

of *o*-aminophenol in 2 l. of ether. After standing for 10 minutes, the reaction mixture was filtered and concentrated; 200 ml. of petroleum ether was added to the residue and the solution again filtered to remove amorphous material. The residue obtained after concentration was crystallized from hexane to give 3.74 g. (33%) of light brown needles,<sup>14</sup> m.p. 73–76°.

*Anal.* Calcd. for C<sub>11</sub>H<sub>15</sub>NO<sub>2</sub>S: N, 6.22; S, 14.23. Found: N, 6.33; S, 14.28.

**Phenyl *p*-Cyanothionocarbaniolate.**—Phenyl chlorothionocarbonyl<sup>15</sup> (10.4 g., 0.06 mole) in 35 ml. of chloroform was

(14) The surmise, ref. 6, that the inhibitory effect of a hydroxyl group in the *o*-position to the amino group is slight, is confirmed by the ability to prepare the desired thionocarbaniolate by method B.

(15) H. Rivier, *Bull. soc. chim. France*, [3] **35**, 837 (1906).

added slowly with cooling to 14.2 g. (0.12 mole) of *p*-aminobenzonitrile dissolved in 75 ml. of chloroform. After standing overnight at room temperature and subsequent filtration, the filtrate was concentrated to an oil which was purified by recrystallization from benzene–petroleum ether to give 9.39 g. (62%) of colorless needles, m.p. 112–122°.

*Anal.* Calcd. for C<sub>14</sub>H<sub>10</sub>N<sub>2</sub>OS: N, 11.02; S, 12.61. Found: N, 11.06; S, 12.59.

**Acknowledgment.**—The author wishes to express his appreciation to Miss Mary Dapero and Mrs. Lois Polansky for their technical assistance and to Mr. Louis Dorfman and his associates for the microanalyses.

SUMMIT, NEW JERSEY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO]

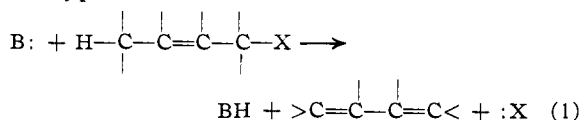
## Mechanisms of Elimination Reactions. XIII. 1,4-Conjugate Eliminations. I. Some *meso*-Dihydroanthracene Derivatives<sup>2</sup>

By STANLEY J. CRISTOL, WERNER BARASCH AND CHARLES H. TIEMAN

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The dibenzoates and diacetates of *cis*- and *trans*-1,5-dichloro-9,10-dihydro-9,10-anthradiol and the *trans*-monobenzoate have been prepared and characterized. The products of alkaline treatment of these compounds have been determined and the rates of their reactions with sodium hydroxide in ethanol–dioxane have been measured at various temperatures. Both thermal and base-promoted 1,4-conjugate elimination of acetic acid or benzoic acid from the diacetates or dibenzoates are considerably faster with the *trans* isomers than with the *cis* compounds, as is base-promoted loss of water from the two diols. Thus *cis* 1,4-conjugate elimination appears to be superior to the corresponding *trans* process. *trans*-1,8-Dichloroanthracene 9,10-dichloride was readily dehydrochlorinated (*cis* elimination) by alkali to give 1,8,10-trichloroanthracene. The ultraviolet absorption spectra of 1,5-dichloro-9-anthryl acetate and benzoate, of 1,5-dichloro-9-anthrone, of 1,5-dichloro-9-anthroxide ion and of 1,5-dichloro-9,10-anthraquinone are tabulated.

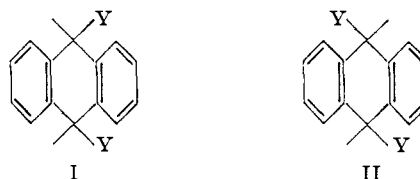
Elimination of groups from vicinal carbon atoms (1,2- or  $\beta$ -elimination) has been subjected to considerable investigation recently. In particular, we have been concerned with the establishment and understanding of the steric requirements of bimolecular 1,2-elimination. Reaction-rate data and quantities of activation have been used as evidence in support of mechanisms for *cis* and *trans* elimination.<sup>2</sup> It seemed worthwhile to extend our studies to include 1,4-conjugate elimination of the type



to determine how important steric factors are in such systems.<sup>3</sup>

9,10-Dihydroanthracene derivatives may lose substituents from the *meso* (9 and 10) positions and thus represent examples in which the stereochemistry of 1,4-conjugate elimination may be studied without the possibility of 1,2-elimination inter-

ference. Thus *cis* isomers of type I and *trans* isomers of type II can be studied in elimination (aromatization) reactions to determine what advantage *cis* or *trans* elimination may have over the other type.



