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Bridged Polycyclic Compounds. XXIV. The Halogenation of Substituted Norbornyl Radicals[1]

STANLEY J. CRISTOL, LYLE K. GASTON, AND TRENT TIEDEMAN

Department of Chemistry, University of Colorado, Boulder, Colorado

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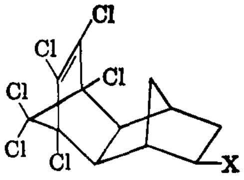
Various procedures for the preparation of the dihydroaldrinyl radical (IV) and the capture of this radical by halogen donors have been studied. The results suggest that the nature of the radical is independent of its source and that the composition of the mixture of epimers produced depends solely on the halogen donor.

Our interest in the stereochemistry of reactions in bicycloheptane systems has led us to the study of a variety of reactions in which the substituted *exo*- and *endo*-2-norbornyl bromides (Ia and IIa) have been produced.[2,3] We now wish to report some work on the preparation of the related chlorides and iodides (Ib, IIb, Ic, and IIc), the stereochemistry of the reactions leading to them, and some additional work on the bromides.



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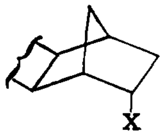
c, X = I
d, X = CO_2H
e, X = H
f, X = CO_2Hlg



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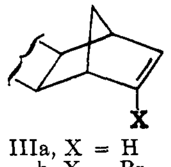

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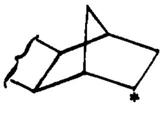

IV

Addition of hydrogen chloride to 1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-1,4-*exo*-*endo*-5,8-dimethanonaphthalene (aldrin, IIIa) with zinc chloride catalysis gave the *exo* chloride (Ib); addition of hydrogen iodide gave the *exo* iodide (Ic). The *exo* structures of these substances was inferred from the syntheses, assuming the usual *exo* addition to norbornenes,[4] and was supported by the observation that mixture melting points of any combinations of Ia, Ib, and Ic were not depressed below that of the lower melting compound of the mixture. Single crystal X-ray diffraction patterns of Ia and Ic were superimposable, thus unequivocally relating the structure of Ic with that of the known Ia.[3,5] The chloride Ib was identical with a sample obtained from Dr. R. E. Lidov, which was produced by the Diels-Alder reaction between hexachlorocyclopentadiene and *exo*-5-chloro-2-norbornene.[6]

Treatment of the silver salt of the acid Id with iodine (Hunsdiecker reaction) gave an 85% yield of a mixture of iodides Ic and IIc in an *exo*–*endo* ratio of 70:30. An identical mixture was obtained in 70% yield by treatment of Id with mercuric oxide and iodine in carbon tetrachloride. Thus the mercuric oxide–halogen procedure[7] has been extended to the formation of alkyl iodides. This procedure is more convenient than the Hunsdiecker reaction, as it avoids the tedious preparation and desiccation of the silver salt. The *endo* iodide (IIc) was separated from the mixture by fractional crystallization.

The *endo* isomers, IIa, IIb,[8] and IIc, did not show melting point depressions when mixed, again indicating structural and crystalline similarities, while mixtures of halide epimers exhibited large melting point depressions. In all the epimeric pairs of halides, the *exo* isomers (I) melted higher than the *endo* isomers (II).

Attempts to prepare *endo*-5-iodo-2-norbornene for Diels–Alder addition to hexachlorocyclopentadiene to form IIc were unsuccessful. Iodine was added to al-

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[1] Previous paper in series: S. J. Cristol, J. R. Mohrig, F. P. Parungo, K. Schwarzenbach, and D. D. Tanner, *J. Am. Chem. Soc.*, **85**, 2675 (1963).

[2] S. J. Cristol and L. K. Gaston, *J. Org. Chem.*, **26**, 4672 (1961).

[3] S. J. Cristol, J. R. Douglass, W. C. Firth, Jr., and R. E. Krall, *ibid.*, **27**, 2711 (1962).

[4] See footnote 14 of ref. 3.

