Bridged Polycyclic Compounds. XXXV. 2-Quadricyclyl Phenyl Sulfone[1]

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Abstract: Benzenesulfonyl bromide adds to norbornadiene (I) under free-radical conditions to give a mixture of *endo*-3-bromo-*exo*-5-norbornen-2-yl phenyl sulfone (II), *exo*-5-bromo-*exo*-3-nortricyclyl phenyl sulfone (III), and *endo*-5-bromo-*exo*-3-nortricyclyl phenyl sulfone (IV). Base-catalyzed epimerization of III gives *exo*-5-bromo-*endo*-3-nortricyclyl phenyl sulfone (V), while IV cannot be epimerized. Strong bases in aprotic solvents eliminated hydrogen bromide from III and V to form 2-quadricycloheptyl phenyl sulfone (VII), while more severe treatment of IV did not result in any apparent reaction.

Since the first attempts by Holz[2] and Sondkuhl[2] in 1935, and until the successful preparation of quadricyclo[2.2.1.0.$^{2,6}0^{3,5}$]heptane-2,3-dicarboxylic acid reported by Cristol and Snell[3,4] in 1954, there were a number of unsuccessful attempts to synthesize the quadricyclene ring system. The synthetic methods that were used all involved attempts to form the fourth ring by closure from the tricyclo[2.2.1.0^{2,6}]heptane ring system. The methods attempted included the oxidation of hydrazones of various appropriate ketones,[2,5] dehydration of 2,3-dihydroxycamphanes,[5] pyrolysis of tricyclic xanthate esters,[5] base-promoted γ elimination from 2,2-dihalocyclocamphane,[6] and decomposition of N-cyclocamphanyl-N-nitrosourethanes.[7] A summary and discussion of these early attempts are available.[8]

More recently, some additional attempts have been made to close the fourth ring from the tricyclo[2.2.1.0^{2,6}]heptane system. Johnson and Landerman[9] studied the elimination of halogen from the 3,5-dibromo- and 3,5-diiodonortricyclenes by the use of lithium and magnesium metals in ether and also by the use of phenyllithium. Although elimination of halogen occurred, the reaction apparently went with cleavage of the cyclopropane ring (homoconjugate elimination) rather than in the desired fashion, and the only product isolated was norbornadiene. Young[10] has again attempted to prepare 1,7,7-trimethylquadricyclo[2.2.1.0.$^{2,6}0^{3,5}$]heptane by the oxidation of isocyclenone hydrazone using a modified procedure wherein the hydrazone was stirred at −20° in a methanolic solution of potassium hydroxide while mercuric chloride in methanol was added dropwise. This method had been shown to be successful in many cases where the normal procedure (use of mercuric oxide) failed. However, again only oxygen-containing products were obtained.

The successful preparation of a quadricyclene was accomplished by Cristol and Snell[3] by valence-bond isomerization of bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylic acid using direct irradiation with ultraviolet light, a technique not previously used. Later, the photochemical preparation of the parent hydrocarbon from norbornadiene was reported by Dauben and Cargill[11] and by Hammond, Turro, and Fischer.[12] Photochemical techniques have also been used to prepare 7-chloroquadricyclene[13] and 7-acetoxyquadricyclene.[14] Recently 1,2,3,4,7,7-hexachloronorbornadiene has been converted photochemically to the corresponding quadricyclene.[15] In another modification of the irradiation technique, Moriarty[16] has prepared the parent hydrocarbon by the irradiation of 6,7-diazaquadricyclo[3.2.1.1.$^{3,8}0^{2,4}$]non-6-ene. The loss of nitrogen from the excited molecule was accompanied by ring closure to give quadricyclene.

To date, all reported successful syntheses of the quadricyclo[2.2.1.0.$^{2,6}0^{3,5}$]heptane ring system have involved the application of irradiation techniques employing ultraviolet light. Schleyer[17] attempted to isomerize norbornadiene to quadricyclene by use of silica–alumina catalyst. However, only starting material was recovered. This failure of norbornadiene to isomerize is not unexpected since Cristol and Snell[3] have demonstrated that, in the case of the isomerization of norbornadienedicarboxylic acid to the quadricyclic diacid, a contrathermodynamic isomerization was involved and the starting diene was thermodynamically more stable than the quadricyclene. Dauben and Cargill[11] have since shown the same situation to hold in the case of the parent hydrocarbons.