Several examples of 1,4-conjugate elimination from such systems have been described previously.<sup>4–7</sup> Barnett and his co-workers<sup>6</sup> have suggested that both thermal and base-promoted elimination of *cis* groups from the *meso* positions occur exclusively. However, this rule appears to be intuitive, the evidence for it appears to be incomplete or faulty, and it has been criticized by Bergmann and Weizmann.<sup>7</sup> In view of the confused picture available from previous work and the fact that no studies had been conducted with *cis*–*trans* pairs, we attempted, without success thus far, the preparation of a pair of isomeric 9,10-dihalides. Such dihalides of anthracene and substituted anthracenes have received considerable

(4) O. Dimroth, *Ber.*, **34**, 219 (1901).

(5) C. Liebermann and M. Beudet, *ibid.*, **47**, 1011 (1914).

(6) E. d. B. Barnett, M. A. Mathews and J. W. Cook, *Rec. trav. chim.*, (a) **43**, 530 (1924); **44**, (b) 217; (c) 728; (d) 818; (e) 894 (1925); **45**, (f) 68, (g) 558 (1926).

(7) E. Bergmann and A. Weizmann, *THIS JOURNAL*, **60**, 1801 (1938).

(1) Previous paper in series: S. J. Cristol, W. P. Norris, A. Begoon and P. S. Ramey, *THIS JOURNAL*, **76**, 4558 (1954). A portion of this work was described at the Conference on Organic Reaction Mechanisms at Bryn Mawr, Penna., September 10, 1952.

(2) See, for example: (a) S. J. Cristol, N. L. Hause and J. S. Meek, *THIS JOURNAL*, **73**, 674 (1951); (b) S. J. Cristol and A. Begoon, *ibid.*, **74**, 5025 (1952).

(3) We have chosen to denote the process described in equation (1) as "1,4-conjugate elimination" in view of its obvious relationship to its opposite, 1,4-conjugate addition. The shorter term, "1,4-elimination," is subject to confusion with closure to a four-membered ring with elimination of groups in 1,4-position and is therefore not as precise a term.

study<sup>5-10</sup>; two isomers of any dihalide have not, however, been reported, although both *cis* and *trans*-dihalides are known, each in a different series.<sup>6,7</sup> In the course of this work we observed that photobromination of 9,10-dihydroanthracene gives 9,10-dibromoanthracene,<sup>10</sup> rather than a second isomer<sup>9</sup> of anthracene dibromide.<sup>6a,b,8</sup>

Both of the isomeric 1,5-dichloro-9,10-dihydro-9,10-anthradiols are known,<sup>6c</sup> however, and their structures have been established by dipole moment measurements.<sup>7</sup> We have prepared the acetates and benzoates of these isomers and have been able to study base-promoted elimination from these materials and from related compounds, as well as from 1,8,9,10-tetrachloro-9,10-dihydroanthracene (*trans*).

The diacetates of 1,5-dichloro-9,10-dihydro-9,10-anthradiol were prepared by treatment of 1,5-dichloro-9,10-dibromo-9,10-dihydroanthracene with sodium acetate in glacial acetic acid or by acetylation of the diols of known configuration,<sup>7</sup> by procedures described by Barnett.<sup>6c</sup> The structures of the *trans* isomer IVa, m.p. 265°, and of the *cis* isomer IIIa, m.p. 246°, may be inferred by their preparations from the corresponding diols<sup>11</sup> and were confirmed by dipole moment studies.<sup>12</sup> Mixtures of the two diols were obtained by reduction of 1,5-dichloro-9,10-anthraquinone (XII) with lithium aluminum hydride. Both diacetates were white, and the higher melting *trans* isomer decomposed at its melting point, eliminating acetic acid (hydrogen and acetoxy *cis*) to give a good yield of 1,5-dichloro-9-anthryl acetate (IXa). This represents a confirmed case of preferred *cis* thermal

1,4-conjugate elimination. The *cis*-diacetate was stable at this temperature.