[5] The authors are indebted to Dr. Walter M. Macintyre for the X-ray data.

[6] R. E. Lidov, U. S. Patent 2,635,979 (April 21, 1953); *Chem. Abstr.*, **47**, 6596*h* (1953).

[7] S. J. Cristol and W. C. Firth, Jr., *J. Org. Chem.*, **26**, 280 (1961).

[8] C. A. Peri, *Gazz. chim. ital.*, **85**, 1118 (1955).

drin (IIIa) photochemically to give a diiodide, presumably another example of the relatively rare class[9] of vicinal diiodides. Whether this is a *cis* or *trans* isomer was not established. Treatment with base gave the iodoaldrin IIIc. Attempts to hydrogenate the *exo* side of the double bond bearing the iodine atom, as had been accomplished with the bromine analog IIIb,[10] without hydrogenolysis of the iodine-carbon bond, were unsuccessful.

Treatment of the silver salts of Id or of IId with chlorine or with iodine, like that with bromine,[3] gives mixtures of I and II halides whose compositions are independent of the *endo* or *exo* stereochemistry of the starting acid, and which in each case contains approximately 70% of the *exo* isomer and 30% of the *endo* isomer. Kooyman and Vegter[11] have given convincing evidence that the *exo–endo* ratio of products of reaction of a norbornyl radical with halogen donors is increased by increasing steric interactions. It would appear that the dihydroaldrinyl radical (IV) involved in these Hunsdiecker reactions[3] finds the acyl hypohalite (If or IIf), with which it reacts of approximately equivalent steric requirement, independent of the halogen. Presumably the larger van der Waals radius of the heavier halogen is offset by the correspondingly longer covalent bond being developed in the transition state.

Further evidence in support of the Kooyman thesis, that the *endo–exo* ratio is affected solely by the bulk of the halogen donor, is given in the data of Table I.

TABLE I

FREE-RADICAL FORMATION OF ALDRIN HYDROHALIDES

Sources of dihydroaldrin radicals	Halogen donor	Initiation process	% *endo* halide (II) in halide mixture[a]
Id, Ag salt, Cl_2	RCO_2Cl (I)	Heat	30
IId, Ag salt, Cl_2	RCO_2Cl (II)	Heat	31
Id, Ag salt, Br_2	RCO_2Br (I)	Heat	31[b,c]
IId, Ag salt, Br_2	RCO_2Br (II)	Heat	31[b,c]
Id, Ag salt, I_2	RCO_2I (I)	Heat	33
IId, Ag salt, I_2	RCO_2I (II)	Heat	34
Id, HgO, I_2	RCO_2I (?)	Heat	34
$(RCO_2)_2$ *exo*	Br_2	Heat	27[c]
$(RCO_2)_2$ *exo*	$BrCCl_3$	Heat	0[c]
$(RCO_2)_2$ *endo*	$BrCCl_3$	Heat	0[c]
Ie + Cl·	Cl_2	Light	30
Ie + Br·	Br_2	Light	30[d]
Ie + $C_4H_4O_2N$·	N-Bromosuccinimide	Light	16
Ie + CCl_3·	$BrCCl_3$	Benzoyl peroxide	4

[a] Infrared analysis; results are probably accurate to ±4%. [b] Similar results were obtained with mercuric oxide and bromine. [c] See ref. 3. [d] See ref. 2.

Here we have summarized our results with a variety of halogen donors and a variety of sources of the dihydroaldrinyl radical (IV). The radical was formed in various cases by the Hunsdiecker procedure from Id and from IId, by the mercuric oxide–halogen procedure on both acids, by decomposition of both acyl peroxides, and by the attack of halogen atoms, succinimide radicals, and trichloromethyl radicals on dihydroaldrin (Ie). One may note that the fraction of *endo* halide in the halide mixture is, within the limits of accuracy of the infrared analytical technique, independent of the source of the radical species. These data are consistent with the idea that the Hunsdiecker reaction, as well as the other reactions, involves a free-radical chain process.[12]

