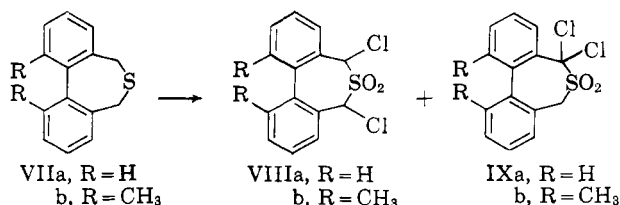
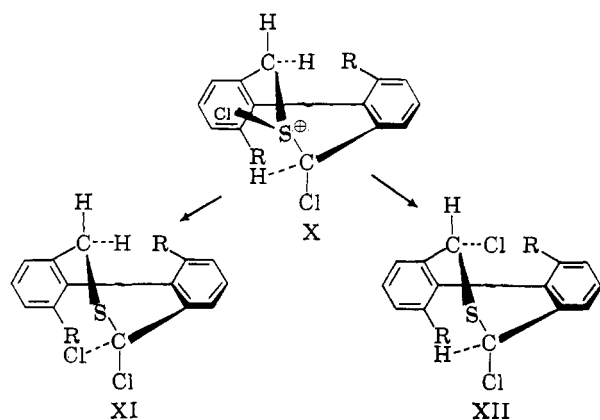


(6) The polychlorination of dimethyl sulfide also resulted in all the hydrogens of one carbon atom being replaced by chlorine before the second methyl group was attacked: W. E. Truce, G. H. Birum, and E. T. McBee, *ibid.*, **74**, 3594 (1952).

In contrast, dichlorination and oxidation of 2,7-dihydro-3,4-5,6-dibenzothiepin (VIIa) afforded the α,α' -dichlorosulfone VIIIa in 2.9% yield and the α,α' -dichlorosulfone IXa in 33.5% yield. The structures were supported by their n.m.r. spectra. Similarly, the dibenzothiepin VIIb gave rise to VIIIb (9.6% yield) and IXb (34.5% yield). In these latter cases are found the first two examples of the α,α' -dichlorination of sulfides. A reasonable explanation for this change in reaction course can be gained from an inspection of Dreiding



models. The initially formed monochlorosulfide reacts with a second mole of chlorinating agent and the salt X is formed. Two reaction alternatives are now open to this intermediate. First, the strong inductive effect of the α -chloro substituent would tend to promote the re-



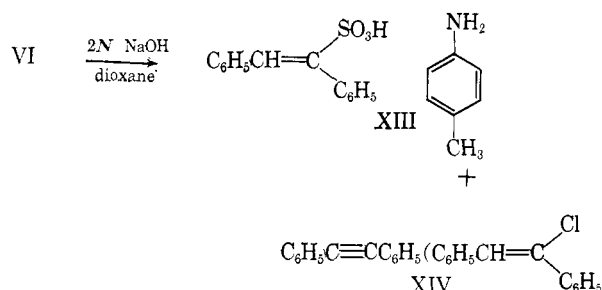
arrangement in favor of the α,α' -dichlorosulfide XI; however, the introduction of a second chlorine atom at that position represents a sterically unfavorable process. On the other hand, X can also rearrange intramolecularly in the opposite direction, that is, away from the first chloro substituent, to afford the sterically unhindered α,α' -dichlorosulfide XII. The relative amounts of the dichlorosulfones (see above) indicate that although the inductive effect of the chlorine atom is the more powerful of the two influences, the steric factor is of a sufficient order of magnitude to inhibit the exclusive formation of the α,α' -dichlorosulfones.

