

Anal. Calcd. for $C_{10}H_{17}NO$: C, 71.81; H, 10.35; N, 8.38. Found: C, 71.77; H, 10.35; N, 8.38.

From the mother liquor, the residue appeared as a mixture of basic products which was not further characterized. If the reaction was allowed to stand overnight before working up, the only isolable product was still 10-hydroxylamino- $\Delta^{1,9}$ -octalin.

Reduction of XVII with Stannous Chloride.—The nitrosochloride adduct XVII (1 g., 0.005 mole) was added to a mixture of 4.5 g. of stannous chloride dihydrate in 6 ml. of concentrated hydrochloric acid with vigorous stirring. The reaction mixture was warmed on a water bath at 55–60°. The blue color disappeared after 30 min. The water bath was removed and stirring continued for another hour. The reaction mixture was diluted with water and washed with petroleum ether three times to remove any neutral products. The acidic solution was neutralized carefully with 10% sodium bicarbonate solution and extracted with ether. The ether layer was washed with saturated sodium chloride solution and dried over magnesium sulfate. Upon removal of solvent, the residue partially solidified. Recrystallization from hexane gave 0.2 g. of 9-hydroxylamino-10-chlorodecalin (XVIII), m.p. 116–117.5° (lit.^{23a} 116–120°); n.m.r. 4.38 τ for amino proton and hydroxyl proton).

Anal. Calcd. for $C_{10}H_{19}ClNO$: C, 58.96; H, 8.90; N, 6.87; Cl, 17.41. Found: C, 58.66; H, 8.89; N, 6.66; Cl, 17.23.

The hydroxylamine hydrochloride was prepared by treatment of this product with ethereal hydrogen chloride; m.p. 169–170° dec. (lit.^{23a} 172–174°).

The hexane mother liquor yielded no other pure components.

Reduction of XVII with Stannous Chloride Followed by Treatment with Base.—Compound XVII (2.0 g., 0.01 mole) was reduced with stannous chloride and concentrated hydrochloric acid as described above. After the same work-up, 1 g. of crude basic product was obtained. The basic mixture was treated with a solution of 6 g. of sodium hydroxide in 50 ml. of water and steam distilled. The distillate was collected in an ice bath until it was no longer cloudy. The distillate was extracted with ether and the ether layer dried with magnesium sulfate. After careful removal of the ether, 0.6 g. of an oil containing some crystals was obtained. Upon trituration with pentane, 0.1 g. of 10-hydroxylamino- $\Delta^{1,9}$ -octalin, m.p. 133–136° dec., was obtained. The

pentane mother liquor was evaporated to dryness, and the oily residue (0.43 g.) was distilled at 60–70° (1.5–2 mm.). Although thin layer chromatography on silica gel of the distilled sample showed two spots with one predominating, the infrared and n.m.r. spectra of this sample are essentially identical with those of the pure ethylenimine XX prepared and characterized by the method described below.

9-Amino-10-chlorodecalin Hydrochloride (XIX).—9-Nitroso-10-chlorodecalin (1 g.) was hydrogenated in ethyl acetate using pre-reduced platinum dioxide catalyst. The hydrogenation was completed in 2 hr. and stopped after 1 molar equivalent of hydrogen was absorbed. After removal of the catalyst and solvent, the solid residue was recrystallized from hexane to give 0.8–0.9 g. of crystals of XVIII, m.p. 116–118° dec.

A solution of XVIII (187 mg.) in 5 ml. of dilute hydrochloric acid and 5 ml. of ethanol was hydrogenated with pre-reduced platinum dioxide in dilute hydrochloric acid. The reduction was over in 3 hr. The catalyst was removed by filtration and the filtrate concentrated by warming on a steam bath under a stream of dry nitrogen. The amine hydrochloride (188 mg.) crystallized as plates, m.p. 233–235° dec. A small sample was recrystallized from water for analysis, yielding colorless crystals, m.p. 235–237° dec.

Anal. Calcd. for $C_{10}H_{19}NCl_2$: C, 53.58; H, 8.54; N, 6.25; Cl, 31.63. Found: C, 53.51; H, 8.59; N, 6.11; Cl, 31.52.

11-Azatricyclo[4.4.1.0^{1,6}]undecane (XX).—A mixture of 1.05 g. of 9-amino-10-chlorodecalin hydrochloride (XIX) and 8 g. of sodium hydroxide in 80 ml. of water was heated to boiling, and the distillate collected in an ice-water bath, until it was no longer cloudy. The aziridine steam distilled with the water and was extracted into ether. The ether extract was dried and evaporated. The residual oil was distilled at 75–90° (1.5 mm., bath temp.) to give 0.545 g. (78%) of XX indicated by thin layer chromatography on silica gel to be a single component. The infrared spectrum showed weak absorption at 3.10 μ . The n.m.r. spectrum showed two unresolved multiplets centered at 8.58 and 8.28 τ . No absorption in the olefinic region was observed.

Anal. Calcd. for $C_{10}H_{17}N$: C, 79.41; H, 11.33; N, 9.26. Found: C, 79.14; H, 11.32; N, 9.12.

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Stereochemistry of the Reaction of Benzal Chloride with Olefins

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Benzal chloride and potassium *t*-butoxide react in cyclohexene to form both 7-chloro-7-phenylnorcaranes. These compounds can be reduced by various reagents with either inversion or retention of configuration to give both 7-phenylnorcaranes. *endo*- and *exo*-7-phenylnorcarane have been separated and characterized. Benzal chloride and potassium *t*-butoxide form the expected cyclopropane derivatives with 1-heptene, 2,4-dimethyl-2-pentene, and *cis*- and *trans*-4-methyl-2-pentene. A study of the products from the latter olefins showed the reaction to be stereospecific and somewhat stereoselective.

In 1954, Doering and Hoffmann¹ obtained 7,7-dichloronorcarane (7,7-dichlorobicyclo[4.1.0]heptane) from the reaction of potassium *t*-butoxide, chloroform, and cyclohexene. This was the first structural evidence of the postulated dichlorocarbene intermediate proposed by Hine² for the alkaline hydrolysis of chloroform. This "divalent carbon reaction" has been extended to include the base-catalyzed reactions of a number of other halogen-substituted compounds in the presence of olefins.^{3a-f} In the more specific case of

phenyl-substituted chloromethanes, Closs and Closs⁴ have shown that benzyl chloride and *n*-butyllithium react with cyclohexene to form a mixture of 7-phenylnorcaranes, which was characterized, but the two isomers were not separated. McElvain and Weyna^{5a,b} have isolated 1,1-dimethyl-2,2-diethoxy-3-phenyl-3-chlorocyclopropane from the reaction of sodium *t*-butoxide and benzal chloride in dimethylketene diethyl acetal. Recently, Moss⁶ studied the reaction of benzal chloride with some olefins and developed an improved reaction employing methyllithium as the base. It was our purpose to study the stereochemistry and behavior of the reaction of benzal chloride and potassium *t*-butoxide with several olefins.