Skell[13] has recently proposed that the course of bromination of aliphatic compounds with N-bromosuccinimide (NBS) involves the transfer of a bromine atom to the alkyl radical from molecular bromine rather than from a molecule of NBS. This cannot be the case in our experiments with NBS, as the mixture of bromides is clearly different from that obtained with bromine (Table I). Perhaps the radical studied by Skell and co-workers is more selective than the dihydroaldrinyl radical we have investigated. Although we have suggested that, in the experiment with NBS, the radical IV is formed from Ie and a succinimidyl radical, our data do not offer any way to distinguish this from the current suggestions that bromine atoms are the chain carriers in NBS brominations.[14]

Experimental

Preparation of *exo*-2,5,6,7,8,9,9-Heptachloro-1,2,3,4,4a,5,8,8a-octahydro-1,4-*exo*-*endo*-5,8-dimethanonaphthalene (Ib).—To 75 ml. of cold glacial acetic acid, saturated with dry hydrogen chloride, were added 10 g. of fused zinc chloride and 5 g. of aldrin (IIIa, Shell Chemical Co.). The mixture was warmed to room temperature with swirling until solution was complete. On standing at room temperature for 5 days, 4.5 g. (82%) of white crystals precipitated. One recrystallization from benzene gave a solid, m.p. 155–157°. The material was identical (infrared and mixture melting point) with a sample supplied by Dr. R. E. Lidov of the Shell Development Co.[6]

Preparation of 5,6,7,8,9,9-Hexachloro-1,2,3,4,4a,5,8,8a-octahydro-*exo*-2-iodo-1,4-*exo*-*endo*-5,8-dimethanonaphthalene (Ic).—To 90 ml. of glacial acetic acid were added 5.0 g. of aldrin (IIIa), 15 g. of sodium iodide, and 10 ml. of 72% perchloric acid. On standing overnight at room temperature, the solution deposited 4.0 g. of yellow solid. Trituration of this material with acetone gave a white solid, 3.3 g. (49%), m.p. 186–187.5°. Recrystallization from methanol gave material melting below 170°, but which resolidified and melted at 186–187.5°. This process could be repeated several times.

Anal. Calcd. for $C_{12}H_9Cl_6I$: C, 29.32; H, 1.84. Found: C, 29.53; H, 1.81.

Single crystal X-ray diffraction patterns were photographed by Dr. Walter M. Macintyre for Ic and the known *exo* bromide (Ia), using a Supper–Weissenberg camera of radius 57.3 mm. A Norelco diffraction apparatus with molybdenum target was used. The two patterns were superimposable, thus establishing the *exo* configuration of the iodide.

Preparation of 5,6,7,8,9,9-Hexachloro-1,2,3,4,4a,5,8,8a-octahydro-*endo*-2-iodo-1,4-*exo*-*endo*-5,8-dimethanonaphthalene (IIc).—A mixture of 1.00 g. (2.43 mmoles) of 5,6,7,8,9,9-hexachloro-1,2,3,4,4a,5,8,8a-octahydro-1,4-*exo*-*endo*-5,8-dimethano-*exo*-2-naphthoic acid (Id),[3] 1.20 g. (5.54 mmoles) of red mercuric oxide, and 1.5 g. (5.9 mmoles) of iodine in 50 ml. of reagent grade carbon tetrachloride (poured through a 15 × 1 cm. column of Merck alumina) was heated at reflux in the dark for 4 hr. The mixture was filtered while hot, and the solvent was removed with a stream of warm air. The residue was dissolved in 100 ml. of carbon tetrachloride, slurried with finely ground sodium thiosulfate to remove traces of iodine, filtered, and poured through a 50 × 1

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[9] T. S. Peterson and J. Robertson, *J. Chem. Soc.*, **125**, 1526 (1924); A. Fairbanks and D. W. Stevens, *ibid.*, 1973 (1932); M. P. Cava and D. R. Napier, *J. Am. Chem. Soc.*, **79**, 1701 (1957); F. R. Jensen and W. E. Coleman, *J. Org. Chem.*, **23**, 809 (1958).