Submission of α,α' -dichlorodibenzyl sulfone (VI) to the conditions of the Ramberg-Bäcklund reaction gave rise to 1,2-diphenylethylene-1-sulfonic acid (70.6%), characterized as its *p*-toluidine salt (XIII),⁵ and tolan (XIV, 17% yield), which was found to be contaminated with $6 \pm 2\%$ of 1-chloro-1,2-diphenylethylene.⁶

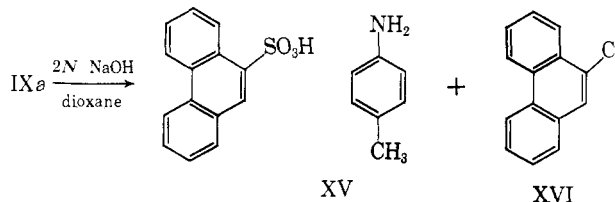
Similarly, solvolytic rearrangement of IXa with dioxane-2 *N* sodium hydroxide under reflux afforded phenanthrene-9-sulfonic acid (isolated as its *p*-toluidine salt XV in 47.3% yield) and 9-chlorophenanthrene (XVI) in 47.6% yield. The structure of both products

(5) We have unfortunately not as yet been able to ascertain the stereochemistry of XIII.

(6) The concentration of 1-chloro-1,2-diphenylethylene was too low to permit unequivocal stereochemical assignment.



were established beyond doubt by mixture melting points and comparison of their infrared spectra with those of authentic samples.⁷



When IXb was refluxed under the same reaction conditions for 16 hr., however, the α,α' -dichlorosulfone was recovered intact in 90% yield. More prolonged reaction periods (to 2.5 days) gave analogous results.

Discussion

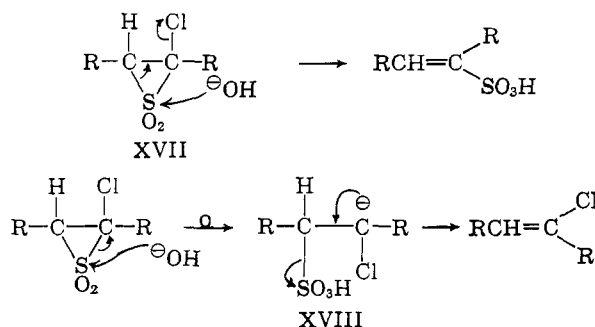
In the preceding paper of this series, evidence was obtained that the Ramberg-Bäcklund rearrangement of 2-chloro-2,7-dihydro-3,4-5,6-dibenzothiepin 1,1-dioxides proceeds *via* an intramolecular S_N2 nucleophilic displacement of chloride ion by an α -sulfonyl carbanion to give rise to an episulfone intermediate. It was shown that in the rearrangement process the benzene rings of the biphenyl system had to attain coplanarity to arrive at this intermediate. Furthermore, additional considerations supported the S_N2 displacement of halide ion as the route to the episulfone. Extrapolation of the argumentation employed earlier¹ to the results obtained herein with the α,α' -dichlorosulfones leads to the conclusion that such rearrangements proceed through a chloroepisulfone intermediate.

Of the three possible pathways considered in the previous paper to account for episulfone formation (carbene insertion, dipolar ions, and S_N2 displacement), only the latter can be applied to the α,α' -dichlorosulfone cases. Obviously, carbene formation is no longer a possibility; the formation of a dipolar ion, already considered unlikely for monochlorosulfones,¹ would be even less likely in the present case because of the added destabilization of the carbonium ion by the attached chlorine atom. These considerations suggest by the process of elimination that the chloroepisulfone intermediates are formed by the intramolecular S_N2 displacement of a chloride ion by a proximate α -sulfonyl carbanion. That hydroxide ion participates in the cleavage of chloroepisulfones is evident from the ultimate isolation of sulfonic acids.

