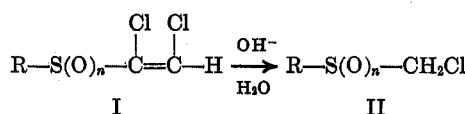


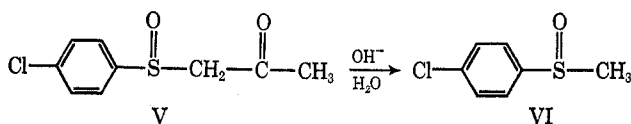
TABLE I



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

would be rapidly protonated to give the base-stable final product II. Such cleavages of  $\beta$ -keto sulfones are well documented.<sup>10</sup>

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, Backer<sup>4</sup> 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  $\beta$ -keto sulfoxides, although the reaction is essentially the reverse of the synthetic method developed by Corey<sup>11</sup> and Russell<sup>12</sup> for their preparation from a sulfinyl carbanion and an ester. We found that the  $\beta$ -keto sulfoxide V was cleaved in 93% yield to the known methyl sulfoxide VI<sup>13</sup> 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 NaHCO<sub>3</sub> solution and water, dried (Mg SO<sub>4</sub>), and concentrated, and the product recrystallized from benzene-hexane to give the following in yields above 80%.

IIc: mp 73-75°; nmr (CDCl<sub>3</sub>)  $\delta$  1.33 (s, 9, (CH<sub>3</sub>)<sub>3</sub>C-), 4.35 (q, 2, CH<sub>2</sub>Cl). *Anal.* Calcd for C<sub>8</sub>H<sub>11</sub>ClOS: S, 20.71; Cl, 22.95. Found: S, 20.60; Cl, 23.05.

IIe: mp 64-67°; nmr (CDCl<sub>3</sub>)  $\delta$  4.36 (m, 4, -CH<sub>2</sub>S(O)CH<sub>2</sub>Cl), 7.36 (s, 5, C<sub>6</sub>H<sub>5</sub>). *Anal.* Calcd for C<sub>8</sub>H<sub>9</sub>ClOS: 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 (CDCl<sub>3</sub>)  $\delta$  2.25 (s, 3, C(O)CH<sub>3</sub>), 3.90 (s, 2, S(O)CH<sub>2</sub>), 7.53 (m, 4, Cl-C<sub>6</sub>H<sub>4</sub>(O)S-). *Anal.* Calcd for C<sub>9</sub>H<sub>9</sub>ClO<sub>2</sub>S: 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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Received December 15, 1969

Compounds containing functional groups having partial sp<sup>2</sup> 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)<sup>1-3</sup> 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 diazomethane<sup>4</sup> resulted in the evolution of nitrogen; formation of the organic products was conveniently monitored by glc,<sup>5</sup> 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 × 1/4 in. SE-30/Chromosorb W columns. Thermal conductivity and flame ionization were used as the methods of detection.

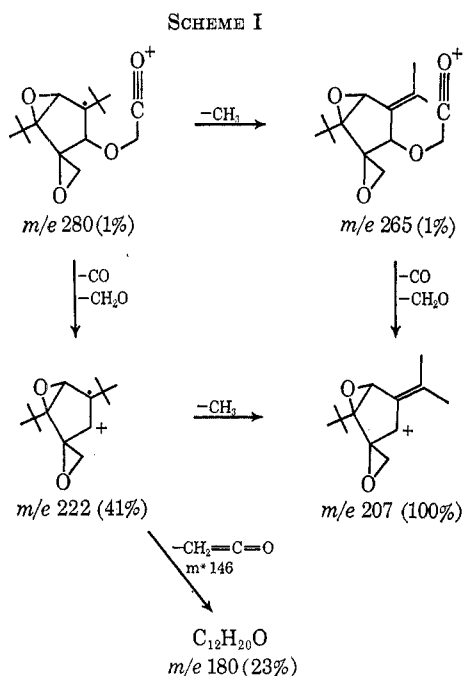
the tetraepoxide **3** and the ring contracted ketone **4**. Termination of the reaction at the appropriate time gave the triepoxide (**2**) in 61% yield, while after complete reaction the only products were **3** and **4** in a ratio of 8:2, respectively. That the triepoxide **2** is a precursor to compounds **3** and **4** was shown by subjecting it to the reaction conditions and observing the formation of the products, **3** and **4**, in the same (8:2) relative ratio.