It has previously been shown[18] that the free-radical addition of benzenesulfonyl bromide to norbornadiene (I) gives a mixture of *endo*-3-bromo-*exo*-5-norbornen-2-yl phenyl sulfone (II) with one or more 5-bromo-3-nortricyclyl phenyl sulfones. The latter compound(s) appeared to be possible intermediates in the prepara-

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(1) (a) Previous paper in series: S. J. Cristol, R. Caple, R. M. Sequeira, and L. O. Smith, Jr., *J. Am. Chem. Soc.*, **87**, 5679 (1965). (b) The authors are indebted to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for generous support of this work.

(2) Unpublished results cited in ref 7.

(3) S. J. Cristol and R. L. Snell, *J. Am. Chem. Soc.*, **76**, 5000 (1954).

(4) S. J. Cristol and R. L. Snell, *ibid.*, **80**, 1950 (1958).

(5) L. Bryusova, *J. Gen. Chem. USSR*, **6**, 667 (1936).

(6) T. Hasselstrom and E. Falasco, Abstracts of Papers, 125th National Meeting of the American Chemical Society, Kansas City, Mo., March 1954, p 39N.

(7) M. Lipp, *Ber.*, **74B**, 1 (1941).

(8) R. T. LaLonde, Ph.D. Thesis, University of Colorado, 1957.

(9) H. W. Johnson and P. N. Landerman, *J. Org. Chem.*, **27**, 303 (1962).

(10) R. L. Young, Ph.D. Thesis, Brown University, 1959.

(11) W. G. Dauben and R. L. Cargill, *Tetrahedron*, **15**, 197 (1961).

(12) G. S. Hammond, N. J. Turro, and A. Fischer, *J. Am. Chem. Soc.*, **83**, 4674 (1961).

(13) H. G. Richey, Jr., and N. C. Buckley, *ibid.*, **85**, 3057 (1963).

(14) P. R. Story and S. R. Fahrenholtz, *ibid.*, **86**, 527 (1964).

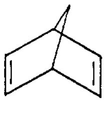
(15) D. I. Davies, private communication.

(16) R. M. Moriarty, *J. Org. Chem.*, **28**, 2385 (1963).

(17) P. von R. Schleyer, *J. Am. Chem. Soc.*, **80**, 1700 (1958).

(18) S. J. Cristol and D. I. Davies, *J. Org. Chem.*, **29**, 1282 (1964).

tion of 2-quadricyclyl phenyl sulfone (VII) *via* a γ-elimination process, which would represent the first chemical synthesis to the quadricyclene ring system. The formation of cyclopropane rings by such a procedure has been demonstrated in the preparation of cyclopropyl phenyl sulfone.[19]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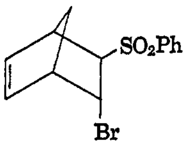

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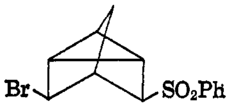

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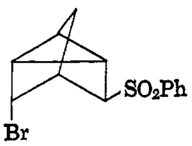

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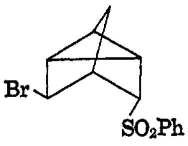

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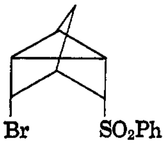

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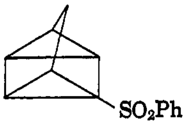