[10] S. B. Soloway, private communication.

[11] E. C. Kooyman and G. C. Vegter, *Tetrahedron*, **4**, 382 (1958).

[12] See ref. 3 for pertinent references.

[13] P. S. Skell, D. L. Tuleen, and P. D. Readio, *J. Am. Chem. Soc.*, **85**, 2850 (1963).

[14] R. E. Pearson and J. C. Martin, *ibid.*, **85**, 354 (1963); G. A. Russell, C. De Boer, and K. M. Desmond, *ibid.*, **85**, 355 (1963).

cm. column of Merck alumina packed in pentane. The column was developed with 200 ml. of pentane, which was removed under vacuum to give 840 mg. (70%) of white solid. Infrared analysis showed this solid mixture was 33-36% *endo* iodide (IIc), and the rest was *exo* iodide (Ic).

Eight grams of material prepared by the foregoing method was triturated with 95% pentane until about 4 g. had dissolved. The pentane-soluble fraction contained most of the *endo* iodide, as judged by absorption peaks at 7.70 and 16.30 μ similar to peaks possessed by the bromo (7.67 and 16.34 μ) and chloro (7.65 and 16.28 μ) analogs. The pentane-soluble material was poured through Merck acid-washed alumina (with carbon tetrachloride as eluent) to remove all traces of carbonyl compounds, slurried with solid sodium thiosulfate to remove iodine, and filtered. Three careful fractional crystallizations from pentane gave 2.0 g. of colorless material very rich in *endo* isomer. Two more crystallizations from pentane and three from methanol gave 0.5 g. of pure IIc, m.p. 140-142°.

Anal. Calcd. for $C_{12}H_9Cl_6I$: C, 29.32; H, 1.84. Found: C, 29.37; H, 1.87.

The pentane-insoluble residues are essentially *exo* iodide, which may be purified by crystallization from methanol.

Mixture Melting Points.—Mixture melting points of the aldrin hydrohalides were taken on an electrically heated calibrated brass block. Melting points of pure *exo* chloride (Ib), bromide (Ia), and iodide (Ic) were, respectively, 155-157°, 183-184°, and 186-187°. Melting points of pure *endo* halides IIb, IIa, and IIc were 94-96°, 109-110°, and 140-142°, respectively. For mixture melting point measurements in the *exo* series, a ratio of five parts of the lower melting isomer to one of the higher was used, and, in the *endo* series, a one-to-one mixture was used. Mixture melting points for Ib-Ia, Ib-Ic, and Ia-Ic were 159-162°, 159-164°, and 183-186°, respectively, while those for IIb-IIa, IIb-IIc, and IIa-IIc were 95-98°, 94-98°, and 109-110°, respectively.

Preparation of 5,6,7,8,9,9-Hexachloro-1,2,3,4,4a,5,8,8a-octahydro-2,3-diiodo-1,4-*exo-endo*-5,8-dimethanonaphthalene.—A solution of 3 g. of aldrin in 100 ml. of 95% ethanol saturated with iodine was irradiated for 24 hr. with a 300-watt tungsten lamp. The solution was poured into 400 ml. of water and decolorized by slowly adding lump sodium thiosulfate. A trace of mineral acid was also added. The solution was extracted with two 50-ml. portions of chloroform. The combined organic layers were dried with magnesium sulfate, and the solvent was removed. The resulting oil was triturated with methanol until a portion solidified, and 1.17 g. (22%) of white solid, m.p. 137-143°, was separated by filtration. Two recrystallizations from hot 95% ethanol and three from Skellysolve B gave material of m.p. 186-189°. The color of iodine began to appear at 180°, and some softening occurred at 184°. The compound is moderately unstable and light sensitive.

Anal. Calcd. for $C_{12}H_8Cl_6I_2$: C, 23.29; H, 1.30. Found: C, 23.47; H, 1.44.