Critical structural data for compounds **2**, **3**, and **4** follow. Compound **2**: mp 111–114°; ir (Nujol) 1693

(C=O), 900–950  $\text{cm}^{-1}$  (C—C); nmr ( $\text{CCl}_4$ )  $\delta$  0.99 [s, 9, C(CH<sub>3</sub>)<sub>3</sub>], 1.05 [s, 9, C(CH<sub>3</sub>)<sub>3</sub>], 2.63 [s, 1, CH], 3.30 (s, 1 CH), 3.14 (AB, 2,  $J = 4.5$  cps, CH<sub>2</sub>); mass spectrum  $M^+$  266. Compound **3**: mp 114–115°; ir (Nujol)

900–960  $\text{cm}^{-1}$  (C—C); nmr ( $\text{CCl}_4$ )  $\delta$  1.00 [s, 18, C(CH<sub>3</sub>)<sub>3</sub>], 2.75 (AB, 4,  $J = 6.8$  cps, CH<sub>2</sub>), 3.36 [s, 2, CH]; mass spectrum  $M^+$  280. Compound **4**, mp 105–107°;

ir (Nujol) 1739 (C=O), 947, 900  $\text{cm}^{-1}$  (C—C); nmr ( $\text{C}_6\text{H}_6$ ) (220 Mc)<sup>6</sup>  $\delta$  0.92 [s, 9, C(CH<sub>3</sub>)<sub>3</sub>], 0.99 [s, 9, C(CH<sub>3</sub>)<sub>3</sub>], 2.82 (AB, 2,  $J = 5$  cps, CH<sub>2</sub>), 3.52 (s, 1, CH), 3.86 (AB, 2,  $J = 17$  cps, CH<sub>2</sub>), 4.61 (s, 1, CH) (in carbon tetrachloride these peaks appear, respectively, at  $\delta$  0.97, 1.12, 3.00, 3.51, 3.78, and 4.42); mass spectrum  $M^+$  280. The mass spectrum of **4** is relatively simple showing only three peaks with relative abundance greater than 15% in the mass range above  $m/e$  57. These peaks appear at  $m/e$  180 (23%), 222 (41%), and 207 (100%) and are rationalized in accordance with structure **4** as shown in Scheme I. A sample of **4** in which the methylene group  $\alpha$  to the carbonyl was deuterated was obtained from the reaction of the triepoxide



(6) The authors are grateful to the California Institute of Technology for the 220 Mc nmr spectrum and to the National Science Foundation for making this instrument available for regional use.

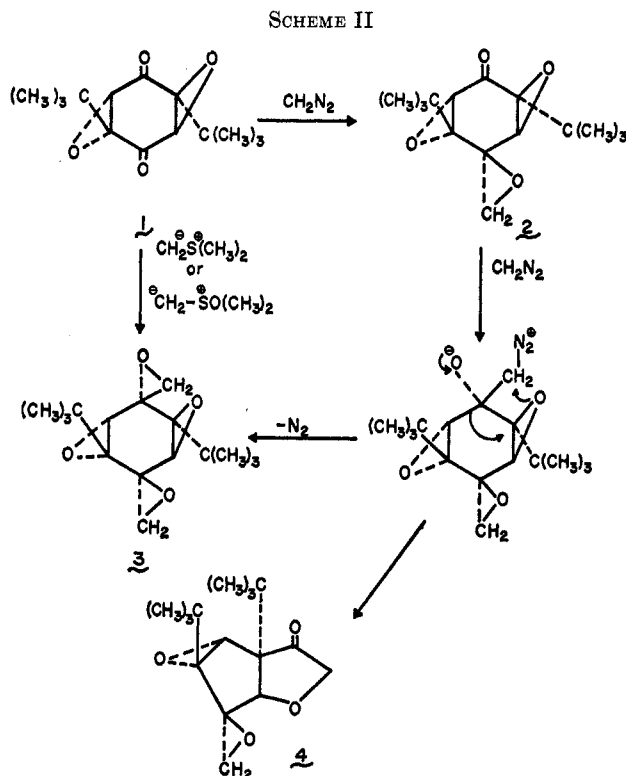
**2** with deuterated diazomethane. The mass spectrum showed the same three major peaks as those reported above for the protected isomer. The only major difference is the molecular ion peak at  $m/e$  282 and the  $M - 15$  peak at  $m/e$  267.