(1) W. von E. Doering and A. K. Hoffmann, *J. Am. Chem. Soc.*, **76**, 6162 (1954).

(2) J. Hine, *ibid.*, **72**, 2438 (1950).

(3) (a) P. S. Skell and A. Y. Garner, *ibid.*, **78**, 5430 (1956); (b) G. L. Closs and L. E. Closs, *ibid.*, **81**, 2579 (1959); (c) W. von E. Doering and W. A. Henderson, *ibid.*, **80**, 5274 (1958); (d) W. E. Parham, E. C. Loew, and E. E. Schweizer, *J. Org. Chem.*, **24**, 1900 (1959); (e) L. Friedman and J. G. Berger, *J. Am. Chem. Soc.*, **82**, 5758 (1960); (f) P. S. Skell and A. P. Krapcho, *ibid.*, **83**, 754 (1961).

(4) G. L. Closs and L. E. Closs, *Tetrahedron Letters*, **No. 24**, 26 (1960).

(5) (a) S. M. McElvain and P. L. Weyna, *J. Am. Chem. Soc.*, **81**, 2579 (1959); (b) R. Breslow, R. Haynie, and J. Mirra, *ibid.*, **81**, 247 (1959).

(6) R. A. Moss, *J. Org. Chem.*, **27**, 2683 (1962).

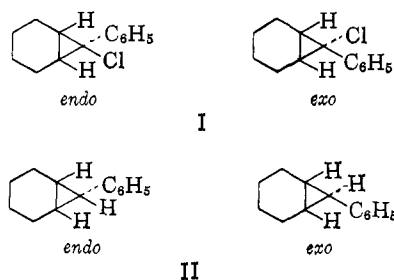
TABLE I
REDUCTION OF 7-CHLORO-7-PHENYLNORCARANE

Method	Benzalcylohexane, %	<i>endo</i> -II, %	<i>exo</i> -II, %
Zn, 5% sodium ethoxide	8	19	73
K in liq. NH ₃ (ethanol)	11 ^a	58	31
H ₂ , Pd-C, ethanol	10 ^a	38	52
Zn, acetic acid	16	29	45 ^b
LiAlH ₄

^a In these two methods the product was actually benzalcylohexane. ^b Reductions with Zn in ethanol or aqueous or pure acetic acid solutions did not go to completion. In this particular case 10% of starting material was recovered.

Benzal chloride reacts with cyclohexene to form 7-chloro-7-phenylnorcarane (7-chloro-7-phenylbicyclo[4.1.0]heptane, I) in the presence of potassium *t*-butoxide, sodium *t*-butoxide, lithium *t*-butoxide, benzoyl peroxide, and ultraviolet light. The best yield, some 27% based on potassium, is given by the first base. Potassium and sodium naphthalene, lithium *t*-butoxide, benzoyl peroxide, and ultraviolet light gave very little yield of I when used in the reaction. The isomers of I were difficult to separate even by gas chromatography, but it was finally accomplished on a ditricinoleate glycol 400 polyethylene column; *endo*- and *exo*-I⁷ are formed in the ratio of about 1:1.5. These compounds could not be separated in the pure state for direct analysis, but the mixture showed elemental analysis, ultraviolet, infrared, and n.m.r. spectra consistent with structure I. Tentative structures can, however, be assigned to the isomers by reasoning from the reduction products, to be discussed later, which indicates that the *exo* isomer is the predominant one produced in the reaction. This stereoselectivity has been substantiated by similar results with other olefins.

Reduction of *endo*- and *exo*-I by the various methods shown in Table I gave different ratios of *endo*- and *exo*-7-phenylnorcarane (7-phenylbicyclo[4.1.0]heptane, II).



Clearly, from Table I, the reductions with Zn in 5% sodium ethoxide give the cleanest stereospecific reductions. (Since the yield of *exo*-II in this particular reduction is somewhat higher than would be expected from the ratio of starting isomers, there must have been some inversion, amounting to 10–15%, of the *endo*-I isomer. We have used the term "stereodirective" to indicate the possibility of a chemical reagent giving either inversion or retention of configuration during a reaction in which there is a large difference in the thermodynamic stability of the products or in the transition-state energies.) In all of the reductions with Zn we have assumed retention of configuration by analogy with other not too related systems.^{3a-c} We have also assumed

(7) The phenyl ring is used here for reference. The *endo* isomer has the phenyl ring adjacent to the ring carbons of the cyclohexane ring.

(8) (a) C. Weygand, "Organic Preparations," Interscience Publishers

that K in liquid NH₃ proceeds with inversion of configuration because of its action in other reductions^{9a,b} and because this follows from the assumption above and the results of Table I. The fact that H₂, Pd-C gives retention of configuration is not too surprising if one considers the affinity the chlorine atom probably has for the Pd surface. The structures of the three products of the reduction were established in the following way: benzalcylohexane could not be separated from the other isomers primarily because of its low yield, so that it was necessary to deduce its structure from a comparison of its v.p.c. retention time to pure synthetic samples of benzalcylohexane,¹⁰ 1-benzylcyclohexene,¹¹ 1-phenylcycloheptene,¹² 1,2,3,4-tetrahydrofluorene,¹³ 1a,1,2,3-tetrahydrofluorene,¹⁴ and the corresponding saturated hydrocarbons. Mixture v.p.c. results also confirmed the structure assignment of the olefin of the reduction as being benzalcylohexane. *exo*-II was separated in pure form from the mixture by first removing benzalcylohexane with ozone and then distilling the olefin-free mixture through a spinning band column. *endo*-II could only be separated by collecting this isomer at the exit port of a gas chromatograph. The purity of both isomers were checked at every stage of their purification by v.p.c. After separation, both compounds were compared to the same isomers prepared by the reaction of phenyldiazomethane with cyclohexene.¹⁵ Both *endo*- and *exo*-II could be reduced to benzylcyclohexane, the first with ease and the second with some difficulty. They both had the correct elemental analysis, the expected ultraviolet spectra for phenylcyclopropanes,¹⁶ and confirmatory infrared spectra. The n.m.r. spectra of the two isomers gave good evidence for the stereochemical assignments. *exo*-II showed a single band in the aromatic region for the phenyl hydrogens, whereas *endo*-II showed a "Christmas tree" splitting of the phenyl hydrogens owing to their close proximity to the cyclohexane hydrogens.¹⁷ The ultraviolet spectra of *exo*- and *endo*-II showed increased conjugation in the *endo* isomer by a shift of the phenylcyclopropane absorption 5 mμ to the red. This may be caused by the inability of the phenyl ring to rotate in this isomer and therefore to no loss of ring-ring electronic interactions as in the *exo* isomer.

