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).

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

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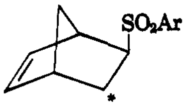
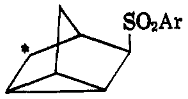
The benzenesulfonyl halides react with norbornadiene under free-radical conditions to give mixtures of *endo*-3-halogeno-*exo*-5-norbornen-2-yl phenyl sulfone (IV) and 5-halogeno-3-nortricyclyl phenyl sulfone (V). The proportion of saturated component decreases along the series (Cl > Br > I). These results 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.

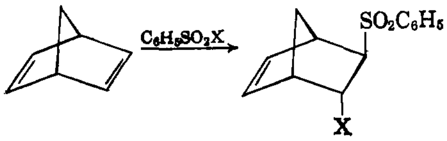


I



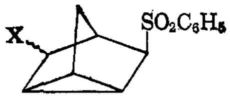
II

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).

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[4] S. J. Cristol, G. D. Brindell, and J. A. Reeder, *J. Am. Chem. Soc.*, **80**, 635 (1958).

[5] S. J. Cristol and J. A. Reeder, *J. Org. Chem.*, **26**, 2182 (1961).

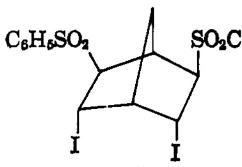
[6] J. H. McNamara and P. S. Skell, Abstracts of Papers, 135th National Meeting of the American Chemical Society, Boston, Mass., April, 1959, p. 13L.

[7] J. D. Roberts, E. R. Trumbull, Jr., W. Bennett, and R. Armstrong, *J. Am. Chem. Soc.*, **72**, 3116 (1950).

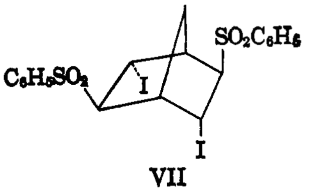
[8] The stereochemistry of the saturated component Va is unknown, and in the crude 1:1 addition product both of the possible products may be present.

[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]

The reactions of benzenesulfonyl bromide and benzenesulfonyl iodide with norbornadiene were then investigated. An equimolar mixture of norbornadiene and benzenesulfonyl bromide on warming gave over 90% of a 1:1 adduct which consisted of 33% of unsaturated IVb and 67% of Vb. Norbornadiene and benzenesulfonyl iodide reacted vigorously when 1 mole of the iodide was added slowly to 1 mole of norbornadiene. The reaction product was predominantly unsaturated, although a weak absorption band at 12.3–12.5 μ in the infrared indicated the presence of some saturated material. This was confirmed by subsequent hydrogenation experiments. When norbornadiene was added to benzenesulfonyl iodide, an extremely violent reaction occurred. The product was a high-melting buff-colored solid with correct analysis for a 2:1 adduct of benzenesulfonyl iodide and norbornadiene. It is believed to have the structure VI or VII.



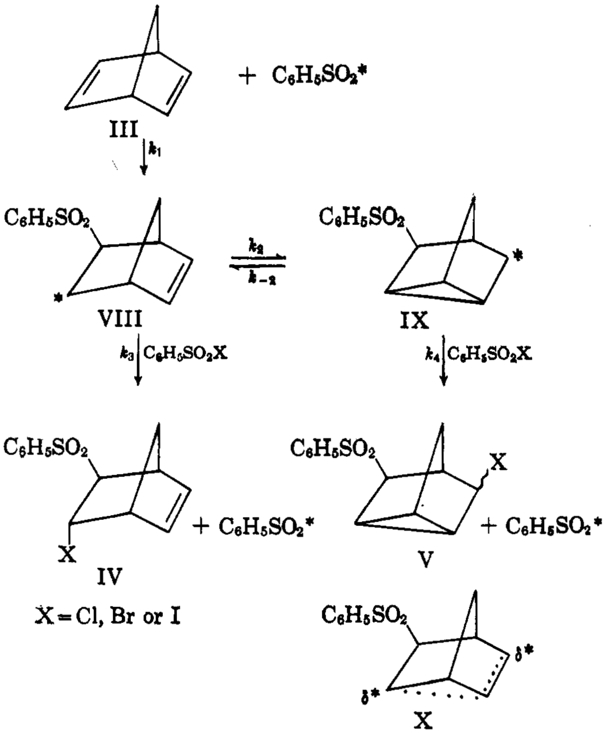
VI



VII

The reaction of the benzenesulfonyl halides with norbornadiene has, most likely, the steps that are shown in Scheme I, which follows, in its chain.

SCHEME I



If this mechanism is correct, and if k_2 and k_{-2} are of the same order of magnitude as $k_3[C_6H_5SO_2X]$, then the following consequences can be predicted. (1) As the nature of X is varied, the ratio of unsaturated IV to saturated V will increase as the tendency to chain transfer (k_3) increases. Thus this ratio should increase as X changes from chlorine to bromine to iodine. (2) As one lowers the concentration of a given halide, the ratio of IV to V will decrease.[10a] On the other hand, if the nonclassical homoallylic radical X were the sole intermediate leading to IV and V isomers, changing the concentration of halide would not affect the ratio of IV to V,[10a] and the effect of varying the nature of X would not necessarily be predictable.