VII

When the reaction product from benzenesulfonyl bromide and norbornadiene was fractionated by chromatography on alumina, three products were separated. These were the unsaturated 1,2 addition product II and two saturated homoconjugate addition products *exo*-5-bromo-*exo*-3-nortricyclyl phenyl sulfone (III) and *endo*-5-bromo-*exo*-3-nortricyclyl phenyl sulfone (IV), the latter two in the ratio 4:3. (The ratio of saturated to unsaturated products varies with the concentration of the reactants.[18]) The product whose structure is assigned as III melted at 130–130.5° and that assigned as IV melted at 105.5–107°. The olefinic bromo sulfone II melted at 126–128°. In the assignment of structures II, III, and IV (and V as well) the following information was considered. The 130 and 107° compounds were saturated to potassium permanganate solution and had infrared absorption bands characteristic of nortricyclenes.[18,20] These isomers must therefore be isomeric at C-2 (sulfone carbon) or at C-5 (bromo carbon) or diastereoisomeric at both positions. The probability that they both have the same configuration (*exo*)[21] at C-2 is suggested by the general observations regarding addition of radicals to norbornenes and norbornadienes, in which there are now many examples of *exo* addition.[23] That they are not C-2 epimers was demonstrated by the fact that the 130° isomer was converted to a 50–50 mixture of itself and a new isomer, mp 106–108°, upon treatment with potassium hydroxide in methanol or with potassium *t*-butoxide in wet ether. This new isomer, which was separated from the mixture by alumina chromatography, was also saturated to potassium permanganate and was converted to the equilibrium mixture with the 130° isomer with base. Furthermore, when the isomerization was carried out with potassium deuteroxide in O-deuterio-*t*-butyl alcohol, one proton was exchanged by a deuterium atom. These data are consistent with structure III for the 130° isomer and V for the 108° compound.

When the 107° material was treated with base under conditions which epimerized III and V, it was recovered unchanged, although deuterium exchange was observed as with III and V. Molecular models suggest that steric strain should make VI a relatively unstable species, and thus IV can be assigned to the 107° substance.

Proton magnetic resonance data are consistent with these assignments. In the C-2 (sulfone) epimers III and V, the environments of the C-2 protons are nearly identical and the chemical shifts in both compounds should be nearly the same, while the protons at C-5 should be different. On this basis, the resonances at τ 6.96 for III and at 6.98 for V were assigned to the C-2 proton and those at τ 6.21 for III and at 6.08 for IV were assigned to the C-5 proton. The disappearance of the *ca.* τ 7.0 resonance for III and V upon deuteration confirmed this assignment. Similarly, one might expect that III and IV would have similar chemical shifts for the C-5 proton and different ones for that at C-2. The resonances at τ 6.21 for III and at 6.08 for IV were therefore assigned to the C-5 proton and that at τ 6.35 for IV was assigned to the C-2 proton. These data give further credence to the structural assignments, in that *endo* sulfone substituents deshield *endo* C-5 protons (compare τ 6.2 for III with 5.08 for V) and *endo* bromine deshields *endo* C-2 protons (compare τ 6.96 for III with 6.35 for IV). The proton magnetic resonance spectrum of II fits the assigned structure nicely. The 3-*exo*-proton at τ 5.58 are coupled to the 2-*endo* (τ 7.07) and 4-bridgehead (τ 6.75) protons at angles such that a triplet with spin–spin couplings of 3 cps is observed. The 2-*endo* proton in turn couples with the 3-*exo* proton and the 7-*anti*-proton (J = 1.5 cps) to give a doublet of doublets. This latter coupling is also seen, of course, in the splitting pattern of the 7-*anti* protons. Other proton magnetic resonance assignments not critical for structure determination are given in the Experimental Section.

When an attempt was made to eliminate the elements of hydrogen bromide from the unsaturated bromo sulfone II, with potassium hydroxide in methanol, an ether was obtained instead, which is tentatively assigned the structure VIII or IX. Analysis of the proton magnetic resonance spectrum of the ether and a comparison with that of II indicates that the ether and phenyl sulfone groups are *trans* (splitting of eclipsed hydrogens is not observed) but does not afford a clear-cut decision between them. The structure VIII is favored by analogy to other known addition reactions in bicyclic systems.[23] The ether is probably formed by elimination to X, followed by base-catalyzed addition of methanol.

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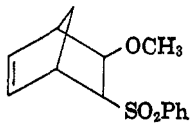
(19) (a) H. E. Zimmerman and B. S. Thyagarajan, *J. Am. Chem. Soc.*, **82**, 2505 (1960); (b) W. E. Truce and L. B. Lindy, *J. Org. Chem.*, **26**, 1463 (1961).