An attempt was made to form other cyclopropane derivatives by the reaction of benzal chloride and potassium *t*-butoxide in the presence of other olefins; these included tetrachloroethylene, 2-methyl-2-butene.

Inc., New York, N. Y., 1945, p. 44; (b) B. S. Rabinovitch and F. S. Looney, *J. Am. Chem. Soc.*, **75**, 2652 (1953); (c) C. Liebermann and W. Scholz, *Ber.*, **25**, 950 (1892).

(9) (a) A. J. Birch and H. Smith, *Quart. Rev. (London)*, **12**, 17 (1958); (b) F. Sondheimer, O. Mancera, G. Rosenkranz, and C. Djerassi, *J. Am. Chem. Soc.*, **75**, 1282 (1953).

(10) H. Christol, A. Laurent, and M. Mousseron, *Bull. soc. chim. France*, 2313 (1961).

(11) This olefin was prepared by dehydration of cyclohexylphenylcarbinol with 85% phosphoric acid. These acid conditions cause a shift of the double bond out of conjugation with the phenyl ring and into the cyclohexane ring; cf. H. J. Schaeffer and C. J. Collins, *J. Am. Chem. Soc.*, **78**, 124 (1956).

(12) J. W. Huffman and J. W. Engle, *J. Org. Chem.*, **26**, 3166 (1961).

(13) J. Colonge and J. Sibeud, *Bull. soc. chim. France*, 75 (1953).

(14) E. D. Bergmann and R. Ikan, *J. Am. Chem. Soc.*, **78**, 2821 (1956).

(15) J. E. Hodgkins, D. H. Gibson, and J. A. King, unpublished work. The *exo* isomer predominates under all reaction conditions and with all catalysts tried.

(16) M. T. Rodger, *J. Am. Chem. Soc.*, **69**, 2544 (1947).

(17) Models show a great deal of crowding of the two rings in the *endo* II isomer and none in the *exo* II isomer.

1-octene, 1-methylcyclohexene, 1,1-diphenylethylene, and cyclohexene at 0°. All these reactions were unsuccessful either because the yields were too low for purification of the products or because the products were unstable. Yields of expected products were obtained from reactions in 1-heptene, 2,4-dimethyl-2-pentene, and in the two olefins discussed below. We have observed independently and in agreement with Moss⁶ that this reaction of benzal chloride and butoxide cannot be considered a good "preparative procedure" for cyclopropanes. The yields of this reaction rarely exceed 30%, and it is remarkably temperature dependent in that no yield of cyclopropane derivatives is obtained at temperatures below 50° (cf. ref. 6). In one experiment with methyl chloroacetate in the reaction with 1-decene and potassium *t*-butoxide at 150°, we obtained definite spectral and elemental evidence for the formation of 1-chloro-1-carbomethoxy-2-octylcyclopropane. The final yield of this purified compound was about 3%. An attempt was made to separate in pure form the cyclopropane derivatives formed from the reaction of benzal chloride and 2,5-dihydrofuran without success. It was hoped that increased splitting of the phenyl ring hydrogens by the oxygen atom of the *endo* isomer would further confirm our assignments made on the n.m.r. spectra of *endo*-II.

Reasonably pure cyclopropane derivatives were obtained from the reaction of benzal chloride, potassium *t*-butoxide, and both *cis*- and *trans*-4-methyl-2-pentene. From each olefin there was obtained two cyclopropane products, giving a total of four different chlorocyclopropane derivatives. These compounds were reduced to four different 1-phenyl-2-isopropyl-3-methylcyclopropanes with Zn in 5% sodium ethoxide. The reduced products were identical with the products formed from *cis*- and *trans*-4-methyl-2-pentene and phenyldiazomethane catalyzed by either Ag-Cu couple or ultraviolet light.¹⁵ The cyclopropanes were characterized by the usual methods. Thus, there can be little doubt that both the benzal chloride and the phenyldiazomethane reactions are stereospecific. Of great interest is the fact that the ratio of the cyclopropanes from the *cis*-olefin was 1:2.5 and the ratio from the *trans*-olefin was 1:1.73. This stereoselectivity indicates either that there is some steric control of the benzal chloride species as it approaches the double bond prior to cyclopropane formation or that some rotation is possible about any *newly formed bond* before ring closure.

As to mechanism, no rigorous statements can be given. By analogy to other chloroform derivatives, it would seem to be a "divalent carbon" reaction but certainly not of the same variety of unstable divalent carbon described by Herzberg.¹⁸ Resonance stabilization (delocalization) of phenylchlorocarbene of the type described by Skell¹⁹ may possibly account for this stability. We performed two separate series of experiments in hopes of gaining some information about the mechanism. The first series evolved the reaction of cumylpotassium,²⁰ cumene (isopropylbenzene), and cyclohexene. Some 5% of dimethylcyclohexylphenylmethane was obtained indicating *anionic* addition to an isolated double bond (see below) by an anion resembling

the anion of benzal chloride. In the former case the product would be formed by hydrogen exchange of the adduct with a donor species such as cumene. We also observed, however, simultaneous formation of *sym*-tetramethyldiphenylethane. Since this result suggests the presence of free radicals, no definite conclusions can be drawn about the addition reaction. In the second series, the bases potassium *t*-butoxide and *n*-butyllithium, dissolved in cyclohexene, were investigated for free radicals by the e.s.r. method.²¹ Definite spectra were obtained for *carbon free radicals* in both cases with *n*-butyllithium showing the lowest concentrations. This suggests the possibility of free-radical reactions. On the other hand, the known free-radical complexes, potassium or sodium naphthalene, gives very little yield of cyclopropane derivative in the reaction with benzal chloride and cyclohexene. Potassium or sodium metal is, however, known to give analogous reactions in other systems.²² All of these rather confusing results suggests that more studies be made of the bases normally used in organic reactions in pure form, in solution of organic solvents, and under "normal" reaction conditions. The other alkali metals, rubidium and cesium, should be included in these studies.