The previously unknown dibenzoates of the two diols were prepared from the diols by esterification with benzoyl chloride. This synthesis established the structure of the esters which were then prepared in larger quantities by the reaction of silver benzoate with 1,5,9,10-tetrachloro-9,10-dihydroanthracene followed by separation of the two isomeric products from the resulting mixture.

In accordance with Barnett's intuitive *cis* rule, the *trans*-dibenzoate IVb, m.p. 254°, decomposed at its melting point to give the theoretical amount of benzoic acid and 45% of 1,5-dichloro-9-anthryl benzoate (IXb). The *cis* isomer IIIb, m.p. 251°, melted without decomposition.

The *trans*-1,5-dichloro-9,10-dihydro-9,10-anthradiol monobenzoate (VIb), was prepared also by benzoylation of the *trans*-diol VIIIb. *trans*-1,8,9,10-Tetrachloro-9,10-dihydroanthracene was prepared by the method of Liebermann and Beudet.<sup>5</sup>

**Reactions of the Esters with Alkali.**—The possible course of reaction of the various esters with alkali may be illustrated with the formulas in Fig. 1.

Combinations of product studies and of kinetic experiments were made to determine the path of the reactions for each of the substances studied. The benzoate systems were studied in greater detail than the acetates and will be discussed first. The reactions were studied in a solvent mixture comprising 75% dioxane and 25% of 92.6 wt. per cent. aqueous ethanol. The medium was found to dissolve the sodium hydroxide used as base as well as the organic substrates. *trans*-1,5-Dichloro-9,10-dihydro-9,10-anthradiol dibenzoate (IVb), was found to give 1,5-dichloro-9-anthryl benzoate (IXb), in excellent yields at 22° as measured by ultraviolet absorption spectra. The anthryl benzoate IXb was saponified more slowly than it was formed, but was converted to the anthrone XI or, by saponification and oxidation, to the anthraquinone XII.

The *cis*-dibenzoate IIIb was converted with alkali principally to the *cis*-diol VIIb, which was almost inert under the conditions of the experiment. In addition to the diol there was formed from IIIb, by elimination followed ultimately by oxidation of X or XI, 3.3 and 7% of the quinone XII (estimated by spectral measurements) at 22 and 62°, respectively. Thus, whereas the *trans*-dibenzoate IVb gives entirely elimination, only a small fraction of the *cis* compound reacts by this path.

The *trans*-monobenzoate VIb was observed to give the anthryl benzoate IXb by base-promoted elimination of water rather than the anthrol X by loss of benzoic acid. The *trans*-diol VIII also lost water by a bimolecular process, as indicated by spectral studies on the product.

The rates of the various elimination reactions were determined as described in the appropriate section below and the significant data are summarized in Table I.

It will be noted that the *trans*-dibenzoate eliminated benzoic acid to alkali at 22° at a rate 1200

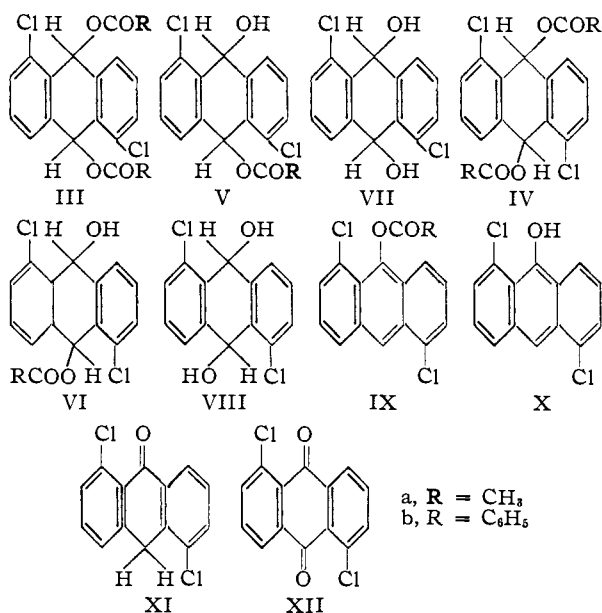


Fig. 1.

(8) W. H. Perkin, *Bull. soc. chim.*, **27**, 464 (1877); *Chem. News*, **34**, 145 (1876).

