

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.<sup>12</sup> m.p. 48°, lit.<sup>14</sup> b.p. 135–140° at 6 mm., m.p. 57°) and a lower boiler fraction which was probably 1a,1,2,3-tetrahydrofluorene,<sup>14</sup> b.p. 120–138° at 12 mm.,  $n_{D}^{25}$  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,  $n_{D}^{25}$  1.5539 (lit.<sup>14</sup>  $n_{D}^{10}$  1.5572, lit.<sup>37</sup>  $n_{D}^{10}$  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.**<sup>40</sup>—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.

**$\alpha$ -Methoxycumene**<sup>20</sup> was prepared by mixing  $\alpha$ -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.,  $n_{D}^{25}$  1.4962.

**Reaction of  $\alpha$ -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°.  $\alpha$ -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 C<sub>15</sub>H<sub>22</sub>: 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,  $n_{D}^{25}$  1.5531.

*Anal.* Calcd. for C<sub>18</sub>H<sub>22</sub>: C, 90.75; H, 9.25. Found: C, 90.81; H, 9.38.

**Reaction of  $\alpha$ -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.

**Acknowledgment.**—The authors wish to acknowledge the financial support (Grant P-058) of the Robert A. Welch Foundation and the assistance of Robert J. Flores with some of the experimental work.

(40) W. B. Smith, *J. Org. Chem.*, **24**, 703 (1959).

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

## $\alpha$ -Halosulfones. I. Conformational Requirements of $\alpha$ -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

RECEIVED FEBRUARY 29, 1964

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  $\alpha$ -sulfonyl carbanion produced in this rearrangement is demonstrated.

The dramatic inertness of  $\alpha$ -halosulfonyl compounds to S<sub>N</sub>2 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.<sup>1</sup> In the midst of these data, there appeared the remarkable report that  $\alpha$ -bromoethyl ethyl sulfone

(1) (a) F. Raschig and W. Prahl, *Ann.*, **448**, 307 (1926); (b) T. Thomson and T. S. Stevens, *J. Chem. Soc.*, 69 (1932); (c) W. M. Ziegler and R. Connor, *J. Am. Chem. Soc.*, **62**, 2596 (1940); (d) T. B. Johnson and I. B. Douglas, *ibid.*, **63**, 1571 (1941); (e) F. G. Bordwell and G. D. Cooper, *ibid.*, **73**, 5184 (1951).

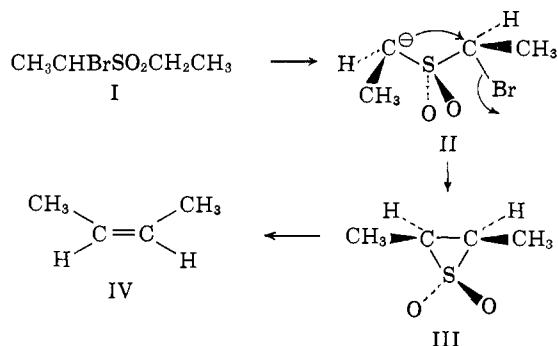
(I) was readily converted by dilute aqueous potassium hydroxide into *cis*-2-butene (IV) in 85% yield.<sup>2</sup> Further studies of this reaction have established its generality for *acyclic* systems<sup>3,4</sup> and have demonstrated the strong likelihood of an episulfone intermediate (III).<sup>3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

(2) L. Ramberg and B. Bäcklund, *Arkiv. Kemi Mineral. Geol.*, **13A**, No. 27 (1940); *Chem. Abstr.*, **34**, 4725 (1940).

(3) (a) F. G. Bordwell and G. D. Cooper, *J. Am. Chem. Soc.*, **73**, 5187 (1951); (b) N. P. Neurieter and F. G. Bordwell, *ibid.*, **85**, 1209 (1963).

(4) T. Bacchetti and A. G. Arnaboldi, *Atti acad. nazl. Lincei Rend. Classe sci. fis., mat. e nat.*, **15**, 75 (1953); *Chem. Abstr.*, **49**, 2301 (1955).