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

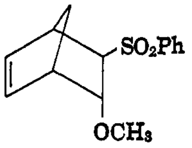
(21) It has been suggested[22] that nomenclature for polysubstituted nortricyclenes with one unsubstituted bridge uses the convention that substituents on the same side as the unsubstituted bridge (*syn* to C-7) be termed *exo* and those *anti* to C-7 be termed *endo*, and this paper utilizes that convention.

(22) S. J. Cristol and R. T. LaLonde, *J. Am. Chem. Soc.*, **80**, 4355 (1958).

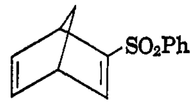
(23) For appropriate references see: S. J. Cristol and D. I. Davies in "Advances in Free Radical Chemistry," Vol. I, G. H. Williams, Ed., Logos Press, London, 1966, pp 155–209.



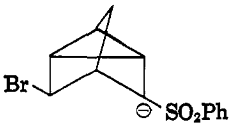
VIII



IX



X



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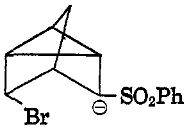

XII

The successful elimination of hydrogen bromide to give the diene X was accomplished by the use of potassium *t*-butoxide in ether at −5°. This product was identical with the product obtained by heating VII over a palladium-on-charcoal catalyst. The diene X was not isolated, but its solution had appropriate pmr absorbances.

When III was heated with potassium hydroxide in refluxing toluene, it was converted first to the III–V equilibrium mixture, and in 15 min about 40% was converted to 2-quadricyclyl phenyl sulfone (VII). The dehydrobromination to VII was complete in 4 hr. Potassium *t*-butoxide in dimethyl sulfoxide converted III to VII in 1 min at room temperature. On the other hand, the *endo*-bromo epimer IV was recovered substantially unchanged upon treatment with potassium *t*-butoxide in dimethyl sulfoxide for 7 hr. There seems to be no doubt that the carbanion XI is the intermediate in the interconversion of III and V and in the dehydrobromination of III and V to VII.

It would appear from these results that the formation of the cyclopropane ring from the carbanion XI has the normally expected[24] requirement for inversion in the nucleophilic attack of the carbanion carbon on the C-5 carbon atom in the formation of the 2,5 bridge. This is not possible with the epimeric *endo*-bromo carbanion XII.[25]

The fact that IV was recovered from severe treatment with base and gave neither the quadricyclene VII nor the norbornadiene X was unexpected in view of the fact that homoconjugate dehalogenation of 3,5-dihalonortricyclenes to give norbornadiene has been observed.[9] It would appear that either the carbanion XII has the wrong geometry to suffer homoconjugate elimination, or that the presence of a sulfonyl group stabilizes the carbanionic center so much that homoconjugate elimination is not allowed. There appears also to be the possibility that the dehalogenation of 2,5-halonortricyclenes is also stereoselective, as yields of norbornadiene were only 45–49% from the dibromo mixture and 70–75% from the diiodo mixture,[9] as well as the possibility that quadricyclene could have been an intermediate in these reactions in view of the observations of Dauben and Cargill[11] on its instability and ready rearrangement to norbornadiene.

Experimental Section

Benzenesulfonyl Bromide. The procedure of Otto and Ostrop[27] gave only a 52% yield in our hands. An improved method was found which simplified the above procedure and gave a yield comparable to that reported by Poshkus, Herweh, and Magnotta.[28]

Sodium benzenesulfinate dihydrate (Eastman Organic Chemicals; 50 g, 0.25 mole) was suspended with vigorous stirring in 150 ml of benzene, and 12.3 ml (0.25 mole) of bromine was added. When the bromine color persisted, about 100 mg of sodium benzenesulfinate was added, turning the solution colorless. The mixture was filtered to remove the precipitated sodium bromide. The benzene was removed from the filtrate using a rotary evaporator and finally a vacuum pump. There remained 48.6 g (98%) of benzenesulfonyl bromide, mp 19.5°.