The yield of the ring contracted ketone **4** ranges from 1.2 to 32.2% depending upon the solvent. The following relative ratios of **3** to **4** are illustrative of its solvent dependence: ether 99:1, ethanolic ether 8:2, aqueous methanolic ether 7:3, lithium bromide methanol (1:1 lithium bromide to substrate) 6.2:3.8.<sup>7</sup>

The stereochemistry of the new compounds reported here are not proved in an unambiguous way. It is assumed, and substantiated partially by experiments, that attack of diazomethane proceeds from the least hindered side of the molecule, *i.e.*, the side opposite the *t*-butyl groups.<sup>8</sup> Since the triepoxide **2** is a precursor to the tetraepoxide **3**, and the nmr spectrum of **3** shows the molecule to be completely symmetrical, the stereochemistries as represented by formulas **2** and **3** are most reasonable.

Consistent with the above steric control argument is the fact that the reaction of **1** with either dimethylsulfoxonium methylide or dimethylsulfonium methylide also give exclusively compounds **2** and **3**. However, it is interesting to note that these ylide reactions give no trace of the ring contracted ketone **4**.

The stereochemistry of **4** is predicted on the basis of the mechanism presented in Scheme II, assuming a con-



(7) These results are in agreement with previous observations concerning the influence of acidic solvents on epoxidation and homologation, *i.e.*, as the acidity of the reaction medium increases, epoxidation is retarded and homologation is enhanced. L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Wiley, New York, N. Y., 1967.

(8) Drieding models show that the diepoxide **1** can exist in two degenerate conformations, and that one of the carbonyl groups is always less sterically hindered on the side opposite the bulky alkyl group, the other carbonyl being coplanar with the alkyl substituent.

certed ring contraction. Note that the epoxide oxygen which is involved in this ring contraction reaction is the one on the same side as the methylene of the diazomethane adduct, thus leading to the *cis* ring junction in 4. One would predict on the basis of a concerted ring contraction that rearrangement would be much less favorable, if possible at all, for those epoxy ketones in which the diazomethane attacks from the side opposite the epoxide function. Such systems are currently under investigation and the results along with those obtained concerning the conjugative influences of the epoxide functions on the spectral and chemical properties of compounds such as 1, 2, and 3 will be reported in a subsequent communication.

### Experimental Section

**Reaction of *trans*-2,3,5,6-diepoxy-2,5-di-*t*-butyl-1,4-benzoquinone (1) with Ethereal Diazomethane.**—Excess freshly distilled ethereal diazomethane was added to a solution of 0.318 g (0.00126 mol) of the diepoxide 1 in 50 ml of anhydrous diethyl ether. Nitrogen slowly evolved and the reaction course was followed by glc which showed the progressive appearance of the triepoxide 2 followed by its disappearance and the formation of the tetraepoxide 3 and the ketone 4. After 24 hr the solvent was removed *in vacuo* leaving 0.339 g of a white crystalline product. Glc analysis of this solid showed it to be a mixture of the tetraepoxide 3 and the ketone 4 in a ratio of 98.8:1.2, respectively. Recrystallization of this solid from ethanol gave the pure tetraepoxide 3, mp 114–115°.

*Anal.* Calcd for C<sub>16</sub>H<sub>24</sub>O<sub>4</sub>: C, 68.55; H, 8.63. Found: C, 68.52; H, 8.65.

The ring contracted ketone 4 was isolated and purified by preparative glc, mp 105–107°.

*Anal.* Calcd for C<sub>16</sub>H<sub>24</sub>O<sub>4</sub>: C, 68.55; H, 8.63. Found: C, 68.43; H, 8.49.

Reaction of the diepoxide 1 with ethereal diazomethane in solvents of varying acidity changed the ratio of the products 3 and 4.

To a solution of 0.278 g (0.0011 mol) of the diepoxide 1 in 100 ml of absolute ethanol was added excess ethereal diazomethane. Concentration of the reaction solution after nitrogen evolution ceased gave 0.292 g (0.0010 mol) of a white crystalline solid. Gas chromatographic analysis of this product showed it to be a mixture of 3 and 4 in a ratio of 79.9 to 20.1, respectively.

Reaction of 0.439 g (0.0017 mol) of 1 in 10 ml of water and 100 ml of absolute methanol with excess ethereal diazomethane gave 0.464 g (0.0017 mol) of a white solid. This solid was shown by gas chromatographic analysis to be a mixture of 3 and 4 in a ratio of 71.7 to 28.3, respectively.

