged Polycyclic Compounds. IV. The Stereochemistry of the Free Radical Addition of *p*-Thiocresol to a Bicyclo[2,2,1]heptene and a Bicyclo[2,2,2]octene[1]

BY STANLEY J. CRISTOL AND ROBERT P. ARGANBRIGHT

RECEIVED JUNE 24, 1957

The addition of *p*-thiocresol to *endo-exo*-1,2,3,4,6,10,10-heptachloro-1,4,4a,5,8,8a-hexahydro-1,4,5,8-dimethanonaphthalene (IV) has been shown to give entirely *cis-exo* addition of the *p*-thiocresoxy radical and the hydrogen atom involved. Free-radical addition of thiocresol to 11-chloro-9,10-dihydro-9,10-ethenoanthracene (V) gave a mixture of isomers of which about $^1/_3$ resulted from *trans* addition and $^2/_3$ from *cis* addition. These results suggest that the product of addition of a thiocresoxy radical to these olefins is a classical free radical, rather than a sulfur-bridged radical.

Some time ago it was shown[2] that the sole 1:1 addition product of *p*-thiocresol to norbornene is *exo*-2-*p*-thiocresoxynorbornane, no rearrangement to the 7-isomer being observed. On the basis of this observation, it was suggested that the intermediate[3] in the addition reaction was the classical radical I rather than the carbon-bridged mesomeric radical II. At that time[2] it was pointed out that structure III was a possible one for the intermediate; this was based upon an analogous suggestion[4] made to explain the *trans* addition observed with hydrogen bromide to 1-bromocyclohexene and 1-methylcyclohexene. During the intervening period of time, a number of papers[5–9] have appeared which make a formulation such as III unlikely, but we wish to report work which makes such a formulation untenable, assuming that a structure such as III would lead to stereospecific *trans* addition.[4] The stereochemistry of the addition reaction could, of course, not be determined with norbornene itself (except with an isotopic label), so we undertook the addition of *p*-thiocresol to a substituted norbornene, 6-chloro-aldrin (IV) (*endo-exo*-1,2,3,4,6,10,10- heptachloro-1,4,4a,5,8,8a-hexahydro-1,4,5,8-dimethanonaphthalene) as well as to a substituted bicyclo[2,2,2]octene, 11-chloro-9,10-dihydro-9,10-ethenoanthracene (V).



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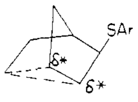

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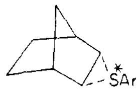

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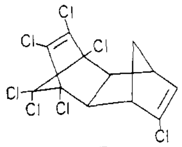

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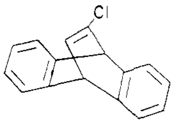

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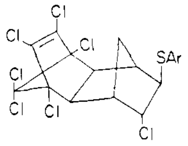

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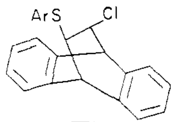

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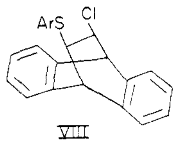

VIII

Addition of *p*-thiocresol to 6-chloro-aldrin gave only one product in isolable quantities. This product was identical with that obtained from the addition of *p*-toluenesulfenyl chloride to aldrin which has been shown[1] to have the *trans* relationship between the chlorine atom and the sulfide group. Thus addition in this system is largely, if not completely, *cis* addition, and this result indicates that neither a bridged sulfur radical analogous to III nor a π-complex[6,10] are important intermediates in the addition of mercaptans to such olefins. The fact of clean *cis* addition appears to be a reflection of the generally observed *exo* addition[1,2,11] to norbornene derivatives, which has been formulated as a rule. The rule applies for the addition of the first ion, radical or atom to the bicyclic double bond, but the position and stereochemistry of the second addend depends upon the type of intermediate formed. For example, with ionic addition, Wagner–Meerwein rearrangements or *trans* additions may occur when the second group is added. However, in this radical addition, the transfer of the hydrogen atom from mercaptan to the radical analogous to I also occurs from the *exo* side. Another example of this is to be found in

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[1] Previous paper in series: S. J. Cristol, R. P. Arganbright, G. D. Brindell and Roger M. Heitz, THIS JOURNAL, **79**, 6035 (1957).

[2] S. J. Cristol and G. D. Brindell, *ibid.*, **76**, 5699 (1954).

[3] M. S. Kharasch, A. T. Read and F. R. Mayo, *Chemistry & Industry*, 752 (1938).

[4] H. L. Goering, P. I. Abell and B. F. Aycock, THIS JOURNAL, **74**, 3588 (1952).

[5] H. L. Goering and L. L. Sims, *ibid.*, **77**, 3465 (1955).

[6] (a) P. S. Skell and R. C. Woodworth, *ibid.*, **77**, 4638 (1955); (b) P. S. Skell, R. C. Woodworth and J. H. McNamara, *ibid.*, **79**, 1253 (1957).

[7] H. L. Goering, D. I. Relyea and D. W. Larsen, *ibid.*, **78**, 348 (1956).

[8] F. G. Bordwell and W. A. Hewett, Abstracts of the 126th Meeting of the American Chemical Society, New York, N. Y., Sept., 1954, p. 6-O.

[9] F. G. Bordwell and N. P. Neureiter, Abstracts of the 131st Meeting of the American Chemical Society, Miami, Florida, April, 1957, p. 10-O.

[10] H. C. Brown and J. D. Brady, THIS JOURNAL, **74**, 3570 (1952).

[11] See for example: K. Alder and G. Stein, *Ann.*, **504**, 216 (1933); R. B. Woodward and H. Baer, THIS JOURNAL, **70**, 1161 (1948); G. Stork, E. E. van Tamelen, L. J. Friedman and A. W. Burgstahler, *ibid.*, **75**, 384 (1953); K. Alder and H. Wirtz, *Ann.*, **601**, 138 (1956).