Deuterium oxide (99.5% pure) was obtained from General Dynamics Corp.

Reagent grade dimethyl sulfoxide (Matheson Coleman and Bell) was passed through a molecular sieve (Linde, type 4A, $^1/_6$-in. pellets) column. The O–H infrared absorption (3500 cm^{-1}) for water was negligible.

Norbornadiene was supplied by the Shell Development Co. and was freshly distilled under reduced pressure prior to use.

Reagent-grade (MSA Research Corp.) potassium *t*-butoxide was used directly.

Proton magnetic resonance spectra were obtained on a Varian A-60 instrument, with materials in carbon tetrachloride solution, and with tetramethylsilane (τ 10.00) as internal standard.

Addition of Benzenesulfonyl Bromide to Norbornadiene.[18] Freshly distilled norbornadiene (55.5 g, 0.6 mole) was added to benzenesulfonyl bromide (111 g, 0.50 mole) in approximately 100 ml of benzene. The mixture was irradiated for 30 min with a 300-w, clear, tungsten-filament light bulb. The reaction was exothermic and the solution turned deep red in color. After a period of several hours the mixture crystallized. Carbon tetrachloride was used for recrystallization. After several recrystallizations, three distinct fractions could be separated. By infrared and proton magnetic resonance, the three fractions were shown to be *endo*-3-bromo-*exo*-5-norbornen-2-yl phenyl sulfone (II), *exo*-5-bromo-*exo*-3-nortricyclyl phenyl sulfone (III), and *endo*-5-bromo-*exo*-3-nortricyclyl phenyl sulfone (IV). IV was separated from the mixture using column chromatography and fractional crystallization. There was 37.5 g (0.12 mole, 24% based on the benzenesulfonyl bromide) of IV obtained from the reaction. A total of 50.0 g (0.16 mole, 32%) of crystalline III was obtained. A total of 13.0 g (0.04 mole, 8%) of II was obtained. Compound II melted at 126–128°, compound III at 130–130.5°, and compound IV at 105.5–107°.

Anal. Calcd for $C_{13}H_{13}BrO_2S$: C, 49.85; H, 4.18. Found for II: C, 49.94; H, 4.24. Found for III: C, 49.73; H, 4.28. Found for IV: C, 49.66; H, 4.16.

Vapor phase chromatographic analysis was conducted on the crude reaction mixture using a 1-m, 0.25-in. o.d. glass column packed with 20% silicone gum rubber (GE SE-30) on 60–80 mesh Chromosorb W at 198° and a flow rate of 69 ml/min of helium. Four major peaks were observed with retention volumes (and percentages in parentheses) of 2070 ml (13%), unidentified; 2415 ml (12%), II; 3100 ml (45%), III; and 3660 ml (30%), IV. These percentages assume that all substances have equal molar responses.

Neither III nor IV reacted with potassium permanganate in acetone, but both gave a precipitate with alcoholic silver nitrate upon heating for a few minutes at 70°.

***exo*-5-Bromo-*endo*-3-nortricyclyl Phenyl Sulfone (V).** To a solution of 1 g of III in 50 ml of ether was added 1 g of potassium *t*-butoxide suspended in ether. The mixture was heated at reflux for 15 min, after which it was poured into cold water. The resulting solution was neutralized by adding 5% sulfuric acid. The ether layer was separated and dried over anhydrous magnesium sulfate. The water layer was extracted with two 200-ml portions

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(24) H. M. Walborsky and C. G. Pitt, *J. Am. Chem. Soc.*, **84**, 4831 (1962).

(25) The requirement of inversion for ready ring closure of the cyclopropane ring is paralleled by another case in one laboratory: S. J. Cristol and B. B. Jarvis, unpublished work. On the other hand, it has been reported[26] that a cyclopropane ring is formed *with retention* at the carbon atom bearing the displaced chlorine in the formation of tricyclo[2.1.1.$0^{5,6}$]hexane-5-*t*-butylcarboxamide from *exo*-5-chloro-bicyclo[2.1.1]hexane-*exo*-6-*t*-butylcarboxamide by dehydrohalogenation with excess *n*-butyllithium. Details of these experiments have not yet appeared, so that mechanistic consideration by us seems unwarranted at this time.