Experimental

A Perkin-Elmer gas chromatograph Model 800, equipped with a 15-ft. 1/8-in. copper column packed with 5% Ucon lubricant on Chromosorb P, was employed for all general analyses. The chromatograph was operated at 150° for all routine analyses, and as low as 120° to separate the C₁₂H₁₄, C₁₃H₁₆, and C₁₄H₁₈ hydrocarbons. A 15-ft. 1/8-in. copper column packed with 5% Apiezon L grease on Chromosorb P operated at 120° was used to separate the 1-phenylcycloheptene and phenylcycloheptane from *endo*-7-phenylnorcarane and *exo*-7-phenylnorcarane, respectively. The *endo*- and *exo*-7-chloro-7-phenylnorcarane were separated on a 15-ft. 1/8-in. 5% copper column packed with di(triisnoleate) glycol 400 polyethylene on Chromosorb P operated at 130°. The carrier gas was nitrogen, and the flow was 10 cc. per 25 sec. An F & M gas chromatograph Model 500, equipped with a 12-ft. 0.25 in. copper column packed with 20% Ucon lubricant on firebrick, was used to purify the 7-phenylnorcaranes. The oven was operated at 175°. The infrared spectra were obtained with a Perkin-Elmer Model 237 grating infrared spectrophotometer using sodium chloride cells. Ultraviolet spectra were obtained with a Beckman Model DK-2 spectrophotometer. The nuclear magnetic resonance spectra were obtained using a Varian Model A-60 spectrometer. Melting points and boiling points are uncorrected.

Potassium *t*-butoxide was prepared by adding 1 l. of dry *t*-butyl alcohol to a 2-l. four-necked flask equipped with a condenser fitted with a calcium chloride tube, mechanical stirrer, thermometer, and a stopper. The temperature was adjusted to approximately 75° and then potassium metal (20 g., 0.512 mole) was added in small pieces. After completion of the reaction, the excess *t*-butyl alcohol was distilled *in vacuo*.

7-Chloro-7-phenylnorcarane was prepared by adding cyclohexene (400 ml.) to the potassium *t*-butoxide prepared above. Purified benzal chloride (82 g., 0.51 mole) was added to the stirred refluxing solution dropwise through a dropping funnel over a period of 1.5 hr. The reaction mixture was refluxed for an additional 6 hr., cooled, and 500 ml. of water added. The organic layer was separated and washed with water until the aqueous layer was neutral, and then it was washed with a saturated solution of sodium chloride and dried over calcium

(21) We wish to thank Dr. J. A. Staples, III, for running the e.s.r. curves.

(22) W. Kirmse and W. von E. Doering, *Tetrahedron*, **11**, 266 (1960). The possibility of free-radical abstractions, exchanges, and displacements were not considered in this work. Since these types of mechanisms represent rather involved paths, they can be argued against but remain possible in low yield reactions, especially when other free-radical products (usually considered to be) are formed. For example, the deuterium results in this work could be explained by a 1,3-exchange-displacement reaction (perhaps with participation of metal or radical in the displacement) of (CH₃)₂C-CH₂ in which the exchanging hydrogen is not available for displacement.

(18) G. Herzberg, *Proc. Roy. Soc. (London)*, **262**, 291 (1961).

(19) See ref. 3a.

(20) K. Ziegler and H. Dislich, *Ber.*, **90**, 1107 (1957).

chloride. The excess cyclohexene was distilled *in vacuo*, and the resulting residue distilled to give 28 g. (27% based on potassium) of 7-chloro-7-phenylnorcarane, b.p. 170–173° at 33 mm. For purposes of analysis this fraction was redistilled through a spinning band distillation column at 3 mm., n_D^{20} 1.5562. Analysis by gas chromatography showed that the ratio of isomers was 1:1.5. The ultraviolet spectrum (cyclohexane) showed bands 221 (ϵ 8360) and 206.5 $m\mu$ (ϵ 8680).

Anal. Calcd. for $C_{13}H_{13}Cl$: C, 75.53; H, 7.31; Cl, 17.15. Found: C, 75.92; H, 7.44; Cl, 16.66.

Activated zinc dust²³ was prepared by adding hydrochloric acid (4 *N*) to zinc dust which had been placed in a beaker. The mixture was stirred for a minute and then filtered and washed quickly with large volumes of 10% sodium hydroxide, water, 95% ethanol, absolute ethanol, acetone, absolute ether, and then dried under vacuum on a hot plate at 200° for 1 hr.

Reduction of 7-Chloro-7-phenylnorcarane. A. Reduction Using Activated Zinc Dust.—A 5% solution of sodium ethoxide was prepared from 300 ml. of ethanol and 12 g. (0.522 g.-atom) of sodium. After completion of the reaction, 35 g. of activated zinc dust and 25 g. (0.121 mole) of 7-chloro-7-phenylnorcarane were added. The mixture was refluxed with vigorous stirring for 40 hr., cooled, and filtered. Water was added to the filtrate and the aqueous solution extracted with ether. The ethereal extract was washed with water and dried over calcium chloride. The ether was evaporated on a steam bath and the residue distilled *in vacuo* to give 15.4 g. (74%) of 7-phenylnorcarane, b.p. 127–128° at 13 mm., n_D^{20} 1.5524. Analysis by gas chromatography showed 7.9% benzaldehyde, 73.2% *exo*-7-phenylnorcarane, and 18.9% *endo*-7-phenylnorcarane.

Anal. Calcd. for $C_{13}H_{18}$: C, 90.61; H, 9.36. Found: C, 90.90; H, 9.39.