Reaction of 0.387 g (0.0015 mol) of 1 in a solution of 100 ml of absolute methanol and 0.133 g (0.0015 mol) of lithium bromide with excess ethereal diazomethane gave 0.407 g (0.0015 mol) of a white crystalline solid. This solid was isolated by concentration of the reaction mixture followed by repeated washing of the precipitate with water to remove all traces of lithium bromide. Gas chromatographic analysis of this product showed it to be a mixture of 3 and 4 in a relative ratio of 61.8 to 38.2, respectively.

**Triepoxide 2.**—Reaction of the diepoxide 1 with diazomethane was carried out according to the method described above. The reaction was worked up when the triepoxide 2 was at its maximum concentration (61%) as evidenced by glc (approximately 6 hr). Recrystallization several times from ethanol gave the pure triepoxide 2, mp 111–114°.

*Anal.* Calcd for C<sub>16</sub>H<sub>22</sub>O<sub>4</sub>: C, 67.68; H, 8.27. Found: C, 67.65; H, 8.33.

**Reaction of the Triepoxide 2 with Deuterated Diazomethane.**—Deuterated diazomethane was prepared in a solvent system of tetrahydrofuran, D<sub>2</sub>O, and phenol-*O-d*.<sup>9</sup> One hundred milligrams of the triepoxide 2 was added to this solution and was allowed to react for 12 hr. The solvent was then removed and the product dried *in vacuo*. Gas chromatographic analysis of the product showed only the tetraepoxide 3 and the ketone 4 in approximately a ratio of 98:2, respectively. The products were separated by preparative glc. The nmr spectrum of the tetra-

epoxide showed at least 96% deuterium incorporation at one of exocyclic epoxy methylenes. The mass spectrum of the ketone 4 is described in the text.

**Reaction of *trans*-2,3,5,6-Diepoxy-2,5-di-*t*-butyl-1,4-benzoquinone (1) with Dimethylsulfonium Methylide.**—To a cold, freshly prepared DMSO solution of dimethylsulfonium methylide<sup>10</sup> was added 2.523 g of finely powdered diepoxide 1 as a DMSO slurry. The reaction solution was allowed to warm to room temperature and then poured into 500 ml of water. The white precipitate (1.917 g, 68.5% yield) was collected and shown to be the tetraepoxide 3 by mixture melting point, and comparison of its ir and nmr spectra to those of an authentic sample. Glc analysis of the crude product showed only the tetraepoxide 3.

**Reaction of *trans*-2,3,5,6-Diepoxy-2,5-di-*t*-butyl-1,4-benzoquinone with Dimethylsulfonium Methylide.**—The reaction of the diepoxide 1 with dimethylsulfonium methylide<sup>10</sup> was carried out in a manner analogous to that described above with dimethylsulfonium methylide. The product was again shown to be only the tetraepoxide 3 by glc, mixture melting point, and its ir and nmr spectra.

**Registry No.**—1, 10476-78-5; 2, 24903-91-1; 3, 24903-92-2; 4, 24903-93-3; diazomethane, 334-88-3.

**Acknowledgment.**—The authors are grateful to the National Science Foundation for partial financial support (GP 8706) of this work. We also express appreciation to Dr. Jean-Claude Gramain for helpful discussions.

(10) E. J. Corey and M. Chaykovsky, *ibid.*, **87**, 1357, 1355 (1966).

## Applications of Rare Earth Nuclear Magnetic Resonance Shift Reagents.

### II.<sup>1</sup> The Assignment of the Methyl Proton Magnetic Resonances of *d*-Camphor

C. C. HINCKLEY

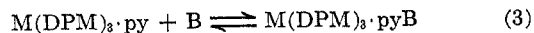
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Received January 23, 1970

When the dipyridine adducts of trisdipivalomethanato rare earth chelates, <sup>2</sup>M(DPM)<sub>3</sub>·2py, are dissolved in carbon tetrachloride, the molecules dissociate according to equations of the type



If an organic compound, B, having a basic coordinating group is added to the above solution, associations with the metal complexes may occur of the type



Contact shifts in the pmr spectrum of B are a consequence of this association if M is paramagnetic. The phenomenon of contact shifts has been known and studied for many years, as has the requirement for the observation of narrow nmr absorptions in paramagnetic systems, eq 4, where  $T_e$  is the electronic relaxation

$$\frac{1}{T_e} > a \quad (4)$$

(1) Part I: C. C. Hinckley, *J. Amer. Chem. Soc.*, **91**, 5160 (1969).

(2) Dipivalomethane, HDPm, is 2,2,6,6-tetramethylheptane-3,5-dione.