(26) J. Meinwald, C. Swithenbank, and A. Lewis, *J. Am. Chem. Soc.*, **85**, 1880 (1963).

(27) R. Otto and H. Ostrop, *Ann.*, **141**, 365 (1867).

(28) A. C. Poshkus, J. E. Herweh, and F. A. Magnotta, *J. Org. Chem.*, **28**, 2766 (1963).

of ether. The ether extracts were combined, dried, filtered, and evaporated to dryness. A crystalline residue (1.0 g) containing III and V was recovered (mp 80–85°).

Anal. Calcd for $C_{13}H_{13}BrO_2S$: C, 49.85; H, 4.18. Found: C, 49.73; H, 4.19.

A mixture of III and V similarly prepared (2.65 g) was separated by column chromatography using 380 g of Merck alumina 71707 and by elution with 50% ethyl ether in carbon tetrachloride. The eleventh 250-ml fraction contained 217 mg of pure V, mp 106–108°. The center fractions contained 2.08 g of a mixture of III and V, mp 75–80°. The last fractions contained 220 mg of pure III, mp 129–130°.

2-Quadricyclyl Phenyl Sulfone (VII). Compound III (14.8 g, 0.0473 mole) was dissolved in 100 ml of dimethyl sulfoxide. To this solution was added quickly 6 g of potassium *t*-butoxide. The mixture was immediately cooled with ice and water. After 5 min, the mixture was neutralized with sodium bicarbonate and 5% sulfuric acid. The aqueous solution was extracted with ether.

The extracts were combined, dried, decolorized with activated charcoal, and evaporated using mild heating (steam bath) and reduced pressure (aspirator).

When the ether and residual dimethyl sulfoxide were gone, yellow crystals of VII remained. The residue (8.2 g, 75%) was dissolved in petroleum ether (bp 35–60°) with a minimum amount of carbon tetrachloride. The warm solution was redried with magnesium sulfate and cleared with activated charcoal. The solution was then filtered and cooled. Colorless crystals (mp 64–65°) of VII precipitated. The pmr spectrum showed aromatic protons (weight 5) between τ 1.9–2.5 and aliphatic protons (weight 7) in the region 7.4–8.6.

Anal. Calcd for $C_{13}H_{12}O_2S$: C, 67.21; H, 5.21. Found: C, 67.08; H, 5.11.

Isomerization of 2-Quadricyclo$[2.2.1.0.^{2,6}0^{3,5}]$heptyl Phenyl Sulfone (VII) to 2-Norbornadienyl Phenyl Sulfone (X). A solution of 409 mg (1.76 mmoles) of VII in 150 ml of reagent grade ethyl acetate, in which 518 mg of 5% palladium-on-charcoal catalyst was suspended, was heated at reflux and stirred for 24 hr. The solution was then cooled, and the catalyst was filtered from the solution. The filtered solution was concentrated on a rotary evaporator with great caution so as not to heat above 50° or remove all of the solvent. Carbon tetrachloride then was added to the solution and the solvent was partially removed under reduced pressure. This procedure was repeated several times until all the ethyl acetate was removed. These precautions were taken because in previous attempts to prepare X, when the solvent was completely removed, a polymeric material was isolated. A sample was removed from the carbon tetrachloride solution and the pmr spectrum was interpreted for structure X as follows: the two bridge protons at τ 7.91, the bridgehead protons at 6.30, the C-5 and C-6 protons at 3.43, and the C-3 proton at about 2.15 (this is at the edge of the absorption due to the aromatic protons, 2.15–2.65, and it was therefore difficult to judge the exact chemical shift).