(9) J. R. Sampey, A. E. McCuen and J. M. Cox, *THIS JOURNAL*, **72**, 1854 (1950).

(10) J. R. Sampey, A. E. McCuen and J. M. Cox, *Furman Studies*, **33**, 56 (1950).

(11) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 356.

(12) M. T. Rogers, personal communication.

TABLE I  
DATA AND SECOND-ORDER REACTION RATE CONSTANTS FOR REACTIONS OF VARIOUS DERIVATIVES OF *meso*-DIHYDROANTHRACENE WITH SODIUM HYDROXIDE IN ETHANOLIC DIOXANE

Compound	Process studied	Temp., °C.	(Compd.) <i>M</i>	(NaOH) <i>M</i>	<i>k</i> , l./sec./mole	Eact., kcal./ mole	$\Delta S^\ddagger$ , cal./ deg./ mole
<i>trans</i> -1,5-Dichloro-9,10-dihydro-9,10-anthradiol dibenzoate (IVb)	Elimin. of benzoic acid	22.44	0.000474	0.00161	0.173	18.2	-2
			.000298	.00079	.172		
			.000548	.00159	.179		
			Ave.	.175			
		9.04	.000448	.00395	.0395		
			.000345	.00395	.0400		
			Ave.	.0398			
		1.97	.000686	.00316	.0178		
			.000251	.00402	.0172		
	Ave.	.0175					
<i>cis</i> -1,5-Dichloro-9,10-dihydro-9,10-anthradiol dibenzoate (IIIb)	Elimin. of benzoic acid	62.36	.000442	.00320	.0174	24	3
		22.44	.000392	.00161	.000149		
			.000466	.00403	.000138		
	Ave.	.000143					
<i>trans</i> -1,5-Dichloro-9,10-dihydro-9,10-anthradiol monobenzoate (VIb)	Elimin. of water	22.44	.000261	.00161	.344		
			.000425	.00159	.368		
				Ave.	.356		
<i>trans</i> -1,5-Dichloro-9,10-dihydro-9,10-anthradiol (VIII)	Elimin. of water	22.44	.00123	.00403	.0108		
			.00113	.00253	.0108		
				Ave.	.0108		
<i>cis</i> -1,5-Dichloro-9,10-dihydro-9,10-anthradiol (VII)	Elimin. of water	62.34	.000411	.00232	.0002 <sup>a</sup>		
<i>trans</i> -1,5-Dichloro-9,10-dihydro-9,10-anthradiol diacetate (IVa)	Elimin. of acetic acid	18.10	.000354	.00362	.0718	16.7	-8
			.000483	.00181	.0715		
				Ave.	.0717		
		10.46	.000283	.00362	.0314		
			.000405	.00724	.0332		
			Ave.	.0323			
		6.39	.000400	.00543	.0217		
			.000380	.00352	.0210		
			Ave.	.0213			
<i>trans</i> -1,8,9,10-Tetrachloro-9,10-dihydroanthracene	Elimin. of hydrogen chloride	18.10	.00165	.00375	.556	15.3	-9
			.00157	.00750	.548		
			.00162	.00281	.547		
			Ave.	.550			
		10.46	.00156	.00302	.270		
			.00161	.00906	.258		
			.00134	.00362	.264		
			Ave.	.264			
		6.39	.00190	.00362	.150		
.00173	.00543		.144				
	Ave.	.147					
1,5-Dichloro-9-anthryl benzoate	Saponification	47.20	.000937	.00319	.163		
			.000624	.00159	.168		
				Ave.	.165		
1,5-Dichloro-9-anthryl acetate (IXa)	Saponification	47.20	.000691	.00409	.921		
			.000944	.00327	.974		
				Ave.	.948		

<sup>a</sup> Estimated from only one reaction sample.

times that observed with the *cis*-dibenzoate in a process which the data show to be first-order in alkali and first-order in dibenzoate. The following argument demonstrates that the path for elimination from the *trans* isomer leads directly to the anthryl benzoate IXb and does not involve any intermediates. The possible intermediates to be considered are the *trans* monobenzoate VIb, arising from normal basic hydrolysis of *trans*-dibenzoate, and *cis*-monobenzoate Vb, arising by a nucleophilic displacement of benzoate ion at one of the *meso*

carbon atoms by hydroxide.<sup>13</sup> It is to be observed from the data in Table I that the *trans*-monobenzoate VIb does eliminate water to give IXb and at a rate twice that of the dibenzoate to IXb reaction. However, this cannot be the process involved in the transformation IVb to IXb, as this reaction gives a good rate constant with the formation of IXb being followed (see Figure 2). It is clear that