B. Reduction Using Potassium in Liquid Ammonia.—Ammonia, *ca.* 100 ml., was introduced into a 500-ml. four-necked flask equipped with a magnetic stirrer bar, Dry Ice condenser, a gas inlet tube, dropping funnel, and a stopper. Potassium (25 g., 0.64 g.-atom) was added in small pieces, and then the 7-chloro-7-phenylnorcarane (21.65 g., 0.105 mole) in 40 ml. of absolute ethanol was added dropwise. After 30 min., an additional 60 ml. of absolute ethanol was added, and the ammonia was allowed to evaporate overnight. Water was added, and the aqueous solution was extracted with ether. The ethereal solution was washed with water and then dried over calcium chloride. The ether was evaporated, and the residue distilled *in vacuo* to give 14.53 g. (80.5%) of 7-phenylnorcarane. Analysis by gas chromatography showed 11.3% benzylcyclohexane, 30.5% *exo*-7-phenylnorcarane, and 58.2% *endo*-7-phenylnorcarane.

C. Reduction Using Hydrogen over Palladium on Charcoal.—Hydrogenation of 7-chloro-7-phenylnorcarane was carried out by the same procedure employed for the hydrogenation of 1-phenylcycloheptene (see below). The pressure of hydrogen was 40 p.s.i., and the catalyst was palladium on charcoal. The reaction was allowed to run for 25 hr. The yield was 70% of 7-phenylnorcarane (see Table I).

D. Reduction Using Zinc Dust in Acetic Acid.—To 10 g. of zinc dust and 5.0 g. of 7-chloro-7-phenylnorcarane was added 20 ml. of acetic acid, and the solution was refluxed for 12 hr. The solution was extracted with ether, washed with 10% sodium hydroxide several times to remove the acid, separated, dried, and distilled *in vacuo* to give 44% total recovered material. See Table I for results of the reduction.

E. Reduction Using Zinc Dust in 90% Acetic Acid.—The reaction was carried out in the same manner as before except that water was added to make a 10% solution of water in acetic acid. The reaction time was 4 hr. The product distilled *in vacuo* to give 42% total recovered material. See Table I for the results of the reduction.

Purification of *endo*- and *exo*-7-Phenylnorcarane. A. Distillation.—The *exo*-7-phenylnorcarane was purified by distilling the mixture from the zinc-ethanol reduction very carefully through a spinning band distillation column at 35 mm. The first fractions containing only benzaldehyde and *exo*-7-phenylnorcarane were combined and treated with ozone as described below, thus yielding pure *exo*-7-phenylnorcarane. The ultraviolet spectrum (cyclohexane) showed bands at 218 (ϵ 7700) and 211 $m\mu$ (ϵ 7700), n_D^{20} 1.5402.

The *endo*-7-phenylnorcarane could be purified in a similar manner by distilling the products from the potassium in liquid ammonia reduction through a spinning band distillation column at 35 mm. The latter fractions were 80% pure in the *endo*-7-phenylnorcarane.

B. Trapping.—The two isomers of 7-phenylnorcarane produced from the zinc-ethanol reduction were purified from the by-product of the reaction, benzaldehyde, by bubbling a stream of 2.2% ozone at a rate of 0.5 l. per min. into a mixture of 9.8 g. of the reduced material in 200 ml. of acetic acid. The gas was then bubbled through a 2% potassium iodide solution. The reaction was allowed to proceed for 10 to 15 min. after iodine first appeared in the potassium iodide trap. After completion of the reaction, 200 ml. of 10% hydrogen peroxide was added, and the solution was allowed to stand overnight. The aqueous solution was extracted with ether. The ethereal solution was washed with dilute base, water, and then dried over calcium chloride. The ether was evaporated, and the residue distilled *in vacuo* to give 8.05 g. (82% recovery) of the 7-phenylnorcaranes. Analysis by gas chromatography and infrared confirmed that all the benzaldehyde had been removed. The 7-phenylnorcaranes were separated from each other by trapping samples on a F & M gas chromatograph, Model 500. The sample was eluted on a 12-ft. 0.25 in. copper tube packed with 20% Ucon lubricant on 60–80 mesh firebrick. Samples were collected at the exit port in a U-shaped 4-mm. tube which was placed in an ice bath. The *exo*-7-phenylnorcarane collected was 95% pure. Determination of the purity of the samples was accomplished by using a Perkin-Elmer gas chromatograph, Model 800.

The 7-phenylnorcaranes prepared by the potassium-liquid ammonia reduction could also be purified by trapping. The *exo*-7-phenylnorcarane obtained in this manner was *ca.* 90% pure, and the *endo*-7-phenylnorcarane obtained in this manner was 90–95% pure. The ultraviolet spectrum (cyclohexane) of *endo*-7-phenylnorcarane obtained in this manner showed bands at 224.5 $m\mu$ (ϵ 11,950) and 205.5 $m\mu$ (ϵ 8730).

Hydrogenation of *endo*-7-phenylnorcarane was carried out by the same procedure employed for the hydrogenation of 1-phenylcycloheptene (see below). The pressure of hydrogen was 75 p.s.i., and the catalyst was platinum. The reaction was allowed to run for 24 hr., and product analysis (v.p.c.) showed complete reduction to benzylcyclohexane.

Hydrogenation of *exo*-7-phenylnorcarane was carried out as stated above except the reaction time was 3 weeks. Analysis (v.p.c.) of the products showed that 58.5% of the material had been reduced to benzylcyclohexane.

Reaction of Benzal Chloride, Potassium *t*-Butoxide, and *cis*-4-Methyl-2-pentene.—To potassium *t*-butoxide (prepared from 9.5 g. of potassium) was added *cis*-4-methyl-2-pentene (73.5 g., 0.875 mole). Benzal chloride (39.7 g., 0.246 mole) was added dropwise over a period of 3 hr. to the refluxing mixture. The reaction was refluxed for an additional 6 hr., cooled, and then 300 ml. of water was added. The organic material was extracted with ether, washed with water, and dried over calcium chloride. The ether and the unreacted *cis*-4-methyl-2-pentene were distilled and the resulting residue distilled *in vacuo* to give 21.08 g. (41.3%) of 1-chloro-1-phenyl-2-methyl-3-isopropylcyclopropane, b.p. 126–135° at 25 mm. This fraction was redistilled through a spinning band distillation column for purposes of analysis; n_D^{20} 1.5174. The ratio of isomers was found to be 1:2.5.

Anal. Calcd. for $C_{13}H_{17}Cl$: C, 74.80; H, 8.21; Cl, 16.90. Found: C, 75.89; H, 8.12; Cl, 15.82.

