

rapid determination of purity. The aldehydes were readily oxidized to the known carboxylic acids for conclusive identification *via* mixture melting point determinations.⁸

Vpc Results.—The injection of up to 50 μ l of **3** ($n = 1, 2$) into the vpc at 190° with an injection port temperature of 230° resulted in apparently quantitative rearrangement of the *endo* isomers to **4** ($n = 1, 2$) without affecting the *exo* isomers.⁹ Typical retention times (min) for a 20 ft \times $\frac{3}{8}$ in. 30% QF-1 column under a helium gas flow rate of 100 cc/min were: *exo*-**3** ($n = 1$), 18; **4** ($n = 1$), 12; *exo*-**3** ($n = 2$), 28; **4** ($n = 2$), 17. Samples were collected from the vpc and subjected to spectral analysis. The *exo* isomers were shown to be unchanged while the nmr and infrared spectra (CHCl_3) of **4** ($n = 1, 2$) were identical with that of authentic material.³

Pyrolysis Results.—The dropwise addition of the *endo* isomer of **3** ($n = 1$) onto a 9 in. column of glass beads in a temperature controlled oven at 240° under helium gas flow and flushing with ether gives a crude pyrolysate containing 25% of **4** ($n = 1$) and 75% of starting material determined by integration of the aldehydic protons at δ 9.85 (t) and 9.55 (d), respectively. At 300°, the nmr spectrum of the crude pyrolysate is identical with that of **4** ($n = 1$). The *exo* isomer of **3** ($n = 1$) remains unchanged at temperatures as high as 400° determined by nmr analysis of the crude pyrolysate.

Photochemical Rearrangements.—A solution of 60 mg of *endo*-**3** ($n = 1$) in 7 ml of ether was irradiated with 3000 Å light in a quartz tube in a Rayonet reactor for 5 hr. Some polymeric material had formed on the sides of the tube. The ether was removed *in vacuo* and CDCl_3 added to the residue (54 mg). Comparison of the nmr spectrum of this material with that of **4** ($n = 1$) allowed an estimation of ca. 30% of **4** ($n = 1$) in the crude mixture from integration of the aldehydic and olefinic protons against the total proton count in the nmr spectrum of the crude reaction mixture. Similar irradiation of 65 mg of *exo*-**3** ($n = 1$) in 7 ml of ether gave a product mixture whose nmr spectrum showed that more than 90% of the starting material had reacted but there were no olefinic absorptions.

Registry No.—*endo*-**3** ($n = 1$), 4729-42-4; *endo*-**3** ($n = 2$), 24874-09-7.

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(8) J. Meinwald, S. S. Labana, and M. S. Chadha, *J. Amer. Chem. Soc.*, **85**, 582 (1963); J. A. Berson and E. S. Hand, *ibid.*, **86**, 1978 (1964). The author is indebted to Professor Berson for an authentic sample of bicyclo-[4.1.1]heptan-7-*endo*-carboxylic acid.

(9) No other peaks are observed in the chromatogram but preparative collection from the vpc results in 80–90% recovery. This loss, due to incomplete trapping of the effluent, is not unusual.

Chloromethyl Sulfoxides and Sulfones from 1,2-Dichlorovinyl Sulfoxides and Sulfones

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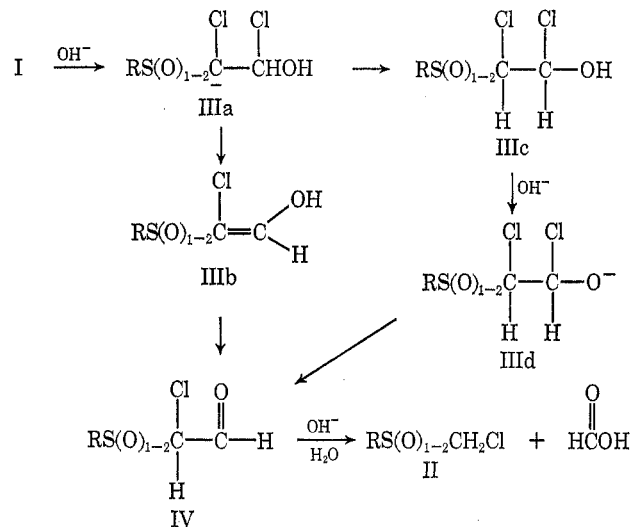
There has been considerable recent interest in the preparation and chemistry of α -chloro sulfoxides¹ and in the chemistry of sulfoxides in general.² We report here the facile preparation of α -chloro sulfoxides and sulfones from the corresponding 1,2-dichlorovinyl com-

(1) (a) R. N. Leoppky and D. C. K. Chang, *Tetrahedron Lett.*, 5415 (1968); (b) M. Hojo and Z. Yoshida, *J. Amer. Chem. Soc.*, **90**, 4496 (1968); (c) T. Durst, *ibid.*, **91**, 1034 (1969).