(13) The relative ease of nucleophilic displacement at a *meso* position has been shown by Barnett,<sup>6</sup> although the mechanisms of these displacements have not been studied.

if the process involved  $IVb \rightarrow VIb \rightarrow IXb$ , there would result an inhibition period (while the concentration of  $VIb$  built up) with an increasing rate constant during the course of reaction.

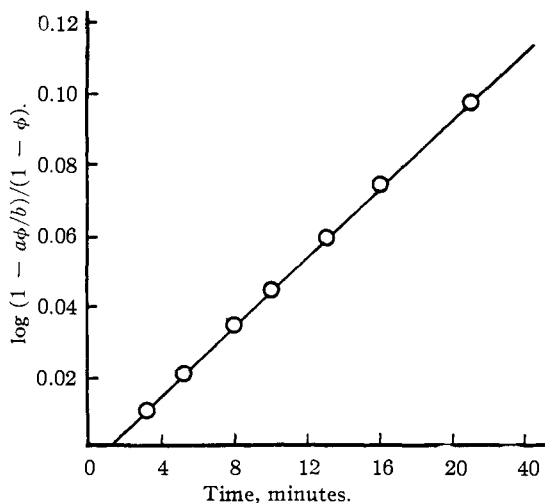


Fig. 2.—Treatment of rate data for the reaction of *trans*-1,5-dichloro-9,10-dihydro-9,10-anthradiol dibenzoate, 0.000548 *M*, with sodium hydroxide, 0.00159 *M*, at 22.44°.

The alternative process  $IVb$  to *cis*-monobenzoate  $Vb$  to  $IXb$  can be discarded for the following reasons. *cis*-Dibenzoate  $IIIb$  is converted by alkali in high yield to *cis*-diol  $VIIb$ . The intermediate in this reaction cannot be *trans*-monobenzoate  $VIb$ , as we have shown that this gives  $IXb$ . Hence the intermediate in this hydrolysis to *cis*-diol must be *cis*-monobenzoate  $Vb$ , and this therefore cannot be involved in the elimination process  $IVb$  to  $IXb$ .

The path of elimination accounting for 3 to 7% of the reaction of the *cis*-dibenzoate is not clear. The reaction may involve a *trans* elimination of benzoic acid from  $IIIb$  to give  $IXb$ , may involve *trans* elimination of water or of benzoic acid from the unknown *cis*-monobenzoate  $Vb$  to give  $IXb$  or  $X$ , or may involve a nucleophilic displacement on a *meso* carbon atom of  $IIIb$  or  $Vb$  to give the *trans* systems  $VIb$  or  $VIIIb$ . In the *cis* case rates were followed by production of the anthraquinone  $XII$  and elimination from either  $VIb$  or  $VIIIb$  is sufficiently fast to allow these as intermediates. Hence the rate indicated in Table I for elimination from the *cis*-dibenzoate represents the *maximum* value for *trans* elimination in this system, and *cis* elimination of the elements of benzoic acid is preferred over *trans* elimination by a factor of at least 1200.

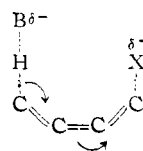
*trans*-1,2-Dichloro-9,10-dihydro-9,10-anthradiol diacetate ( $IVa$ ) eliminated acetic acid smoothly to give the anthryl acetate  $IXa$ . Good rate constants were observed of magnitude slightly lower than that of the corresponding dibenzoate  $IVb$ . The *cis* diacetate  $IIIa$  did not eliminate smoothly, if at all, and no clean-cut assignment of the ultraviolet absorption spectrum could be made. The products of the reaction of  $IIIa$  with alkali were not analyzed. However evidence for the relative slowness of the reaction was obtained by isolating 87% of the

starting material under conditions where over 99.9% of the *trans* isomer would be estimated to have reacted. This leads to a *maximum* value for the rate constant for elimination from the *cis*-acetate at 50° of about 0.01 l./sec./mole, which may be compared with the value of 1.0 l./sec./mole extrapolated from the data of Table I for the *trans* isomer. Here again, *cis*-1,4-conjugate elimination is favored by a large amount over the corresponding *trans* elimination.