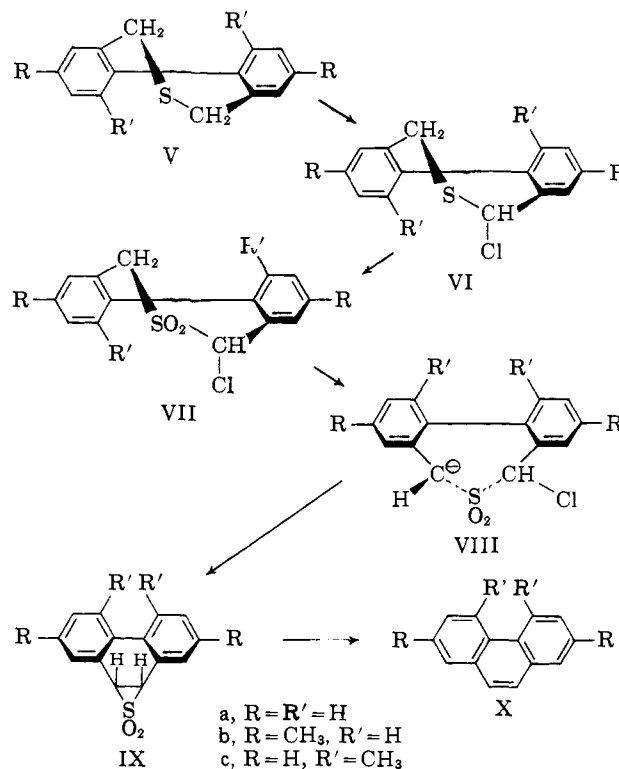
The Ramberg-Bäcklund reaction<sup>2</sup> is therefore analogous to the base-catalyzed rearrangement of  $\alpha$ -halo ketones, the Favorskii reaction.<sup>5</sup>



Despite the success of this procedure in acyclic systems, this reaction has previously failed in the conversion of an  $\alpha$ -bromothiophane 1,1-dioxide to a cyclobutene,<sup>4</sup> and has been shown to give a poor yield of cyclopentene when applied to  $\alpha$ -bromothiacyclohexane 1,1-dioxide.<sup>6</sup> The failure of this approach to cyclic olefins might be attributed to the fact that, whereas rotational freedom in aliphatic sulfones would permit a conformation in which the  $\alpha$ -sulfonyl carbanion sphere could easily adopt a geometry highly favorable to the  $S_N2$  displacement of halide ion (see II), such a desirable situation would be difficult to achieve in the more conformationally fixed cyclic systems.<sup>7</sup> The conformation of aliphatic  $\alpha$ -halosulfones required for this rearrangement is actually the one preferred on the basis of sulfonyl group field effects.<sup>8</sup>

While considering cyclic  $\alpha$ -halosulfones which would be expected to be more susceptible to the Ramberg-Bäcklund rearrangement because of their inherently suitable geometrical features for facile intramolecular  $S_N2$  displacement of halide ion, we were attracted to the 2-chloro-2,7-dihydro-3,4,5,6-dibenzothiepin 1,1-dioxides (VII). Examination of Dreiding models revealed that such systems, in totally strainless conformations, contain a diene system which is considerably distorted from planarity.<sup>9</sup> Further study of these models indicated, however, that a quasi-stable configuration could be attained in which all six carbon atoms of the seven-membered ring are in the same plane and the sulfonyl group is bent below (or above) this plane (see VIII). In VIII, the conformation of the carbanion bonding-orbital sphere is ideally oriented for the  $S_N2$  displacement of the covalently bound halogen atom. Furthermore, the large negative electric field of the sulfonyl oxygens is more than adequately removed from the site of this displacement reaction because of the strict steric requirement inherent in this molecule which forces the sulfone group to the underside of the molecule. A final important characteristic of the 2-chloro-2,7-dihydro-3,4,5,6-dibenzothiepin 1,1-dioxide molecule rests in the fact that the episulfone intermediate IX

which would result from the rearrangement process would undoubtedly rapidly lose the elements of sulfur dioxide to arrive at a resonance-stabilized aromatic species.