Finally, it should be noted that the solvolytic fate of the chloroepisulfone intermediate varies with the nature of the molecule of which it is a segment. Thus, whereas I has been reported² to yield exclusively the

(7) The author is indebted to Professors D. J. Hennessy and P. B. D. de la Mare for the authentic samples of XV and XVI, respectively.

sulfonic acid III, IV affords predominantly the sulfonic acid XIII but also a substantial amount of a vinylic chloride (or its subsequent transformation product, the acetylene XIV), and IXa produces equal amounts of both possible products, XV and XVI. The following mechanistic pathways are consistent with the experimental observations. First, it seems likely that the sulfonic acids arise by the concerted attack of hydroxide ion at tetravalent sulfur and concomitant ejection of chloride ion (see XVII). This mechanism is in line



with the relative ease of cleavage of carbon-sulfur and carbon-chlorine bonds in other displacement reactions.⁸

The vinylic chlorides most probably result from stepwise cleavage of the episulfone ring to give the anion XVIII. This anion, which in suitable cases may enjoy an appreciable lifetime, may then invert and subsequently displace bisulfite ion from the normal rearward position. That vinylic chlorides arise only in those cases where R is an aromatic system is evident from the stability gained by carbanion XVIII upon the introduction of such substituents.

Experimental⁹

α,α -Dichlorodibenzyl Sulfone (VI).—To a stirred solution of 42.8 g. (0.20 mole) of dibenzyl sulfide (IV) in 200 ml. of carbon tetrachloride at room temperature was added dropwise a solution of 58.0 g. (0.428 mole) of sulfuryl chloride in 80 ml. of carbon tetrachloride. When the addition was completed, the solution was stirred at room temperature for approximately 60 min. and warmed to 60° for 10 min. until gas evolution ceased. After cooling, the solvent was evaporated under reduced pressure to give the α,α -dichlorosulfide V as a pale yellow oil.

To a stirred solution of V in 800 ml. of chloroform cooled to 0–5° was added 69.0 g. (0.40 mole) of *m*-chloroperbenzoic acid in portions at such a rate that the temperature did not exceed 30°. The mixture was stirred for 3.5 hr. at room temperature. The precipitated *m*-chlorobenzoic acid was removed by filtration and washed with a small amount of chloroform. The combined filtrate and washings were shaken with saturated sodium bicarbonate solution, dried, and evaporated. Trituration of the oily product with hexane gave 40.2 g. (63.6%) of white solid, m.p. 124–127°. Three recrystallizations of this material and benzene-hexane gave pure VI, m.p. 134–135°.

Anal. Calcd. for $C_{14}H_{12}Cl_2O_2S$: C, 53.34; H, 3.84; Cl, 22.49; S, 10.17. Found: C, 53.40; H, 3.75; Cl, 22.65; S, 10.07.

In additional experiments, VI was occasionally obtained in a polymorphic form, m.p. 111–112°. The n.m.r. and solution infrared spectra of the polymorphs were identical.

Anal. Found: C, 53.75; H, 3.84; Cl, 22.48; S, 10.15.

2,2-Dichloro-2,7-dihydro-3,4,5,6-dibenzothiepin 1,1-Dioxide (IXa) and 2,7-Dichloro-2,7-dihydro-3,4,5,6-dibenzothiepin 1,1-Dioxide (VIIIa).—To a stirred solution of 21.2 g. (0.10 mole) of 2,7-dihydro-3,4,5,6-dibenzothiepin (VIIa)¹⁰ in 100 ml. of carbon

tetrachloride at room temperature was added a solution of 29.0 g. (0.214 mole) of sulfuryl chloride in 40 ml. of carbon tetrachloride during 45 min. Approximately midway through the addition, a solid separated which subsequently redissolved. When the addition was completed, the solution was stirred at 60° for 45 min., cooled, and evaporated. The crude mixture of dichloro sulfides was obtained as a pale orange oil.

To a stirred solution of 34.5 g. (0.20 mole) of *m*-chloroperbenzoic acid in 400 ml. of chloroform cooled to 0–5° was added dropwise a solution of the crude chlorination product in 50 ml. of chloroform at such a rate that the temperature did not exceed 5–10°. The mixture was then allowed to stand overnight at room temperature. Utilization of a work-up similar to that described above for VI afforded a colorless gum. Crystallization of this gum from benzene-hexane yielded 13.7 g. (43.7%) of white solid, m.p. 145–170°. Careful chromatography of this solid on silica gel (elution with benzene-chloroform 1:1) gave 900 mg. of VIIIa, m.p. 220–225°, and 10.5 g. of IXa, m.p. 194–196°. In addition, there was an overlapping fraction of both components, m.p. 198–200°.