Table I lists the composition of the 1:1 adducts from the various benzenesulfonyl halides and norbornadiene, as estimated by quantitative hydrogenation. It may be noted that the ratio of unsaturated IV to V varies from 0.05 to 5 (neat reactions) as the benzenesulfonyl halide is varied from chloride to iodide,[10b] and that there is an analogous variation in the experiments with reactants dissolved in ten volumes of chlorobenzene. Excepting the benzenesulfonyl chloride experiments, where the yields were very poor, the dilution experiments also are consistent with the proposed mechanism.

In the early work on dilution experiments in the addition of mercaptans to norbornadiene,[4] it was also shown that two intermediates were involved in the free-radical addition reaction. However, the minimum amount of nortricyclyl species found was 60%, so that it was not possible to state with complete assurance that the intermediates were the classical radicals VIII and IX, as the data could be accommodated to the intermediates X and IX. In the present work, where we have now succeeded in trapping the initial intermediate by transfer with benzenesulfonyl iodide before more than 17% has rearranged to the nortricyclyl radical, one may have considerable confidence in excluding X as a product-producing intermediate and in relegating it to the position of a transition state in the rearrangement of VIII to IX.

TABLE I

PROPORTIONS OF IV AND V FORMED IN THE REACTION OF BENZENESULFONYL HALIDES WITH NORBORNADIENE

Type of adduct	Yield, %	IV, %	V, %	IV/V	Hydrogenation time, hr.
Norbornadiene and Sulfonyl Halide in 1:1 Proportions (Neat)					
Norbornadiene + $C_6H_5SO_2Cl$	7.3	5	95	0.05	3
Norbornadiene + $C_6H_5SO_2Br$	90	33	67	0.5	4
Norbornadiene + $C_6H_5SO_2I$	68	83	17	5	48
Norbornadiene and Sulfonyl Halides in 1:1 Proportions, Dissolved in 10 Volumes of Chlorobenzene					
Norbornadiene + $C_6H_5SO_2Cl$	11.4	7	93	0.07	3
Norbornadiene + $C_6H_5SO_2Br$	93	13	87	0.15	5
Norbornadiene + $C_6H_5SO_2I$	72.5	73	27	2.7	48

This conclusion is consistent not only with results in this laboratory, but also with those of other workers on free-radical additions to norbornadiene and other related bridged bicyclic systems, where no evidence could be found in favor of nonclassical homoallylic radicals,[11-14] and it seems possible to state that non-

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[10] (a) For a complete discussion of this situation, see ref. 4; (b) the data on the chloride may be unconvincing, in view of the poor yields, but they are consistent with those on the bromide and iodide.

[11] E. S. Huyser and G. Echegaray, *J. Org. Chem.*, **27**, 429 (1962).

[12] M. M. Martin and D. C. DeJongh, *J. Am. Chem. Soc.*, **84**, 3526 (1962).

[13] J. A. Berson and C. J. Olsen, *ibid.*, **84**, 3178 (1962); J. A. Berson, C. J. Olsen, and J. S. Walia, *ibid.*, **84**, 3337 (1962).

[14] H. Hart and F. J. Chloupek, *ibid.*, **85**, 1155 (1963).

classical homoallylic radicals of type X do not exist in the dehydronorbornyl–nortricyclyl series.

Experimental

Reagents.—Norbornadiene supplied by the Shell Development Company was freshly distilled prior to use, b.p. 84° (620 mm.). Benzenesulfonyl chloride was Eastman Kodak reagent grade. Benzenesulfonyl bromide and iodide were prepared, respectively, by the reaction of benzenesulfinic acid with bromine[6] and with iodine.[6,15,16]

Addition of Benzenesulfonyl Chloride to Norbornadiene. A.—Benzenesulfonyl chloride, 115 g. (0.65 mole), and norbornadiene, 60 g. (0.65 mole), were mixed, and a few crystals of benzoyl peroxide were added. The solution was stirred magnetically and irradiated with a 150-watt clear electric light bulb for 56 hr., during which time the solution darkened appreciably. Distillation gave 87 g. of unchanged benzenesulfonyl chloride followed by 12.8 g. (7.3%) of 1:1 adduct as a pale yellow liquid which solidified on standing. An intractable black tar remained in the distillation flask. The crude 1:1 adduct did not decolorize potassium permanganate in acetone, and its infrared spectrum showed absorption of medium intensity in the 12.3–12.5-μ range, characteristic of a nortricyclene structure. Several recrystallizations of a small portion from methanol gave 5-chloro-3-nortricyclyl phenyl sulfone as crystals, m.p. 114–116°.