Reduction of 1-Chloro-1-phenyl-2-methyl-3-isopropylcyclopropane (from *cis*-4-Methyl-2-pentene).—A 5% sodium ethoxide solution in 34 ml. of absolute ethanol was prepared as before. To this solution was added 6 g. of activated zinc dust and 1-chloro-1-phenyl-2-methyl-3-isopropylcyclopropane (3.85 g., 0.0184 mole, prepared from *cis*-4-methyl-2-pentene). The solution was refluxed with vigorous stirring for 40 hr., cooled, and filtered. The filtrate was worked up as before. Distillation afforded 2.65 g. of total distillate (81.5% of 1-phenyl-2-methyl-3-isopropylcyclopropane, b.p. 115–122° at 19 mm. The fourth fraction which boiled at 121–122° at 19 mm., n_D^{20} 1.5120, was analyzed.

Anal. Calcd. for $C_{13}H_{18}$: C, 89.59; H, 10.41. Found: C, 88.63; H, 10.31.

Reaction of Benzal Chloride, Potassium *t*-Butoxide, and *trans*-4-Methyl-2-pentene.—This reaction was carried out in exactly the same manner and with the same quantities of reagents as the

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reaction of benzal chloride and *cis*-4-methyl-2-pentene. The yield was 26.83 g. (53.7%) of 1-chloro-1-phenyl-2-methyl-3-isopropylcyclopropane, b.p. 112–128° at 12 mm. This fraction was redistilled through a spinning band distillation column for purposes of analysis; n_D^{20} 1.5294. The ratio of isomers was found to be 1:1.73. Analysis showed the compound to be impure; however, upon reduction, the impurity, which was most likely benzal chloride, was reduced to toluene which could be separated from the cyclopropane derivatives (see below). The yield stated is obviously in error owing to the impurities present.

Reduction of 1-Chloro-1-phenyl-2-methyl-3-isopropylcyclopropane (from *trans*-4-Methyl-2-pentene).—A 5% sodium ethoxide solution in 68 ml. of absolute ethanol was prepared as before. To this solution was added 20 g. of zinc dust and 1-chloro-1-phenyl-2-methyl-3-isopropylcyclopropane (10.02 g., 0.048 mole, prepared from *trans*-4-methyl-2-pentene). The solution was refluxed with vigorous stirring for 40 hr., cooled, and filtered. The filtrate was worked up as before. Distillation afforded 6.21 g. of total distillate (75%) of 1-phenyl-2-methyl-3-isopropylcyclopropane, b.p. 115–125° at 20 mm. The third fraction which boiled at 120–125° at 20 mm., n_D^{20} 1.5017, was analyzed.

Anal. Calcd. for $C_{13}H_{15}$: C, 89.59; H, 10.41. Found: C, 88.68; H, 10.18.

1-Chloro-1-phenyl-2-pentylcyclopropane was prepared by adding 1-heptene (325 ml.) to potassium *t*-butoxide (prepared from 16.20 g., 0.415 g.-atom, of potassium). Purified benzal chloride (66.4 g., 0.413 mole) was added dropwise over a period of 1.5 hr. to the stirred solution heated to 87°. The mixture was stirred at this temperature for an additional 6 hr., cooled, and worked up as before. The product distilled *in vacuo* to give 9.62 g. (10%) of 1-chloro-1-phenyl-2-pentylcyclopropane, b.p. 164–167° at 28 mm. For purposes of analysis a small sample of this material was eluted through alumina with petroleum ether-ether.

Anal. Calcd. for $C_{14}H_{19}Cl$: C, 75.48; H, 8.60; Cl, 15.92. Found: C, 75.55; H, 8.63; Cl, 15.93.

1-Phenylcycloheptanol²⁴ was prepared in 72.5% yield, b.p. 161–163° at 14 mm., n_D^{20} 1.5478. The alcohol was crystallized from petroleum ether (b.p. 30–60°), m.p. 24–25° (lit.²⁴ n_D^{20} 1.5515, lit.²⁵ b.p. 136° at 8 mm., m.p. 23°, n_D^{20} 1.5493; lit.²⁶ b.p. 119–120° at 0.4 mm., m.p. 24–25°).

1-Phenylcycloheptene.—1-Phenylcycloheptanol (9.65 g., 0.0508 mole) and 85% phosphoric acid (3.5 ml.) were placed in a 100-ml. flask equipped with a magnetic stirring bar and a reflux condenser. The mixture was heated to 120° for 1 hr. with vigorous stirring. After completion of the reaction, water was added, and the organic material was extracted with ether, washed with water, and dried over calcium chloride. The ether was evaporated, and the residue distilled *in vacuo* to give 6.72 g. (77%) of 1-phenylcycloheptene, b.p. 131–132° at 14 mm., n_D^{16} 1.5559. The ultraviolet spectrum (cyclohexane) showed bands at 247 (ϵ 14,500) and 208.5 μ (ϵ 16,750) (lit.²⁵ b.p. 113–115° at 8 mm., n_D^{20} 1.5624; lit.¹² b.p. 74–75.5° at 0.3 mm., n_D^{20} 1.5575, λ_{max}^{alc} 247 μ (ϵ 14,000); lit.²⁶ b.p. 115–116° at 10 mm., λ_{max}^{alc} 247 μ (ϵ 11,500)).

Phenylcycloheptane.—1-Phenylcycloheptene (3.97 g., 0.023 mole) was hydrogenated in 20 ml. of ethanol with 0.1 g. of 5% palladium on charcoal for 3 hr. in a Paar hydrogenator (50 p.s.i.). The solution was filtered through Celite, and the alcohol evaporated yielding 3.82 g. (95%) of phenylcycloheptane, b.p. 123–124° at 12 mm., n_D^{20} 1.5256 (lit.²⁷ b.p. 80–82° at 0.65 mm., n_D^{20} 1.5287, n_D^{20} 1.5309; lit.²⁸ n_D^{20} 1.5290).

Cyclohexylphenylcarbinol²⁹ was prepared from benzaldehyde and cyclohexyl chloride³⁰ in 75% yield, b.p. 181–183° at 30 mm. The alcohol was crystallized from ligroin (b.p. 60–90°), m.p. 48–49° (lit.²⁹ m.p. 49–50°, lit.³¹ b.p. 139–142° at 5 mm.; lit.²⁹ b.p. 141° at 20 mm.).

Anal. Calcd. for $C_{13}H_{18}O$: C, 82.06; H, 9.54; O, 8.41. Found: C, 82.00; H, 9.43.