The third case in this series arises in the diols where the *trans*-diol  $VIII$  eliminates water with alkali in a bimolecular process at a fairly high rate at 22°, whereas the *cis*-diol  $VII$  is much less reactive under similar conditions at 62°.

**Reaction of *trans*-1,8-Dichloroanthracene 9,10-Dichloride with Alkali.**—The product of the elimination reaction from this dichloride has been described by Liebermann and Beudet<sup>5</sup> and by Barnett, Cook and Mathews.<sup>6f</sup> However, the structure could be either 1,8,9- or 1,8,10-trichloroanthracene. Dr. Rogers<sup>12</sup> has informed us that the product is the 1,8,10-isomer. Thus in the elimination the *meso* proton removed is from the 10-position (*i.e.*, that more remote from the two benzenoid chlorine atoms). One might expect that the *meso* hydrogen in the 9-position would be more acidic in view of its closer station with respect to the electron-attracting 1- and 8-chlorine atoms; however, it may be that the steric bulk and electrical charge on the combined 1-, 8-, and 9-chlorine atoms are sufficient to discourage attack on the 9-hydrogen atom by an hydroxide ion.<sup>14</sup> Alternatively, the results may reflect the preferred conformation of the carbon-hydrogen and the carbon-chlorine bonds at the 9- and 10-positions (see below).

**Discussion of Results.**—The results above indicate a clear superiority in rate in bimolecular *cis*-1,4-conjugate elimination over the corresponding *trans* process. The results may be interpreted in terms of a concerted *cis* process involving inversions at carbons 1 and 3, *viz.*



This process might be considered to be analogous with the abnormal bimolecular allylic displacement reaction<sup>15,16</sup> in the same manner that *trans*-1,2-elimination formally has been considered analogous to ordinary bimolecular direct displacement processes.<sup>2,17</sup>

At the present time, however, we hesitate to generalize on the results for several reasons. It has been reported<sup>18</sup> that *trans*-1,4-conjugate elimination is favored over *cis* in isomeric 3,4,5,6-

(14) In this regard see ref. 2 and W. Hüchel, W. Tappe and G. Legutke, *Ann.*, **543**, 191 (1940).

(15) R. E. Kepner, S. Winstein and W. G. Young, *THIS JOURNAL*, **71**, 115 (1949); W. G. Young, I. D. Webb and H. L. Goering, *ibid.*, **73**, 1076 (1951).

(16) G. Stork and W. N. White, *ibid.*, **75**, 4119 (1953).

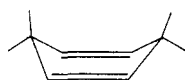
(17) S. J. Cristol, *ibid.*, **69**, 338 (1947).

(18) H. D. Orloff and A. J. Kolka, *ibid.*, **76**, 5484 (1954).

tetrachlorocyclohexenes. Also Bergmann and Weizmann<sup>7</sup> have shown that 1,5,9,10-tetrachloro-9,10-dihydroanthracene is *cis*, yet Liebermann and Beudet<sup>8</sup> and Barnett and his co-workers<sup>6c</sup> have stated that alkali eliminates hydrogen chloride (*trans*) from this system.

The superiority in *cis*-1,4-conjugate thermal elimination over the corresponding *trans* process may be understood readily by recourse to a cyclic transition state analogous to those proposed for thermal 1,2-eliminations.<sup>19</sup>

Bond angles about carbon-carbon double bonds require the central ring in the *meso*-dihydroanthracene system to be a boat-form cyclohexadiene ring of shape XIII such that the bond orientations at the 9- and 10-positions are not equivalent. Two



XIII

*cis* bonds may be designated as axial and two as equatorial.<sup>20</sup> In the *trans* system one bond is equatorial and one axial. There appears to be no reason to assume that interconversion from one conformation to the other would have a high enough energy requirement to be involved as the rate-determining step in reactions such as we are studying, but recent work on 1,2-elimination<sup>21,22</sup> makes it quite likely that 1,4-conjugate elimination may have a preferred conformation in the transition state in the same sense as does 1,2-elimination. If this is the case, preference for *cis* or *trans* conjugate elimination may depend upon certain conformations. Just as the presence of halogen atoms on the 1 and 3 rings in the anthracene molecule influences the course of addition of chlorine to yield *cis* or *trans* isomers,<sup>7</sup> so may elimination also be altered by electronic or steric influences of halogen substituents. Although, as indicated above, an attractive mechanism may be conceived to suggest reasons for preference for *cis* elimination, it is clear that much more experimental work is necessary to establish the generality or lack of generality of stereochemical preferences in 1,4-conjugate elimination. We hope to continue such work.