Sulfonyl chloride monochlorination<sup>10</sup> of the 2,7-dihydro-3,4,5,6-dibenzothiepins Va-c in carbon tetrachloride solution gave the  $\alpha$ -chlorosulfides VIa-c which were not purified, but directly oxidized to the  $\alpha$ -chlorosulfones VIIa-c in good yields. The structures of VIIa-c followed from their elemental analyses and infrared and proton resonance spectra. Treatment of a dioxane solution of VIIa with excess 25% aqueous sodium hydroxide under reflux for several hours led to the isolation of phenanthrene (Xa) in 95.8% yield. Similarly, solvolytic rearrangement of VIIb gave rise in 92% yield to 2,7-dimethylphenanthrene (Xb). In contrast, the  $\alpha$ -chlorosulfone VIIc, as anticipated (see Discussion), proved to be remarkably inert to the reaction conditions which had successfully converted VIIa and VIIb to phenanthrenes. Thus, solutions of VIIc in 25% aqueous sodium hydroxide-dioxane, when refluxed for periods of 17 to 72 hr., were found to contain only unreacted  $\alpha$ -chlorosulfone which could be recovered in virtual quantitative yield. No traces of 4,5-dimethylphenanthrene (Xc) were detected.

Recently, Neurieter and Bordwell<sup>3</sup> found that aliphatic  $\alpha$ -halosulfones undergo rapid deuterium exchange at all the  $\alpha$ -hydrogens with NaOD-D<sub>2</sub>O prior to Ramberg-Bäcklund rearrangement. Should rapid deuterium exchange likewise precede rearrangement in the 2-chloro-2,7-dihydro-3,4,5,6-dibenzothiepin 1,1-dioxides, then a simple route to the unknown 9,10-dideuterated phenanthrenes would become available. This was indeed found to be the case.<sup>10a</sup> For example, VIIa

(5) A. S. Kende, *Org. Reactions*, **11**, 261 (1960).

(6) I. Nischon, Ph.D. Thesis, Technische Hochschule zu Karlsruhe (Germany), 1955.

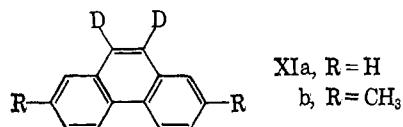
(7) It is interesting to note that this type of unreactivity exactly parallels the situation in the mechanistically similar Favorskii rearrangement which is apparently unsuccessful with cyclic  $\alpha$ -halo ketones of less than six members.<sup>5</sup>

(8) C. V. Meyers, *Tetrahedron Letters*, No. 24, 1125 (1962).

(9) The noncoplanarity and accompanying asymmetry of seven-membered  $\sigma,\sigma'$ -bridged biphenyls containing sulfur has been elegantly demonstrated by W. E. Truce and D. D. Emrick [*J. Am. Chem. Soc.*, **78**, 6130 (1956)].

(10) For an exposé of the limitations and probable mechanistic pathway of this chlorination reaction, see W. E. Truce, G. H. Birum, and E. T. McBee, *ibid.*, **74**, 3594 (1952); F. G. Bordwell and B. M. Pitt, *ibid.*, **77**, 572 (1955); F. G. Bordwell, G. D. Cooper, and H. Morita, *ibid.*, **79**, 376 (1957).

was readily converted to 9,10-dideuteriophenanthrene (XIa) in 91.7% yield when treated with 25% NaOD-D<sub>2</sub>O-dioxane. Similarly, VIIb afforded 9,10-dideu-



terio-2,7-dimethylphenanthrene (XIb) in 90.7% yield.

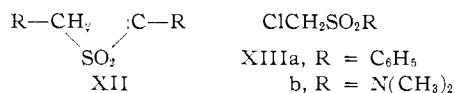
The proton magnetic resonance spectra of the 9,10-dideuteriophenanthrenes (the nondeuterated counterparts are included for comparison purposes) are illustrated in Fig. 1.

### Discussion

From kinetic investigations of the Ramberg-Bäcklund rearrangement of several  $\alpha$ -chlorosulfones, Bordwell and Cooper<sup>3a</sup> found that the rate of release of chloride ion was first order in both hydroxide ion and sulfone. These authors indicated that the kinetics were consistent with a mechanism which would involve the formation of an intermediate episulfone *via* the intramolecular displacement of halogen by an  $\alpha$ -sulfonyl carbanion (as in II); the episulfone could then rapidly decompose to produce the observed olefinic products. The subsequent findings of Neurieter and Bordwell<sup>3b</sup> that pure episulfones readily decompose when warmed neat or in solution to give olefins appear to provide conclusive evidence for the formation of episulfone intermediates.