Preparation of 5,6,7,8,9,9-Hexachloro-1,4,4a,5,8,8a-hexahydro-2-iodo-1,4-*exo-endo*-5,8-dimethanonaphthalene (IIIc).—A mixture of 5.0 g. (8.1 mmoles) of the diiodide and 0.46 g. (8.2 mmoles) of potassium hydroxide in 200 ml. of 95% ethanol was slowly warmed to reflux with stirring. At the end of 20 min., solution was complete. Heating at reflux was continued for 30 min.; the solution stood overnight at room temperature and was then poured into water. Organic materials were extracted into chloroform, washed with water, and dried with magnesium sulfate. Evaporation of the solvent gave an oil which on crystallization from 25 ml. of hot methanol gave 3.12 g. (78%) of white crystals, m.p. 110-120°. Recrystallizations from methanol sharpened the melting point to 113-115°. An absorption peak at 6.46 μ indicates the vinyl iodide structure.[15]

Anal. Calcd. for $C_{12}H_7Cl_6I$: C, 29.36; H, 1.44. Found: C, 29.29; H, 1.60.

A mixture of 0.25 g. of IIId, 40 mg. of 10% palladium on charcoal, and 50 ml. of methanol was shaken under 630 mm. of hydrogen for 18 hr. at room temperature. The solution was filtered and the solvent was removed. The infrared spectrum of the residue was essentially that of unchanged starting material.

A mixture of 0.5 g. of IIId, 40 mg. of 10% palladium on charcoal, and 100 ml. of methanol was charged to 39 p.s.i. (gage pressure) with hydrogen and shaken at room temperature for 27 hr. The mixture was filtered and the solvent was removed. The residue possessed an infrared spectrum quite similar to that of dihydroaldrin (Ie), thus establishing the aldrin ring system for IIIc. The residue was poured through a 20 × 1 cm. column of Merck neutral alumina in pentane and washed out with 200 ml. of pentane, which was then distilled. Recrystallization from methanol gave a solid, m.p. 75-77°. A mixture melting point with authentic dihydroaldrin was 75-77°.

Infrared Analysis Procedure.—Analyses of aldrin hydrohalides were done on a Perkin-Elmer Model 137 Infracord equipped with potassium bromide optics, using a differential technique.[2] Sample and reference concentrations were 0.1 *M* for the chlorides and bromides, and 0.08 *M* for the iodides. Tetrachloroethylene, freshly distilled from phosphorus pentoxide, was used as solvent. The cell length was 1.0 mm. The analytical absorption band was at 16.3 μ, characteristic of all *endo* aldrin hydrohalides.

Reaction of *exo* Id Silver Salt[3] with Chlorine.—To 60 ml. of reagent carbon tetrachloride was added 500 mg. (1.01 mmoles) of the silver salt of Id. Ten milliliters of solvent was distilled to ensure dryness, and 1.0 ml. of 1.5 *M* chlorine in dry carbon tetrachloride was added. The mixture was heated at reflux for 2 hr. in the dark and solids were filtered. The filtrate was poured through a 50 × 1 cm. column of Merck acid-washed alumina packed in carbon tetrachloride. The epimeric halides were washed out with 200 ml. of carbon tetrachloride, leaving the carbonyl-containing side products on the column. Evaporation of solvent gave 111 mg. (28%) of a mixture of Ib and IIb. Differential analysis showed that there was approximately 30% of *endo* chloride (IIb).

Reaction of *endo* IId Silver Salt[3] with Chlorine.—Reaction and work-up of 500 mg. (1.01 mmoles) of IId silver salt with 1.5 mmoles of chlorine, exactly as above, gave 175 mg. (44%) of a mixture of Ib and IIb. The *endo* (IIb) chloride content of the mixture lay between the limits 30-33%.

Reaction of *exo* Id Silver Salt with Iodine.—Reaction and work-up of 500 mg. (1.01 mmoles) of Id silver salt with 1 g. (7.9 mmoles) of iodine, exactly as above, gave 441 mg. (89%) of a mixture of Ic and IIc, with the *endo* iodide content between the limits 30-36%.