Anal. Calcd. for $C_{13}H_{13}ClO_2S$: C, 58.08; H, 4.88. Found: C, 57.92; H, 5.00.

B.—A similar reaction with norbornadiene, benzenesulfonyl chloride, and chlorobenzene in the ratio 1:1:10 gave an 11.4% yield of 1:1 adduct, b.p. 180° (0.2 mm.), which was redistilled twice prior to hydrogenation experiments.

Addition of Benzenesulfonyl Bromide to Norbornadiene. A.—Benzenesulfonyl bromide, 6 g. (0.027 mole), was added dropwise to 2.5 g. (0.027 mole) of well-stirred norbornadiene. No reaction appeared to take place, and the solution was irradiated with a 150-watt clear electric light bulb for 27 hr. to give a pale yellow viscous liquid. Distillation afforded no unchanged norbornadiene or benzenesulfonyl bromide, and 7.6 g. (90%) of 1:1 adduct was obtained as a pale yellow, very viscous liquid, b.p. 180° (0.15 mm.), which solidified on standing. The product decolorized dilute potassium permanganate in acetone, and its infrared spectrum showed only medium absorption in the 12.3–12.5-μ range. Several recrystallizations of a portion of the product gave a 5-bromo-3-nortricyclyl phenyl sulfone as white crystals, m.p. 100–105°.

Anal. Calcd. for $C_{13}H_{13}BrO_2S$: C, 49.84; H, 4.19. Found: C, 50.03; H, 4.11.

B.—In a similar reaction with norbornadiene, benzenesulfonyl bromide, and chlorobenzene in ratio 1:1:10, a 93% yield of 1:1 adduct was obtained as a pale yellow liquid, b.p. 186° (0.3 mm.). It was twice redistilled prior to hydrogenation.

Addition of Benzenesulfonyl Iodide to Norbornadiene. A.—To 6.0 g. (0.065 mole) of well-stirred norbornadiene, 17.5 g. (0.065 mole) of benzenesulfonyl iodide was added in small portions. Much heat was evolved, and the reaction was moderated by ice cooling, and then allowed to stand at room temperature overnight to yield a pale yellow semisolid material. The product was boiled with Skellysolve B to remove any unchanged norbornadiene and then boiled with 175 ml. of methanol, the product completely dissolving which indicated the absence of any 2:1 adduct. Most of the methanol was removed by distillation and, on cooling, 16 g. (68%) of material, m.p. 115–120°, was deposited. The material decolorized potassium permanganate in acetone, indicating the presence of unsaturated material, but the infrared spectrum showed some absorption in the 12.3–12.5-μ region of the infrared, characteristic of a nortricyclene system. A portion of material was recrystallized several times from methanol to give *endo*-3-iodo-*exo*-5-norbornen-2-yl phenyl sulfone as crystals, m.p. 152–153°, which had no absorption at 12.3–12.5 μ in the infrared.

Anal. Calcd. for $C_{13}H_{13}IO_2S$: C, 43.34; H, 3.64. Found: C, 43.69; H, 3.80.

B.—A similar reaction with norbornadiene, benzenesulfonyl iodide, and chlorobenzene in the ratio 1:1:10 gave a 72.5% yield of 1:1 adduct.

C.—Benzenesulfonyl iodide, 51.5 g. (0.19 mole), was placed in a flask equipped with a reflux condenser, and 13.3 g. (0.14 mole) of norbornadiene was added dropwise through the top of the condenser. The mixture was stirred magnetically during the addition. Much heat was evolved and the product was a blackish tarry material. On boiling this with benzene, a solution was obtained which deposited a buff-colored solid on cooling. Several recrystallizations from toluene gave material, m.p. 237°, which would not decolorize potassium permanganate in acetone, and which showed no absorption in the 12.3–12.5-μ region of the infrared.

Anal. Calcd. for $C_{19}H_{18}I_2O_4S_2$: C, 36.32; H, 2.89. Found: C, 36.62; H, 3.04.

Estimation of Unsaturation.—In a typical experiment, 150 mg. of 10% palladium-on-charcoal catalyst was weighed into a hydrogenation flask, 80 ml. of 95% ethanol was added, and the flask was shaken on a quantitative (atmospheric pressure) hydrogenation apparatus for 10–15 min. The flask was detached, and the hydrogen atmosphere in it was removed. Then 0.5–1.5 g. of 1:1 adduct was added to the flask and was washed in with 25 ml. of 95% ethanol. The flask was then shaken on the quantitative hydrogenator until hydrogenation was complete. This took approximately 3, 4–5, and 48 hr., respectively, for the adducts of norbornadiene with benzenesulfonyl chloride, bromide, and iodide. The volume of gas absorbed was corrected to standard conditions by the use of the ideal gas law.

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(15) R. Otto and J. Tröger, *Ber.*, **24**, 478 (1891).

(16) P. S. Skell and J. H. McNamara, *J. Am. Chem. Soc.*, **79**, 85 (1957).