Evidently, in the case of the dihydrodibenzothiepin dioxides VII, formation of an episulfone intermediate would, of necessity on the basis of conformational reasoning, demand that the two benzene rings of the biphenyl system attain coplanarity. Thus, if the  $\alpha$ -halosulfones VII are transformed to phenanthrenes *via* a structure such as IX, then the phenyl rings must achieve coplanarity to permit its formation. Fortunately, this requirement of the aromatic system can be easily tested by placing methyl groups in the R'-positions; this structural change will produce a situation in which the large degree of steric crowding of the R'-methyl groups should effectively prohibit the attainment of coplanarity. The failure of VIIc to yield 4,5-dimethylphenanthrene and its successful recovery after prolonged heating in alkaline solution conclusively substantiate this assumption. Thus, the formation of phenanthrenes from 2-chloro-2,7-dihydro-3,4-5,6-dibenzothiepin 1,1-dioxides is entirely consistent only with the formation of an episulfone intermediate.

With the establishment of episulfone intermediates in the rearrangement of  $\alpha$ -halosulfones, there appear to be three reasonable pathways which will account for their formation. The first that we might consider would be the generation of an  $\alpha$ -sulfonyl carbene (XII), followed by intramolecular insertion of this species into the C-H bond of the methylene group two atoms removed. However, evidence which would infer that



(10a) NOTE ADDED IN PROOF.—B. Chenon, L. C. Leitch, R. N. Renaud, and L. Pichot [*Bull. Soc. Chim. France*, 38 (1964)] have recently prepared 9,10-dideuteriophenanthrene by the hydrolysis of the di-Grignard of 9,10-dibromophenanthrene in D<sub>2</sub>O.

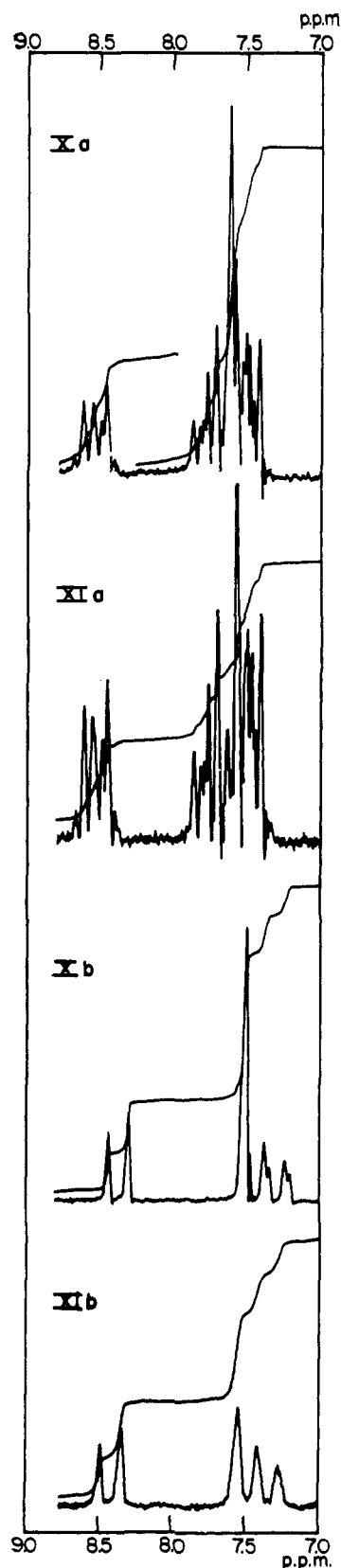


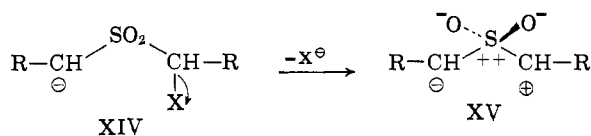
Figure 1.

such a mechanistic sequence is untenable was derived from chloromethyl phenyl sulfone (XIIIa) and N,N-dimethylchloromethanesulfonamide (XIIIb).<sup>11</sup> Prolonged heating of XIIIa or XIIIb with several strong bases in the presence of cyclohexene gave no adducts

(11) L. A. Paquette, unpublished observations.

derivable from carbenoid intermediates.<sup>12</sup> Instead, the chloromethylsulfonyl compounds were recovered in good yield. Furthermore,  $\alpha,\alpha$ -dichlorosulfones, systems which are incapable of forming carbenes, have been found to undergo readily Ramberg-Bäcklund rearrangements.<sup>13</sup> On the basis of these data, it appears that this mechanism can be discarded.