Reaction of *endo* IId Silver Salt with Iodine.—Reaction and work-up of 500 mg. (1.01 mmoles) of IId silver salt with 1 g. (7.9 mmoles) of iodine, exactly as above, gave 423 mg. (85%) of a mixture of Ic and IIc, with the *endo* iodide content between the limits 33-36%.

Attempted Equilibration of *endo* Chloride (IIb).—*endo* chloride (IIb) (200 mg., 0.5 mmole) and 170 mg. (1 mmole) of silver acetate were placed in 70 ml. of reagent grade carbon tetrachloride, and 10 ml. of solvent was distilled. Two millimoles of chlorine was added in carbon tetrachloride, and the mixture was heated in the dark at reflux for 2 hr., and then filtered; the solvent was removed to give 202 mg. of oil. The infrared spectrum is essentially that of IIb. It has been shown[3] that the corresponding bromides, Ia and IIa, do not rearrange under Hunsdiecker reaction conditions, or under other free-radical conditions.[2]

Chlorination of Dihydroaldrin (Ie).—Dihydroaldrin,[6] 1.835 g. (5.00 mmoles), was dissolved in 50 ml. of carbon tetrachloride, and the vapor volume was swept out with dry nitrogen. Chlorine, 11.2 ml. (STP or 0.5 mmole), was bubbled in at −30°, and the solution was irradiated with a GE AH-4 lamp. The addition took 150 sec. After approximately 1 min., the chlorine color had disappeared. The solvent was removed under reduced pressure and the residue was chromatographed on 160 g. (1.8 × 63 cm. column) of neutral, activity grade I alumina.[16] Starting material that was recovered amounted to 94.9% of the initial amount. The aldrin hydrochloride weighed 79.4 mg. (3.96%), and contained 30 ± 5% *endo* chloride (IIb).

Bromination of Dihydroaldrin (Ie) with N-Bromosuccinimide.—Dihydroaldrin, 1.835 g. (5.00 mmoles), and N-bromosuccinimide, 89.3 mg. (0.514 mmole), were dissolved in 50 ml. of carbon tetrachloride. The flask was irradiated with a 100-watt light bulb for 46 hr. The solvent was removed under reduced pressure, and the residue was chromatographed on 160 g. (1.8 × 62 cm. column) of neutral, activity grade I alumina, as above. The material was put on the column in pentane, in which N-bromosuccinimide and succinimide are virtually insoluble. Starting material recovered amounted to 85.4% of the initial quantity.

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(15) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, p. 50.

(16) H. Brockmann and H. Schodder, *Ber.*, **74B**, 73 (1941); see ref. 2 for the detailed chromatographic procedure.

The aldrin hydrobromide portion recovered weighed 128.4 mg. (5.75% yield). Analysis of this material indicated that the mixture contained 16 ± 3% *endo* bromide (IIa).

Bromination of Dihydroaldrin (Ie) with Bromotrichloromethane.—Dihydroaldrin, 1.835 g. (5.00 mmoles), and benzoyl peroxide, 32 mg. (0.124 mmole), were dissolved in 50 ml. of bromotrichloromethane. This solution was heated at 83° for 15 hr. in the dark. The solvent was removed under reduced pressure, and the residue was chromatographed on 160 g. (1.8 × 64 cm. column) of neutral, activity grade I alumina, as above. Fractions 2 through 5 contained 87.0% of recovered starting material. Fractions 6 through 12 contained traces of a colorless oil. Fractions 13 through 30 contained 11.7% of a mixture of aldrin hydrobromides. Differential infrared analysis of this material indicated 4 ± 1% *endo* bromide (IIa).

Acknowledgment.—The authors are indebted to the National Science Foundation for generous support of this work.