Two recrystallizations of VIIIa from benzene-hexane gave pure white needles, m.p. 234–235°; $\lambda_{\text{max}}^{\text{EtOH}}$ 225 (35,250) and 270 μ (ϵ 3400).

Anal. Calcd. for $C_{14}H_{10}Cl_2O_2S$: C, 53.68; H, 3.22; Cl, 22.64; S, 10.24. Found: C, 53.99; H, 3.51; Cl, 22.49; S, 10.57.

Two recrystallizations of IXa from benzene gave white needles, m.p. 198.5–199°; $\lambda_{\text{max}}^{\text{EtOH}}$ 213 (36,250), 250 sh (8200), and 279 μ (ϵ 4050).

Anal. Found: C, 53.53; H, 3.35; Cl, 22.37; S, 10.36.

2,2-Dichloro-2,7-dihydro-4',1''-dimethyl-3,4,5,6-dibenzothiepin 1,1-Dioxide (IXb) and 2,7-dichloro-2,7-dihydro-4',1''-dimethyl-3,4,5,6-dibenzothiepin 1,1-Dioxide (VIIIb).—To a stirred solution of 4.8 g. (0.02 mole) of 2,7-dihydro-4',1''-dimethyl-3,4,5,6-dibenzothiepin (VIIb)¹ in 30 ml. of carbon tetrachloride was added dropwise a solution of 6.1 g. (0.045 mole) of sulfuryl chloride in 10 ml. of the same solvent. When the addition was completed, the solution was slowly warmed to 60° with stirring during 15 min. The solution was cooled and evaporated under reduced pressure and the residual pale yellow oil was dissolved in 25 ml. of chloroform.

With stirring, this solution was added slowly below 25° to an externally cooled solution of 7.8 g. (0.045 mole) of *m*-chloroperbenzoic acid in 50 ml. of chloroform. The resulting mixture was allowed to stand at room temperature overnight and was worked up as above. The residual gum was fractionally crystallized from a benzene-hexane mixture to afford 2.35 g. of crude IXb, m.p. 198–205° dec., and 650 mg. of crude VIIIb, m.p. 133–145° dec. (total yield, 3.0 g., 44.1% for the two steps).

Pure IXb was obtained as small white prisms from benzene-hexane; m.p. 208–210°.

Anal. Calcd. for $C_{16}H_{14}Cl_2O_2S$: C, 56.31; H, 4.13; Cl, 20.78. Found: C, 56.35; H, 4.20; Cl, 20.99.

Pure VIIIb was obtained as white beads from benzene-hexane; m.p. 173–175°.

Anal. Found: C, 56.14; H, 4.23; Cl, 20.82.

Ramberg-Bäcklund Rearrangement of VI.—A solution of 6.4 g. (0.02 mole) of VI in 60 ml. of 2 *N* sodium hydroxide and 30 ml. of dioxane was refluxed with stirring for 18 hr. After cooling, the solution was treated with 60 ml. of water and extracted with three 40-ml. portions of chloroform. The aqueous layer was acidified with concentrated hydrochloric acid and this solution was treated with 3.0 g. (0.03 mole) of *p*-toluidine. A precipitate formed immediately which was filtered, washed thoroughly with water, and dried. There was obtained 5.15 g. (70.6%) of the *p*-toluidine salt of 1,2-diphenylethylene-1-sulfonic acid (XVI) as a buff-colored solid, m.p. 198° dec. Recrystallization of this salt from water gave the analytical sample as long pale yellow needles, m.p. 198° dec.

Anal. Calcd. for $C_{21}H_{21}NC_3S$: C, 68.64; H, 5.76; N, 3.81. Found: C, 68.53; H, 5.87; N, 3.45.