Elimination reactivities of the *trans*-dibenzoate IVb, *trans*-monobenzoate VIb and *trans*-diol VIII (see Table I) are of interest. The monobenzoate lost water at a rate about twice that at which the dibenzoate eliminated benzoic acid and at a rate 33 times faster than the *trans*-diol eliminated water. It therefore appears as if the loss of both fragments may be concerted in *cis*-1,4-conjugate elimination as is believed to be the case in *trans*-1,2 elimination,<sup>2a</sup> with the relative rates in the first comparison (IVb *vs.* VIb) the result of the nature of

the departing anion. A second comparison (VIb *vs.* VIII) shows that a benzoxy group is more effective in labilizing a hydrogen as a proton than is a hydroxy group. This is probably an inductive effect and would probably therefore be anticipated in view of the relative acid strengths of benzoic acid and water.

The ease of base-promoted elimination of water from the *trans*-diol and the *trans*-monobenzoate was of interest as this type of reaction is not well known. The dehydration of alcohols is generally accomplished with acid catalysts or by pyrolysis of esters of the alcohols.<sup>23</sup> The dehydration which sometimes occurs in a base-catalyzed aldol condensation may be analogous to the reactions observed here.<sup>24</sup>

A comparison of reactivities of 1,5-dichloro-9,10-dihydro-9,10-anthradiol diacetate IVa and dibenzoate IVb and 1,8-dichloroanthracene 9,10-dichloride seems of interest. It will be noted (Table I) that these three compounds all eliminate with alkali at approximately the same order of magnitude (within one power of 10) in rate. Although the comparisons are somewhat restricted because of the fact that the positions of the chlorine atoms on the benzene rings are not identical, we were surprised that the diesters eliminated acetic and benzoic acid at about the same rate as the other compound lost hydrogen chloride. We have been unable to find direct analogies in the literature, but apparently base-promoted elimination from esters is not generally observed because of the much greater rate of saponification of ordinary esters as compared with elimination from analogous chlorides. For example, an extrapolation of the data of Rylander and Tarbell<sup>25</sup> for alkaline saponification of isopropyl acetate in 62% aqueous acetone indicates a rate constant about 10<sup>4</sup> times greater than that found for base-promoted elimination of hydrogen chloride from isopropyl chloride in 80% aqueous ethanol at 80°.<sup>26</sup>

Further evidence that the diacetate IVa and the dibenzoate IVb react by direct elimination rather than rate-determining saponification followed by elimination may come from the relative rates, IVa being somewhat slower than IVb. This order of reactivity is opposite to that observed<sup>27</sup> for the alkaline hydrolysis of the corresponding ethyl esters in 85–90% aqueous ethanol, where the acetate was saponified 8–10 times as rapidly as the benzoate. On the other hand, 1,5-dichloro-9-anthryl acetate (IXa) was saponified about 6 times as fast as the benzoate IXb, analogous with the hydrolysis of the ethyl esters.

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(23) C. Weygand, "Organic Preparations," Interscience Publishers, Inc., New York, N. Y., 1945, p. 318.

(24) See also R. P. Linstead, L. N. Owen and R. F. Webb, *J. Chem. Soc.*, 1211 (1953).

(25) P. N. Rylander and D. S. Tarbell, *THIS JOURNAL*, **72**, 3021 (1950).

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### Experimental

**1,5-Dichloroanthracene**, m.p. 186° (cor.), was prepared as described by Bergmann and Weizmann.<sup>7</sup> Bromination of this compound in dry carbon tetrachloride<sup>8</sup> gave 1,5-dichloro-9,10-dibromo-9,10-dihydroanthracene, m.p. 176–180° dec. Barnett<sup>6</sup> reported an m.p. of 186° for this compound. We were unable to recrystallize the compound from dioxane or nitromethane without loss of bromine and regeneration of 1,5-dichloroanthracene.