A second mechanism which must be considered involves a dipolar ion such as XV. This route differs from the third possibility, namely intramolecular S<sub>N</sub>2 displacement of halide ion (see II), solely in the manner in which the halide ion X<sup>-</sup> is lost. The direct dis-



placement of halide ion would, of course, lead to an episulfone directly whereas the rate-determining loss of halide ion as in XIV or a concerted proton abstraction and ionization would produce the intermediate zwitterion XV.

Although a somewhat analogous situation appears to exist in the Favorskii rearrangement,<sup>14</sup> there are in fact a number of important differences. First, whereas the halide ionization process in the Favorskii reaction can be facilitated by overlap of the developing p-orbital with the  $\pi$ -orbital of the enolate anion without requiring the localization of negative charge or distortion of the geometry of the enolate anion implied in the direct displacement,<sup>14</sup> such  $\pi$ -orbital assistance is not available to  $\alpha$ -sulfonyl carbanions. Furthermore, the dipolar intermediate XV would not be expected to be endowed with a substantial resonance stabilization like that predicted in the Favorskii case.<sup>15</sup>

In actuality, the pyramidal  $\alpha$ -sulfonyl carbanion which is stabilized by p-d overlap having no strict configurational or conformational requirements<sup>16</sup> would not be expected to assist in the heterolysis of the carbon-chlorine bond. In addition, an important deterrent factor to the formation of a zwitterion such as XV resides in the highly unfavorable proximity of positive centers of the sulfone sulfur and incipient carbonium ion. This electrostatic repulsion should be sufficient to raise the free energy of activation too high for the heterolysis to occur easily.

The present results and theoretical considerations therefore strongly suggest the likelihood of the intramolecular S<sub>N</sub>2 nucleophilic displacement pathway to episulfone formation as the mechanism of the Ramberg-Bäcklund rearrangement.

### Experimental<sup>17</sup>

**2-Chloro-2,7-dihydro-3,4-5,6-dibenzothiepin 1,1-Dioxide (VIIa).**—To a stirred solution of 9.5 g. (0.045 mole) of 2,7-dihydro-3,4-5,6-dibenzothiepin (Va)<sup>9</sup> in 40 ml. of carbon tetrachloride

(12) Chloromethyl phenyl sulfide, on the other hand, readily yields phenylmercaptocarbene with several bases: U. Schlölkopf and G. J. Lehmann, *Tetrahedron Letters*, No. 4, 185 (1962).

(13)  $\alpha$ -Halosulfones. II. L. A. Paquette, *J. Am. Chem. Soc.*, **86**, 4089 (1964).

(14) For a discussion of this topic, see ref. 5 and H. O. House and W. F. Gilmore, *ibid.*, **83**, 3980 (1961).

(15) J. G. Burr and M. J. S. Dewar, *J. Chem. Soc.*, 1201 (1934).

(16) D. J. Cram and A. S. Wingrove, *J. Am. Chem. Soc.*, **85**, 1100 (1963), and leading references found therein.

(17) Melting points are uncorrected. Combustion analyses were determined by the Scandinavian Microanalytical Laboratory, Herley, Denmark. Deuterium analyses (falling drop method) were performed by J. Nemeth, Urbana, Ill.

was added in small portions over a 10-min. period a solution of 7.5 g. (0.055 mole) of sulfuryl chloride in 20 ml. of carbon tetrachloride. When the addition was completed, the solution was warmed to 60° and kept at that temperature for approximately 1 hr. After cooling, the solvent was evaporated under reduced pressure and the residual yellow solid was dissolved in 150 ml. of chloroform. To this stirred solution was added portionwise with external cooling 15.5 g. (0.09 mole) of *m*-chloroperbenzoic acid. As the reaction proceeded, the resulting *m*-chlorobenzoic acid crystallized from the solution. The reaction mixture, after standing overnight, was filtered, shaken well with aqueous bicarbonate solution, dried, and evaporated to give 7.8 g. (62.8%) of crude sulfone, m.p. 196–198°. Recrystallization of this material from benzene-hexane afforded pure VIIa as white prisms, m.p. 204.5–205.5°.