(2) C. R. Johnson and J. R. Sharp, "The Chemistry of Sulfoxides," Intra Science Research Foundation, Santa Monica, Calif., 1969.

pounds by treatment with dilute aqueous base. In Table I are listed a number of examples of this reaction and the recrystallized yields of the products.^{3–6} Crude yields were generally 10 to 15% higher, and the crude products were quite clean, impurities being soluble in the basic aqueous phase. Identification of products was made by elemental analyses and spectral (ir and nmr) and melting point comparison with authentic samples prepared by oxidation of the corresponding α -chloro sulfides.^{7,8}

In only one case, that of the *t*-butyl sulfoxide IIc, was a relatively poor yield obtained. Part of the starting material was converted into unidentified base-soluble products under all conditions explored. The use of organic solvents such as dioxane, tetrahydrofuran, dimethyl sulfoxide, and dimethylformamide in conjunction with the aqueous base for the hydrolysis of Ia–c led uniformly to lower yields of IIa–c. Milder conditions were necessary with the benzyl derivatives Ie–f, as heating led to styrene from the chloromethyl sulfone II f *via* a Ramberg–Bäcklund reaction and to unidentified products from the sulfoxide IIe.



The chemistry of β -chlorovinyl sulfoxes has been extensively investigated and reaction with various nucleophiles (RO^- , RS^- , RSO_2^- , R_2NH) leads to β -substituted vinyl sulfoxes with displacement of chloride.^{4,9} Thus, it is reasonable to postulate that the initial step in the present reaction is nucleophilic attack by hydroxide to give the carbanion IIIa, which can be converted to the aldehyde IV either by direct elimination of chloride to give the tautomeric enol IIIb, or by protonation of IIIa followed by elimination of HCl through IIIc. The aldehyde would be highly susceptible to attack by hydroxide followed by cleavage to give formic acid and the α -sulfinyl or sulfonyl anion which

(3) E. Ayca, *Fac. Sci. Univ. Istanbul, Ser. C*, **22**, 371 (1957); *Chem. Abstr.*, **53**, 11287f (1959).

(4) H. J. Backer, *et al.*, *Rec. Trav. Chim. Pays-Bas*, **72**, 813 (1953); *Chem. Abstr.*, **49**, 11538g (1955).

(5) F. G. Bordwell and G. D. Cooper, *J. Amer. Chem. Soc.*, **73**, 5187 (1964).

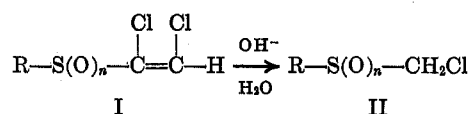
(6) J. Metivier, U. S. Patent 2,793,234 (1957).

(7) H. Bohme, *Ber.*, **69**, 1610 (1936).

(8) In agreement with Durst,¹⁰ we find that *m*-chloroperbenzoic acid oxidation, using chloroform or methylene chloride as solvent, gives excellent yields of the sulfoxides.

(9) F. Montanari and A. Negrini, *Gazz. Chim. Ital.*, **87**, 1068 (1957); *Chem. Abstr.*, **52**, 9987g (1958). L. Maioli and G. Modena, *ibid.*, **89**, 854 (1959); *Chem. Abstr.*, **54**, 22451i (1960).

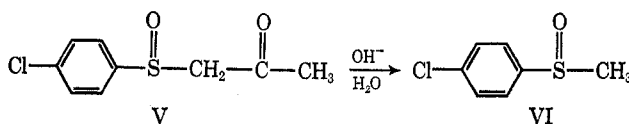
TABLE I



Compd	R	n	Reaction conditions	Mp, °C	% yield	References	
						Product	Starting material
IIa	<i>p</i> -CH ₃ C ₆ H ₄ -	1	3 hr, reflux	60-62	81	3	6
IIb	<i>p</i> -CH ₃ C ₆ H ₄ -	2	4 hr, reflux	80-82	79	3	6
IIc	(CH ₃) ₃ C-	1	0.5 hr, reflux	73-75	48		4
IId	(CH ₃) ₃ C-	2	4 hr, reflux	83-85	81	4	4
IIe	C ₆ H ₅ CH ₂ -	1	44 hr, ambient	64-67	78		6
IIf	C ₆ H ₅ CH ₂ -	2	48 hr, ambient	97-99	77	5	6

would be rapidly protonated to give the base-stable final product II. Such cleavages of β -keto sulfones are well documented.¹⁰

The aldehydes IV have not been observed by us, even in basic and acidic extracts of reactions terminated when greater than 50% of starting material I remains. However, Backer⁴ reported the preparation of the *t*-butylsulfonylaldehyde IVd by acid cleavage of the corresponding dimethyl acetal and its ready basic hydrolysis to the chloromethyl sulfone IId. There appears to be no report of the basic cleavage of β -keto sulfoxides, although the reaction is essentially the reverse of the synthetic method developed by Corey¹¹ and Russell¹² for their preparation from a sulfinyl carbanion and an ester. We found that the β -keto sulfoxide V was cleaved in 93% yield to the known methyl sulfoxide VI¹³ by refluxing with 5% sodium hydroxide for 18 hr.