Treatment of II with Bases. A solution prepared by dissolving 255 mg (0.81 mmole) of II in 50 ml of 0.026 *M* potassium methoxide in methanol was allowed to stand at room temperature for 2 hr. The reaction mixture was then poured into 150 ml of 5% ammonium chloride solution. The aqueous solution was extracted with three 100-ml portions of ether. The ether extracts were combined, extracted with saturated sodium chloride solution, dried over magnesium sulfate, filtered, and concentrated. The solvent was removed under reduced pressure (0.3 mm). The residue was recrystallized from carbon tetrachloride. The solid weighed 128 mg (61%) and melted at 95–97.5°. From spectral data and chemical data the product was shown to be 3-methoxy-5-norbornen-2-yl phenyl sulfone; pmr spectrum τ 2.1–2.6 (five aromatic protons), 3.7–4.1 (two olefinic protons), 6.4 (proton α to methoxy, a broad unresolved singlet, $w_{1/2} = 5$ cps), 6.8 (three methyl protons and proton α to sulfone), 7.2 (two bridgehead protons), and 8.4 (two bridge protons). Although this spectrum has not been analyzed in detail, the only large couplings were in the aromatic and vinyl proton regions. The fact that the resonance at τ 6.4 was *not* a doublet ($J = 6$ cps) is evidence that this proton is *trans* to the proton on the sulfone carbon atom.[29]

Anal. Calcd for $C_{14}H_{16}O_3S$: C, 63.61; H, 6.10. Found: C, 63.85; H, 5.97.

Potassium *t*-butoxide (69 mg, 0.62 mmole) was dissolved in 100 ml of *t*-butyl alcohol. To this solution was added 181 mg (0.58 mmole) of II. After 5 min the solution was poured into a solution of 15% ammonium chloride forming two liquid phases. The solution was extracted with three 100-ml portions of ether. The ether extracts were treated as those above. The oily residue was estimated by pmr to be a 3:2 mixture of X and II.

To a solution of II (0.1172 g, 0.374 mmole) in 100 ml of dry ether was added potassium *t*-butoxide (43 mg, 0.383 mmole). The temperature was maintained at −5° for 2.5 hr using an ice–salt bath. The solution was then filtered cold and the ether removed under reduced pressure (0.3 mm), keeping the contents of the flask close to 0°. Carbon tetrachloride was quickly added to avoid polymerization (refer to the section on the isomerization of VII). The proton magnetic resonance spectrum was identical with that of the product X from isomerization of VII.

Treatment of IV with Bases. When IV was treated with base under the same conditions of isomerization (potassium *t*-butoxide in ether) as its isomer II for 1.5 hr, it was recovered unchanged.

Even when treated with stronger base (potassium *t*-butoxide in dimethyl sulfoxide) starting material was recovered. II (300 mg, 0.96 mmole) was dissolved in 30 ml of dimethyl sulfoxide. To this solution was added potassium *t*-butoxide (173 mg, 1.53 mmoles). After 7 min, half of the solution was removed and quenched in water. The aqueous solution was acidified with dilute sulfuric acid, extracted with ether, dried over anhydrous magnesium sulfate, and filtered. The solvent was removed from the filtered extract using a rotary evaporator. The oily residue (115 mg) crystallized upon standing, mp 95–97.5°. The second half of the reaction was quenched after 7 hr by being poured into water. The aqueous solution was treated in the same manner as the 7-min aliquot, leaving a white crystalline solid (100 mg), mp 105–105.5°. The infrared spectra of the recovered materials from the two aliquots were identical with the spectrum of starting material IV. From similar treatment with higher ratios and concentrations of base, starting material was recovered, but in smaller yield.

A solution of potassium deuteroxide in O-deuterio-*t*-butyl alcohol was prepared from deuterium oxide (1.00 g, 0.050 mole) and potassium *t*-butoxide (3.20 g, 0.30 mole). To the slurry of base was added 201 mg (0.642 mmole) of IV. After 20 min, a small amount of supernatant liquid was decanted and the solvent was removed. The crude residue, mp 85–100°, was combined with the product extracted from the neutralized base solution. The pmr spectrum of the isolated product showed that the chemical shift at τ 6.2 assigned to the C-3 (sulfone) proton was absent. When IV was treated under identical conditions with undeuterated solvent, the pmr spectrum of the product was unchanged, showing that no significant epimerization had occurred.

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(29) S. J. Cristol, L. K. Gaston, and D. W. Johnson, *Tetrahedron Letters*, 185 (1963).