1-Benzylcyclohexene.—Cyclohexylphenylcarbinol (50 g., 0.263 mole) and 85% phosphoric acid (13 ml.) were placed in a 100-ml. flask equipped with a magnetic stirring bar and a reflux condenser. The mixture was heated to 120° for 4 hr. with vigorous stirring. The reaction was worked up as before yielding 35.06 g. (77.5%) of a mixture which was 82% 1-benzylcyclohexene and 18% benzaldehyde, b.p. 120° at 14 mm. The distillate was redistilled through a spinning band distillation column, and the second fraction was found to be 95% pure in 1-benzylcyclohexene, n_D^{20} 1.5375 (lit.³² b.p. 125° at 11 mm., n_D^{20} 1.5419).

Anal. Calcd. for $C_{13}H_{16}$: C, 90.64; H, 9.36. Found: C, 90.61; H, 9.34.

Hydrogenation of 1-Benzylcyclohexene.—1-Benzylcyclohexene (4.10 g., 0.0238 mole) was hydrogenated in the same manner as 1-phenylcycloheptene. The yield of benzylcyclohexane was 3.69 g. (89%), n_D^{20} 1.5194 (lit.³³ b.p. 239.5–241.5° at 736 mm., n_D^{20} 1.5132; lit.³⁴ b.p. 250–255°, 113–115° at 5 mm., n_D^{20} 1.5210; lit.³⁵ b.p. 122.5–123° at 16 mm., n_D^{20} 1.5264).

Benzaldehyde.¹⁰—Cyclohexylphenylcarbinol (12.30 g., 0.666 mole) and anhydrous powdered potassium bisulfate (8 g., 0.0583 mole) were placed in a 100-ml. round-bottom distilling flask. The mixture was allowed to reflux for 15 min. under a vacuum of 25 mm., and then the vacuum was increased to 15 mm., and the product was distilled. The distillate was taken up in ether, washed with water, and dried over calcium chloride. The ether was evaporated, and the residue distilled *in vacuo* to give 7.42 g. (67%) of a mixture which was 23% 1-benzylcyclohexene and 77% benzaldehyde, b.p. 129–133° at 16 mm. The distillate was redistilled through a spinning band distillation column at 23 mm. A latter fraction which was ca. 95% pure was obtained, n_D^{20} 1.5562. An ultraviolet spectrum (cyclohexane) showed bands at 246 (ϵ 14,150) and 208.5 μ (ϵ 16,200); lit.¹⁰ b.p. 130° at 20 mm., λ_{max}^{alc} 247 μ (ϵ 10,839); lit.³⁶ b.p. 128–130° at 14 mm.; lit.³² b.p. 117–118.5° at 10 mm., n_D^{20} 1.5437).

Hydrogenation of Benzaldehyde.—Benzaldehyde (1.31 g., 0.00763 mole) was hydrogenated in the same manner as 1-phenylcycloheptene. The yield was 1.21 g. (91%) of benzylcyclohexane, n_D^{20} 1.5169 (lit.³³ b.p. 239.5–241.5° at 736 mm., 1.5132; lit.³⁴ b.p. 250–255°, 113–115° at 5 mm., n_D^{20} 1.5210; lit.³⁵ b.p. 122.5–123° at 16 mm., n_D^{20} 1.5264).

***trans*-2-Benzylcyclohexanol.**³⁷—*trans*-2-Benzylcyclohexanol was prepared from benzyl chloride (52.3 g., 0.413 mole), cyclohexene oxide (35 g., 0.356 mole), magnesium (10.5 g., 0.432 g.-atom), and 250 ml. of anhydrous ether in a manner similar to the preparation of 1-phenylcycloheptanol. The yield was 37.98 g. (56%) of *trans*-2-benzylcyclohexanol, b.p. 134–136° at 7 mm., m.p. 76–77° (crystallized from ligroin, b.p. 60–90°) (lit.³⁷ b.p. 130° at 5–6 mm., m.p. 76.5–77.5°; lit.³⁸ b.p. 154° at 11 mm., m.p. 75.5–76°).

Anal. Calcd. for $C_{13}H_{18}O$: C, 82.06; H, 9.54; O, 8.41. Found: C, 81.98; H, 9.51.

2-Benzylcyclohexanone.³⁷—*trans*-2-Benzylcyclohexanol (31.50 g., 0.166 mole) and 460 ml. of glacial acetic acid were placed in a 1-l. three-necked flask equipped with a condenser, a mechanical stirrer, and a dropping funnel. To this mixture was added, dropwise, a solution of chromium trioxide (18.3 g., 0.183 mole) in 69 ml. of 80% acetic acid. The solution was stirred at room temperature for 15 hr. The organic material was then extracted with a large volume of ether, washed with 10% base, water, and then dried over calcium chloride. The ether was evaporated, and the residue distilled *in vacuo* to give 25.54 g. (82%) of 2-benzylcyclohexanone, b.p. 155–157° at 12 mm., n_D^{20} 1.5322 (lit.³⁸ b.p. 155° at 10 mm.).

Cyclodehydration of 2-Benzylcyclohexanone.³⁹—2-Benzylcyclohexanone (23 g., 0.122 mole), anhydrous aluminum chloride (49 g., 0.367 mole), and 112 ml. of ligroin (b.p. 60–90°) were placed in a three-necked 500-ml. flask equipped with a reflux condenser, a mechanical stirrer, and a thermometer; the solution was heated to 60° for 4 hr. After the mixture had cooled,

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6 *N* hydrochloric acid was added to hydrolyze the complex. The organic layer was separated and worked up as usual. The yield was 8.15 g. (40%) of 1,2,3,4-tetrahydrofluorene, b.p. 138° at 12 mm., m.p. 56–57° (lit.¹² m.p. 48°, lit.¹⁴ b.p. 135–140° at 6 mm., m.p. 57°) and a lower boiler fraction which was probably 1a,1,2,3-tetrahydrofluorene,¹⁴ b.p. 120–138° at 12 mm., n_{D}^{28} 1.5495.

Hydrogenation of the Tetrahydrofluorenes. A.—1,2,3,4-Tetrahydrofluorene (1.03 g., 0.00606 mole) was hydrogenated in the same manner as 1-phenylcycloheptene. The yield was 0.95 g. (91%) of 1,2,3,4,1a,4a-hexahydrofluorene.