*Anal.* Calcd. for C<sub>14</sub>H<sub>11</sub>ClO<sub>2</sub>S: C, 60.32; H, 3.98; Cl, 12.72; S, 11.50. Found: C, 60.57; H, 4.15; Cl, 12.33; S, 11.29.

**Phenanthrene (Xa).**—To a solution of 5.5 g. (0.02 mole) of VIIa in 40 ml. of dioxane was added 60 ml. of 25% aqueous sodium hydroxide solution and the mixture was refluxed with stirring for 18 hr. The mixture was cooled in a refrigerator at -5° for 4 hr. and the resulting solid was separated by filtration, washed thoroughly with water, and dried. There was obtained 3.35 g. (95.8%) of crude phenanthrene as a very pale yellow solid, m.p. 92–94°. Recrystallization of this material from ethanol yielded shiny white platelets of phenanthrene, m.p. 98–99°, identical by the usual criteria with an authentic sample of Xa.

**9,10-Dideuteriophenanthrene (XIa).**—A mixture of 2.8 g. (0.01 mole) of VIIa, 28 ml. of approximately 25% sodium deuterioxide in deuterium oxide,<sup>18</sup> and 20 ml. of dioxane was stirred at room temperature for 0.5 hr. and refluxed with stirring for 4.5 hr. The mixture was cooled and diluted with 350 ml. of ice-water. The precipitated product was filtered and dried to give 1.65 g. (91.7%) of pale yellow solid, m.p. 92.5–94.5°. Two recrystallizations of this material from ethanol sufficed to yield shiny white flakes of pure XIa, m.p. 98.5–99.5°.

*Anal.* Calcd. for C<sub>14</sub>H<sub>8</sub>D<sub>2</sub>: 20 atom % excess D. Found: 19.97 atom % excess D.

**2,7-Dihydro-2',3''-dimethyl-3,4-5,6-dibenzothiepin (Vb).**—A mixture of 29.5 g. (0.08 mole) of 4,4'-dimethyl-2,2'-bis(bromomethyl)biphenyl,<sup>19</sup> 60 g. (0.25 mole) of sodium sulfide nonahydrate, 1200 ml. of methanol, and 70 ml. of water was refluxed with stirring for 20 hr. The solvent was evaporated under reduced pressure and the residue was treated with water. The resulting insoluble solid was filtered, washed thoroughly with water, and dried to yield 19.05 g. (99.3%) of tan crystals, m.p. 122–126°. Recrystallization from absolute ethanol afforded white plates, m.p. 128.5–129.5°.

*Anal.* Calcd. for C<sub>16</sub>H<sub>16</sub>S: C, 79.95; H, 6.71. Found: C, 79.90; H, 6.81.

**2-Chloro-2,7-dihydro-2',3''-dimethyl-3,4-5,6-dibenzothiepin-1,1-Dioxide (VIIb).**—To a stirred solution of 3.6 g. (0.015 mole) of Vb in 20 ml. of carbon tetrachloride was added in portions 2.5 g. (0.019 mole) of sulfuryl chloride. The solution was stirred at room temperature for 1.5 hr. and evaporated under reduced pressure. The residual pale yellow oil was dissolved in 35 ml. of chloroform and treated with 6.0 g. (0.035 mole) of *m*-chloroperbenzoic acid in portions with external cooling. The mixture was worked up as described above and the residue was recrystallized from benzene-hexane to give 2.8 g. (62.0%) of pale yellow solid, m.p. 177–183°. Two additional recrystallizations from the same solvent mixture served to afford pure VIIb as very pale yellow prisms, m.p. 189–190°.

*Anal.* Calcd. for C<sub>18</sub>H<sub>18</sub>ClO<sub>2</sub>S: C, 62.63; H, 4.93; Cl, 11.56. Found: C, 63.01; H, 5.18; Cl, 11.60.

**2,7-Dimethylphenanthrene (Xb).**—A mixture of 700 mg. (2.29 moles) of VIIb, 5 ml. of 25% sodium hydroxide solution, and 5 ml. of dioxane was refluxed with stirring for 4 hr. The cooled mixture was diluted with 150 ml. of water and the precipitated solid was separated by filtration. The wet solid was dissolved in chloroform, and the solution was dried, filtered, and evaporated to give 430 mg. (92.0%) of very pale yellow solid, m.p. 85–92°. Recrystallization of this material from methanol and sublimation yielded white crystals, m.p. 101.5° (lit.<sup>20</sup> m.p. 101–102°).