The combined organic layers were dried, filtered, and evaporated to give a pale yellow oil which was chromatographed on Florisil (elution with hexane) to yield 600 mg. (ca. 17% yield) of white solid, m.p. 40–43°. Recrystallization of this solid from aqueous ethanol afforded shiny white plates, m.p. 49–51°. An infrared spectrum of this solid was very similar to that of tolan (XIV).¹¹ Elemental analysis indicated the presence of

(8) F. G. Bordwell and G. D. Cooper, *J. Am. Chem. Soc.*, **73**, 5187 (1951).

(9) Melting points are uncorrected. Combustion analyses were determined by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

(10) W. E. Truce and D. D. Emrick, *J. Am. Chem. Soc.*, **78**, 6130 (1956).

(11) The reported melting point of tolan, however, is 60–62°.

2.06% chlorine, signifying the presence of $6 \pm 2\%$ of 1-chloro-1,2-diphenylethylene (unknown stereochemistry).

Rambert-Bäcklund Rearrangement of IXa.—A mixture of 3.1 g. (0.01 mole) of IXa, 25 ml. of dioxane, and 15 ml. of 2 *N* sodium hydroxide solution was refluxed with stirring for 16 hr. Upon cooling the solution, there was added 60 ml. of water. The aqueous solution was extracted with three 30-ml. portions of methylene chloride, acidified with concentrated hydrochloric acid, and treated with 1.5 g. (0.015 mole) of *p*-toluidine. The mixture was warmed with scratching until the resulting oil had crystallized. After cooling, this solid was filtered and dried to afford 1.7 g. (47.3%) of the *p*-toluidine salt of phenanthrene-9-sulfonic acid (XV), m.p. 210–216°. Recrystallization of this salt from water yielded pale yellow needles of XV, m.p. 231–232° [reported m.p. 229° (235° cor.),¹² m.p. 230–232°¹³]. The infrared spectrum of this material (in Nujol) was identical with that of an authentic specimen.⁷

The combined organic layers were dried, filtered and evaporated to give 1.0 g. (47.6%) of 9-chlorophenanthrene, m.p. 49–50°. Recrystallization of this sample from aqueous ethanol

afforded white needles, m.p. 52.5–53° (reported¹⁴ m.p. 53–53.5°). The infrared spectrum of this material was likewise superimposable on that of an authentic specimen.⁷

Attempted Ramberg-Bäcklund Rearrangement of IXb.—A mixture of 1.0 g. (2.93 mmoles) of IXb, 5 ml. of dioxane, and 8 ml. of 2 *N* sodium hydroxide solution was refluxed with stirring for 16 hr. The cooled solution was treated with 25 ml. of water and extracted with three 20-ml. portions of chloroform. The combined organic layers were dried, filtered, and evaporated to give 900 mg. (90% recovery) of IXb, m.p. 165–175°.

Treatment of the acidified aqueous layer with *p*-toluidine gave no detectable quantities of a salt. Longer reaction times gave analogous results.

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.

(12) L. F. Fieser, *J. Am. Chem. Soc.*, **51**, 2460 (1929).

(13) Sr. M. G. Solomon and D. J. Hennessy, *J. Org. Chem.*, **22**, 1649 (1957).

(14) P. B. D. de la Mare, N. V. Klassen, and R. Koenigsberger, *J. Chem. Soc.*, 5285 (1961).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UPJOHN CO., KALAMAZOO, MICH.]

Unsaturated Heterocyclic Systems. VIII. 2,3-Dihydro-1H-azepines¹⁻³

BY LEO A. PAQUETTE⁴

RECEIVED APRIL 15, 1964

The lithium aluminum hydride reduction of 1,3-dihydro-2H-azepin-2-ones has been found to afford seven-membered cyclic dienamines. Although the secondary cyclic dienamine **3a** is quite unstable, tertiary analogs are remarkably stable when the proper precautions are observed. Treatment of the 2,3-dihydro-1H-azepines with perchloric acid afforded crystalline perchlorates resulting from protonation at the δ -carbon atom. The cyclic dienamines have been found to enter very vigorously into Diels-Alder reactions and to photoisomerize as normal conjugated cycloheptadienes.