B.—Procedure A was repeated using the lower boiling fraction mentioned above in the preparation of cyclodehydration of 2-benzylcyclohexanone. The yield was 3.31 g. (93%) of 1,2,3,4,1a,4a-hexahydrofluorene, n_{D}^{29} 1.5539 (lit.¹⁴ n_{D}^{10} 1.5572, lit.³⁷ n_{D}^{10} 1.5572).

Reaction of Benzal Chloride, Sodium *t*-Butoxide, and Cyclohexene.—Reaction of sodium *t*-butoxide (sodium 12 g., 0.5 g.-atom and 1.400 g. of *t*-butyl alcohol) with benzal chloride (82 g., 0.51 mole) and cyclohexene (324 g., 3.95 moles) was carried out exactly as the procedure described above for the preparation of 7-chloro-7-phenylnorcarane. Distillation afforded 15.29 g. (15% based on sodium) of 7-chloro-7-phenylnorcarane, b.p. 170–173° at 33 mm.

Reaction of Lithium *t*-Butoxide, Benzal Chloride, and Cyclohexene.—Reaction of lithium *t*-butoxide (lithium 3.5 g., 0.505 g.-atom and 1.400 g. of *t*-butyl alcohol) with benzal chloride (82 g., 0.51 mole) and cyclohexene (324 g., 3.95 moles) was carried out in the same manner described above for the preparation of 7-chloro-7-phenylnorcarane. Analysis of the residue by gas chromatography showed that only traces of 7-chloro-7-phenylnorcarane had been formed.

Sodium Naphthalene.⁴⁰—Tetrahydrofuran (380 g., 5.8 moles) and naphthalene (57 g., 0.45 mole) were introduced into a 2-l. four-necked flask equipped with a condenser fitted with a calcium chloride tube, mechanical stirrer, thermometer, and stopper. Sodium (10 g., 0.45 g.-atom) was added carefully to the heated mixture, and the solution was refluxed for an additional 2 hr.

Reaction of Sodium Naphthalene, Benzal Chloride, and Cyclohexene.—Cyclohexene (324 g., 3.95 moles) was carefully added to the solution of sodium naphthalene prepared above, and then benzal chloride (82 g., 0.51 mole) was added dropwise through a dropping funnel over a period of 45 min. The mixture was refluxed for 4 hr., and the tetrahydrofuran distilled. The residue in the reaction vessel was cooled, washed with water, and dried over calcium chloride. The cyclohexene was distilled *in vacuo*, and analysis of the residue by gas chromatography confirmed that

a very small quantity of 7-chloro-7-phenylnorcarane had been formed.

Potassium naphthalene was prepared by the same procedure described above for the preparation of sodium naphthalene. Tetrahydrofuran (380 g., 5.8 moles), naphthalene (57 g., 0.45 mole), and potassium (18 g., 0.46 g.-atom) were used for the reaction.

Reaction of Benzal Chloride, Potassium Naphthalene, and Cyclohexene.—The potassium naphthalene solution was treated with benzal chloride (82 g., 0.51 mole) and cyclohexene (324 g., 3.95 moles) in the same manner as the sodium naphthalene solution. Analysis of the residue by gas chromatography showed that a very small amount of 7-chloro-7-phenylnorcarane had been formed.

α -Methoxycumene²⁰ was prepared by mixing α -methylstyrene (912 g., 7.70 moles), methanol (492 g., 15.4 moles), and 8.2 ml. of 60% perchloric acid and allowing it to stand for 48 hr. at 50°. The solution was then neutralized, and the organic material washed several times with water and then with a saturated solution of sodium chloride and then dried over calcium chloride. The oily material distilled *in vacuo* to give 425 g. (37%) of methoxycumene, b.p. 91–94° at 34 mm., n_{D}^{26} 1.4962.

Reaction of α -Methoxycumene, Potassium, and Cyclohexene.—Into a 100-ml. flask was introduced cyclohexene (75 ml.) and potassium (3.9 g., 0.10 g.-atom), and the whole was heated with stirring to 70°. α -Methoxycumene (8.05 g., 0.0538 mole) was added and the suspension was allowed to stir at about 70° for 3 hr. The reaction was then quenched (for a control reaction to be compared to the following reaction) with methanol and worked up as usual. Distillation afforded 0.061 g. (1.2%) of the cyclohexene adduct, b.p. 195–202° at 34 mm., n_{D}^{21} 1.5308.

Anal. Calcd. for C₁₅H₂₂: C, 89.11; H, 10.89. Found: C, 88.96; H, 10.33.

The residue which was left in the distillation pot was eluted on alumina, yielding 0.678 g. (13.44%) of the dimer *sym*-diphenyltetramethylethane, n_{D}^{28} 1.5531.

Anal. Calcd. for C₁₈H₂₂: C, 90.75; H, 9.25. Found: C, 90.81; H, 9.38.

Reaction of α -Methoxycumene, Potassium, Cyclohexene, and Cumene.—The reaction was run the same as above up to the point of adding methanol. Instead of adding the methanol, cumene (6.46 g., 0.0538 mole) was added and the solution refluxed while stirring for an additional 6 hr., then worked up as before yielding 0.447 g. (4.97%) of dimethylcyclohexylphenylmethane and 0.984 g. (10.93%) of *sym*-diphenyltetramethylethane.

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[CONTRIBUTION FROM THE EVANS CHEMISTRY LABORATORY, THE OHIO STATE UNIVERSITY, COLUMBUS 10, OHIO]

α -Halosulfones. I. Conformational Requirements of α -Sulfonyl Carbanions in the Synthesis of Phenanthrenes from 2-Chloro-2,7-dihydro-3,4-5,6-dibenzothiepin 1,1-Dioxides

BY LEO A. PAQUETTE

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The conversion of 2-chloro-2,7-dihydro-3,4-5,6-dibenzothiepin 1,1-dioxides to phenanthrenes and 9,10-deuteriophenanthrenes is described. The conformational requirement of the α -sulfonyl carbanion produced in this rearrangement is demonstrated.

The dramatic inertness of α -halosulfonyl compounds to S_N2 displacement reactions, owing to the repulsion of the nucleophilic species by the negative field of the sulfonyl oxygen atoms, has been well documented over the years.¹ In the midst of these data, there appeared the remarkable report that α -bromoethyl ethyl sulfone

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(I) was readily converted by dilute aqueous potassium hydroxide into *cis*-2-butene (IV) in 85% yield.² Further studies of this reaction have established its generality for *acyclic* systems^{3,4} and have demonstrated the strong likelihood of an episulfone intermediate (III).³

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