(18) Prepared by the addition of the calculated amount of sodium metal under a nitrogen atmosphere to deuterium oxide of 99.9+% isotopic purity.

(19) The author is indebted to Prof. M. S. Newman for providing him with the directions for the preparation of this dibromide prior to publication.

(20) R. D. Haworth, C. R. Mavin, and G. Sheldrick, *J. Chem. Soc.*, 454 (1934).

This material was identical by the usual criteria with an authentic sample of Xb.<sup>21</sup>

**9,10-Dideuterio-2,7-dimethylphenanthrene (XIb).**—A mixture of 700 mg. (2.29 moles) of VIIb, 5 ml. of 25% NaOD in D<sub>2</sub>O, and 5 ml. of dioxane was refluxed with stirring for 3.5 hr. The work-up proceeded as above to give 425 mg. (90.7%) of crude product, m.p. 96.5–98°. Sublimation and recrystallization from methanol yielded white crystals, m.p. 102°.

*Anal.* Calcd. for C<sub>16</sub>H<sub>12</sub>D<sub>2</sub>: 14.30 atom % excess D. Found: 14.20 atom % excess D.

**2,7-Dihydro-4',1'-dimethyl-3,4-5,6-dibenzothiepin (Vc).**—A mixture of 25.0 g. (0.068 mole) of 6,6'-dimethyl-2,2'-bis-(bromomethyl)biphenyl,<sup>22</sup> 48 g. (0.20 mole) of sodium sulfide nonahydrate, 1200 ml. of methanol, and 60 ml. of water was refluxed with stirring for 18 hr. The solvent was evaporated under reduced pressure and to the residue was added 300 ml. of water. The insoluble gray solid was separated by filtration, washed thoroughly with water, and dried. There was obtained 16.1 g. (98.8%) of crude sulfide, m.p. 95–98°, which after recrystallization from ethanol was obtained as white prisms, m.p. 98.5–99°.

(21) The author is grateful to Prof. M. S. Newman for the authentic sample of Xb.

(22) E. D. Bergmann and Z. Pelchowicz, *J. Am. Chem. Soc.*, **75**, 2663 (1953).

*Anal.* Calcd. for C<sub>16</sub>H<sub>16</sub>S: C, 79.95; H, 6.71. Found: C, 79.81; H, 6.74.

**2-Chloro-2,7-dihydro-4',1'-dimethyl-3,4-5,6-dibenzothiepin 1,1-Dioxide (VIIc).**—A 7.9-g. (0.0329 mole) sample of Vc was chlorinated and oxidized as described above to give 7.25 g. (71%) of white crystals from ethanol, m.p. 192–195°.

*Anal.* Calcd. for C<sub>16</sub>H<sub>16</sub>ClO<sub>2</sub>S: C, 62.63; H, 4.93; S, 10.45. Found: C, 62.71; H, 5.07; S, 10.79.

**Attempted Ramberg-Bäcklund Rearrangement of VIIc.**—An 800-mg. sample of VIIc was refluxed with 10 ml. of dioxane and 10 ml. of 25% sodium hydroxide solution for 24 hr. The cooled solution was diluted with water and extracted with chloroform. The combined organic layers were washed with water, dried, filtered, and evaporated to give 800 mg. of recovered VIIc, m.p. 186–191°. Infrared comparisons of starting material and product showed them to be identical. Longer reactions periods (to 72 hr.) likewise resulted solely in the isolation of VIIc.

**Acknowledgment.**—The author gratefully acknowledges support of this work in part by Petroleum Research Fund Grant 169G, administered by the American Chemical Society, and in part by a grant awarded through the office of the Vice President for Research, The Ohio State University.