Experimental Section

Hydrolysis of Dichlorovinyl Sulfoxides and Sulfones.—The appropriate starting material, 4.5 g, was added to 100 ml of 5% aqueous sodium hydroxide plus a small amount of a surfactant (Aerosol OTB). The mixture was stirred under the conditions given in Table I. The products were isolated by extraction with chloroform and purified by recrystallization from a benzene-hexane mixture. Direct comparison of physical properties was made in each case with authentic samples prepared according to the literature or as indicated below to substantiate the structure of the products.

Preparation of Sulfoxides IIc, IIe, and V.—To a solution of the corresponding sulfide (0.1 mol) in 250 ml of chloroform cooled in an ice bath was added as a solid over 1 hr *m*-chloroperbenzoic acid (0.1 mol). The solution was left at room temperature for 24 hr, filtered to remove precipitated *m*-chlorobenzoic acid, washed with saturated NaHCO₃ solution and water, dried (Mg SO₄), and concentrated, and the product recrystallized from benzene-hexane to give the following in yields above 80%.

IIc: mp 73-75°; nmr (CDCl₃) δ 1.33 (s, 9, (CH₃)₃C-), 4.35 (q, 2, CH₂Cl). *Anal.* Calcd for C₈H₁₁ClOS: S, 20.71; Cl, 22.95. Found: S, 20.60; Cl, 23.05.

IIe: mp 64-67°; nmr (CDCl₃) δ 4.36 (m, 4, -CH₂S(O)CH₂Cl), 7.36 (s, 5, C₆H₅). *Anal.* Calcd for C₈H₉ClOS: S, 16.95; Cl, 18.82. Found: S, 16.72; Cl, 18.68.

(10) (a) A. Otto, *J. Prakt. Chem.*, **36**, 401 (1888). (b) M. Ohta, *et al.*, *J. Pharm. Soc. Jap.*, **69**, 43 (1949); *Chem. Abstr.*, **44**, 1485c (1950). (c) J. J. Looker, *J. Org. Chem.*, **31**, 2714 (1966).

(11) E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **86**, 1639 (1964).

(12) H. D. Becker, G. J. Mikol, and G. A. Russell, *ibid.*, **85**, 3410 (1963).

(13) A. Cerniani and G. Modena, *Gazz. Chim. Ital.*, **89**, 843 (1959); *Chem. Abstr.*, **54**, 22446i (1960).

V: mp 109-111°; nmr (CDCl₃) δ 2.25 (s, 3, C(O)CH₃), 3.90 (s, 2, S(O)CH₂), 7.53 (m, 4, Cl-C₆H₄(O)S-). *Anal.* Calcd for C₉H₉ClO₂S: S, 14.75; Cl, 16.35. Found: S, 14.40; Cl, 16.56.

Registry No.—IIa, 24824-93-9; IIb, 7569-26-8; IIc, 24824-95-1; IId, 24824-96-2; IIe, 24824-97-3; IIf, 5335-44-4; V, 17530-95-9.

Conjugated Epoxy Compounds. An Unusual Ring Contraction of *trans*-2,3,5,6-Diepoxy-2,5-di-*t*-butyl-1,4- benzoquinone upon Reaction with Diazomethane

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Compounds containing functional groups having partial sp² character which are specifically oriented in close proximity around a small carbon framework are of potential interest in regard to unusual spectral and chemical properties. Reported here is an investigation leading to such a system, *i.e.*, the tri- and tetraepoxides, 2 and 3, respectively. These compounds are obtained from the reaction of *trans*-2,3,5,6-diepoxy-2,5-di-*t*-butyl-1,4-benzoquinone (1)¹⁻³ with either diazomethane or sulfonium methylides. Reaction of 1 with the former reagent also results, in addition to epoxidation, in an unusual ring contraction to the ketone (4). This result, to our knowledge, constitutes the first such rearrangement involving diazomethane and suggests an interesting area for subsequent investigations utilizing simpler epoxy ketones.

Reaction of an ethanolic solution of 1 with excess freshly distilled ethereal diazomethane⁴ resulted in the evolution of nitrogen; formation of the organic products was conveniently monitored by glc,⁵ showing the gradual formation of the triepoxide 2 which subsequently disappeared with the synchronous formation of

(1) H. W. Moore, *J. Org. Chem.*, **32**, 1996 (1967).

(2) F. R. Hewgill and S. L. Lee, *J. Chem. Soc. C*, 1549 (1968).

(3) D. H. Williams, J. Ronayne, H. W. Moore, and H. R. Sheldon, *J. Org. Chem.*, **33**, 998 (1968).

(4) J. A. Moore and D. E. Reed, *Org. Syn.*, **41**, 16 (1961).

(5) Analysis was carried out isothermally at 190° on 6 ft \times 1/4 in. SE-30/Chromosorb W columns. Thermal conductivity and flame ionization were used as the methods of detection.