Among the many intriguing areas of organic chemistry currently under investigation, study of the properties and reactivities of enamines has contributed most significantly to the progress of synthetic methods. Evidence to this effect is given by the wide variety of problems in which enamines have found application.⁵ The reactions of enamines have been so varied and numerous that studies in this area have only in rare circumstances progressed beyond the use of simple enamines and cyclic enamines. We wish now to report, in some detail, the preparation and selected reactions of a class of novel seven-membered cyclic dienamines, the 2,3-dihydro-1H-azepines.⁶

(1) Unsaturated Heterocyclic Systems. VII: L. A. Paquette, *J. Am. Chem. Soc.*, **85**, 4053 (1963).

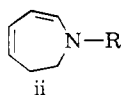
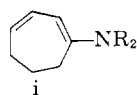
(2) For a preliminary account of a portion of this work, see L. A. Paquette, *Tetrahedron Letters*, 2027 (1963).

(3) Presented in part at the Gordon Research Conference on Heterocyclic Chemistry, New Hampton, N. H., Aug. 24–28, 1964.

(4) Correspondence should be addressed to the Department of Chemistry, The Ohio State University, Columbus 10, Ohio.

(5) For a recent review of enamine chemistry, see J. Szmuszkovicz, "Advances in Organic Chemistry, Methods and Results," Vol. IV, R. A. Raphael, E. C. Taylor, and H. Wynberg, Ed., Interscience Publishers, Inc., New York, N. Y., 1963; see also G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovicz, and R. Terrell, *J. Am. Chem. Soc.*, **85**, 207 (1963).

(6) In keeping with the nomenclature of enamines,⁵ we propose that i be termed a "dienamine," and ii be referred to as a "cyclic dienamine."



(7) For examples of dienamines such as i, see A. A. Bothner-By, R. S. Schutz, R. R. Dawson, and M. L. Solt, *J. Am. Chem. Soc.*, **84**, 52 (1962); E. Leete, *ibid.*, **84**, 55 (1962).

Preparation.—Recently, the interesting ring expansion of the sodium salts of 2,6-dialkyl- and 2,4,6-trialkylphenols with ethereal chloramine at 120–150° was reported from this laboratory.⁸ The unique 1,3-dihydro-2H-azepin-2-ones which result from this reaction appeared to represent, because of the degree of unsaturation present in this heterocyclic system, excellent substrates for the preparation of cyclic dienamines.

Lithium aluminum hydride reduction of 1,3-dihydro-3,5,7-trimethyl-2H-azepin-2-one (**1**) in ethereal solution under an atmosphere of nitrogen afforded, after appropriate alkaline work-up, a white solid (**3a**, see below) which rapidly decomposed exothermically on exposure to the atmosphere with the liberation of white fumes. Although a very small amount of unreduced dihydroazepinone **1** could be isolated from the dark residue, the remainder of the decomposition product was a dark intractable resin. This result, despite the fact that product isolation was not achieved, suggested that cyclic dienamine formation was occurring and prompted further study.

In earlier papers of this series,^{8,9} it was shown that treatment of **1** with sodium hydride in dimethylformamide produced an anion which when alkylated gave rise to N-substituted derivatives such as **2a** and **2b**. When 1,3-dihydro-1,3,5,7-tetramethyl-2H-azepin-2-one (**2a**) was prepared by this method and subjected to lithium aluminum hydride reduction, there was obtained in 91.8% yield a colorless liquid which yellowed

(8) L. A. Paquette, *ibid.*, **84**, 4987 (1962); **85**, 3288 (1963).

(9) L. A. Paquette and J. K. Reed, *J. Med. Chem.*, **6**, 771 (1963).