Bridged Polycyclic Compounds. XXV. Free-Radical Addition of Benzenesulfonyl Halides to Norbornadiene[1]

STANLEY J. CRISTOL[2] AND DAVID I. DAVIES[3]

Department of Chemistry, University of Colorado, Boulder, Colorado

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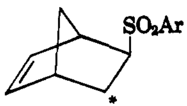
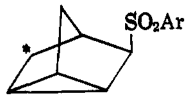
The benzenesulfonyl halides react with norbornadiene under free-radical conditions to give mixtures of *endo*-3-halogeno-*exo*-5-norbornen-2-yl phenyl sulfone (IV) and 5-halogeno-3-nortricyclyl phenyl sulfone (V). The proportion of saturated component decreases along the series (Cl > Br > I). These results combined with dilution experiments provide evidence favoring the two separate intermediates VIII and IX, rather than the nonclassical homoallylic radical (X) as an intermediate.

Some time ago Cristol, Brindell, and Reeder[4] reported that the addition of aryl mercaptans to norbornadiene under free-radical conditions gave a mixture of *exo*-5-norbornen-2-yl aryl thioether *via* 1,2-addition and 3-nortricyclyl aryl thioether *via* homoconjugative addition. Conclusive evidence was provided against the intermediacy of a single nonclassical homoallylic radical and in favor of two separate intermediates. Further work by Cristol and Reeder[5] showed that *p*-toluenesulfonyl chloride added to norbornadiene to give a 1:1 product which was largely saturated, and which, on crystallization, gave a 42% yield of a product which was almost certainly 5-chloro-3-nortricyclyl *p*-tolyl sulfone. The relative completeness of the rearrangement to the nortricyclene ring system was rationalized on the basis of the slow chain transfer of the intermediate radicals with the sulfonyl chloride allowing sufficient time for rearrangement of radical I to II.

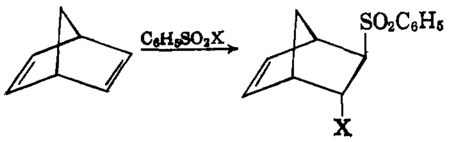


I



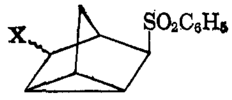
II

In 1959 McNamara and Skell[6] investigated free-radical addition reactions of benzenesulfonyl halides to reactive olefins and found that, when equimolar quantities of freshly prepared olefin and sulfonyl halide were irradiated for a few minutes with a nonfrosted light bulb, the β-halosulfone addition product, in many cases, crystallized within a few minutes, often in better than 90% yields. In our hands, application of this method to the reaction of benzenesulfonyl chloride with norbornadiene met with only moderate success. If equimolar amounts of reactants were irradiated for several days, the reaction mixture slowly darkened and yielded, on distillation, unchanged benzenesulfonyl chloride, about 10% of the 1:1 addition product, and a large quantity of an intractable black tar. The reaction could proceed to give the following products in the absence of major skeletal rearrangement.



III

IVa, X = Cl
b, X = Br
c, X = I



Va, X = Cl
b, X = Br
c, X = I

The product had an infrared absorption band of medium intensity in the 12.3–12.5-μ range characteristic of a nortricyclene structure[7] and did not readily decolorize potassium permanganate in acetone. This indicates that the product is predominantly Va,[8] possibly together with a small amount of IVa.[9] This was confirmed by hydrogenation experiments. Crystallization of the crude 1:1 adduct from methanol gave a pure saturated component, Va, the stereochemistry of the chlorine atom being unknown.

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[1] Previous paper in series: S. J. Cristol, L. K. Gaston, and T. Tiedeman, *J. Org. Chem.*, **29**, 1279 (1964).

[2] To whom all inquiries should be addressed.

[3] Shell Development Co. Post-Doctorate Fellow, University of Colorado, 1958–1959.

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[8] The stereochemistry of the saturated component Va is unknown, and in the crude 1:1 addition product both of the possible products may be present.

[9] In the unsaturated IVa the benzenesulfonyl and chlorine groups presumably have the *trans* relationship by analogy with the addition product of *p*-toluenesulfonyl chloride to norbornene where a *trans* relationship of sulfur and chlorine groups has been proved.[5]