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

## $\alpha$ -Halosulfones. II. The Ramberg-Bäcklund Rearrangement of $\alpha, \alpha'$ -Dichlorosulfones. The Solvolytic Fate of $\alpha$ -Chloroepisulfones<sup>1</sup>

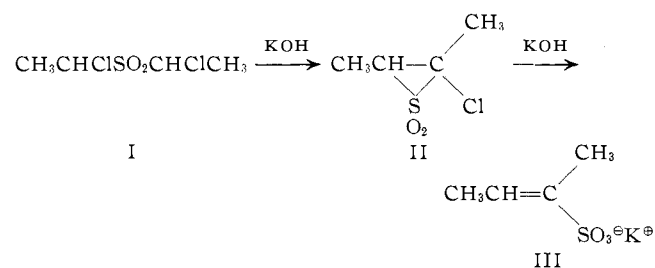
BY LEO A. PAQUETTE

RECEIVED FEBRUARY 29, 1964

Dichlorination and oxidation of dibenzyl sulfide has yielded exclusively  $\alpha, \alpha'$ -dichlorodibenzyl sulfone. Dichlorination and oxidation of the 2,7-dihydro-3,4-5,6-dibenzothiepins VIIa and VIIb has given rise to mixtures of  $\alpha, \alpha'$ - and  $\alpha, \alpha'$ -dichlorosulfones. These cases represent the first two examples of the  $\alpha, \alpha'$ -dichlorination of sulfides. The Ramberg-Bäcklund rearrangements of the  $\alpha, \alpha'$ -dichlorosulfones were studied; discussion of the solvolytic fate of the chloroepisulfones formed as intermediates in these reactions is presented.

In the previous paper of this series,<sup>1</sup> the preparation of 2-chloro-2,7-dihydro-3,4-5,6-dibenzothiepin 1,1-dioxides and a study of their rearrangement to phenanthrenes was reported. The present communication is concerned with the preparation and Ramberg-Bäcklund rearrangement of  $\alpha, \alpha'$ -dichlorosulfones. Of especial interest to us was the question of whether such sulfones would be susceptible to alkali-induced rearrangement, and also the solvolytic fate of the intermediate chloroepisulfones.

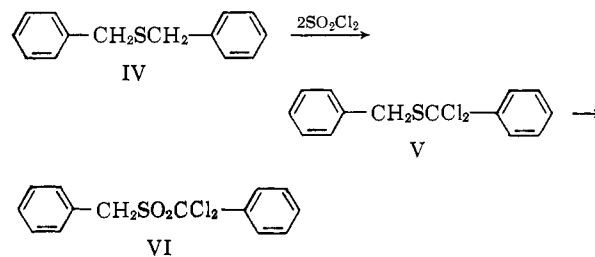
The only report in the literature to date which bears somewhat on this question is that of Ramberg and Bäcklund<sup>2</sup> in which the reaction of bis( $\alpha$ -chloroethyl) sulfone (I) with aqueous potassium hydroxide was found to give rise to potassium 2-butene-2-sulfonate (III). The formation of III can easily be formulated



as proceeding in a manner totally analogous to the rearrangement of  $\alpha$ -halosulfones<sup>1,3</sup>; that is, SN<sub>2</sub> displacement of either chlorine atom by the other  $\alpha$ -sulfonyl carbanion to give the chloroepisulfone II, which upon attack by hydroxide ion affords III. Despite the attractiveness of this mechanism, however, several other possibilities can be visualized which are consistent with the results. The ensuing report delineates our efforts to provide evidence for the formation of chloroepisulfone intermediates.

### Results

Addition of 2 equivalents of sulfonyl chloride to a solution of dibenzyl sulfide (IV) in carbon tetrachloride, followed by direct oxidation of the resulting dichlorosulfide, gave the  $\alpha, \alpha'$ -dichlorosulfone VI as the only product.<sup>4</sup>



(1)  $\alpha$ -Halosulfones. I. L. A. Paquette, *J. Am. Chem. Soc.*, **86**, 4085 (1964).

(2) L. Ramberg and B. Bäcklund, *Arkiv. Kemi Mineral. Geol.*, **13A**, No. 27 (1940); see also further mention of this reaction by F. G. Bordwell and G. D. Cooper, *J. Am. Chem. Soc.*, **73**, 5187 (1951).

(3) N. P. Neurieter and F. G. Bordwell, *ibid.*, **85**, 1209 (1963).

(4) The polychlorination of dimethyl sulfide also resulted in all the hydrogens of one carbon atom being replaced by chlorine before the second methyl group was attacked: W. E. Truce, G. H. Birum, and E. T. McBee, *ibid.*, **74**, 3594 (1952).