***cis*- and *trans*-1,5-Dichloro-9,10-dihydro-9,10-anthradiol Diacetates (IIIa and IVa).**—Four grams (10 mmoles) of 1,5-dichloroanthracene dibromide was added to a hot solution of 7 g. of anhydrous sodium acetate in 35 ml. of glacial acetic acid, and the solution was heated under reflux for 25 minutes. After the solution had cooled to room temperature, the mixture was poured onto 150 g. of ice. The precipitate was filtered and was triturated with acetone until the residue was white. This residue, m.p. 235–255° (2.2 g., 60%), was fractionally crystallized from 40% dioxane in acetone to give 1.0 g. of *cis*-1,5-dichloro-9,10-dihydro-9,10-anthradiol diacetate (IIIa), m.p. 246°, and 0.5 g. of the *trans* isomer IVa, m.p. 263–265° dec.

*Anal.* Calcd. for C<sub>18</sub>H<sub>14</sub>Cl<sub>2</sub>O<sub>4</sub>: C, 59.19; H, 3.86. Found (*cis* isomer): C, 59.08; H, 3.96. Found (*trans* isomer): C, 58.84; H, 3.82.

Barnett and co-workers<sup>6</sup> reported only the isolation of the *cis* isomer, m.p. 246°, by this procedure, although the lack of stereospecificity in displacement reactions at the *meso* positions has been observed in a number of other cases.<sup>6,7</sup> The mechanisms of these displacement reactions apparently have not been studied. The diacetates were also prepared by treatment of the corresponding diols with acetic anhydride in pyridine, substantially as described by Barnett and co-workers.<sup>6</sup> Their *trans* product was reported to melt at 259°.

***cis*- and *trans*-1,5-Dichloro-9,10-dihydro-9,10-anthradiols (VII and VIII).**—A solution of 0.09 mole of lithium aluminum hydride and 13.8 g. (0.05 mole) of 1,5-dichloro-9,10-anthraquinone (XII), m.p. 247–248.5°, in 200 ml. of dry ether was allowed to stand at room temperature for 20 days (with occasional shaking). The mixture was then cooled in an ice-salt-bath and was decomposed by the addition of 200 ml. of commercial ether, followed by 100 ml. of water and 50 ml. of 2 *N* sulfuric acid. The ethereal solution was separated, and the ether was removed by distillation. Extraction with 80 ml. of hot acetone gave a mixture from which 1.0 g. of starting material and 1.0 g. (7%) of *cis*-1,5-dichloro-9,10-dihydro-9,10-anthradiol (VII), m.p. 210–212°, were isolated, the latter by crystallization from toluene. Subsequent extraction of the residue with boiling dioxane or pyridine gave 7.2 g. (52%) of the *trans*-diol VIII, m.p. 244–245°.

This preparation of the diols by reduction of the quinone is more convenient than the preparation *via* 1,5-dichloroanthracene 9,10-dibromide described by Barnett.<sup>6</sup> Barnett reported a m.p. of 210° for the *cis*-diol and one of 244° for the *trans* isomer. The structures of these diols have been elaborated by Bergmann and Weizmann.<sup>7</sup>

***trans*-1,5-Dichloro-9,10-dihydro-9,10-anthradiol Dibenzoate (IVb).**—*trans*-1,5-Dichloro-9,10-dihydro-9,10-anthradiol (400 mg., 1.4 mmoles) in 5 ml. of pyridine containing 0.6 ml. (5.2 mmoles) of benzoyl chloride was allowed to stand overnight in an ice-box. The white product was then filtered and after washing with ether melted with decomposition at about 230°. Recrystallization from dioxane and then xylene gave 430 mg. (62%) melting at 248–250°. Two more crystallizations from dioxane yielded material melting at 253.5–254° dec.

*Anal.* Calcd. for C<sub>28</sub>H<sub>18</sub>Cl<sub>2</sub>O<sub>4</sub>: C, 68.72; H, 3.71. Found: C, 68.44; H, 3.91.

***cis*-1,5-Dichloro-9,10-dihydro-9,10-anthradiol Dibenzoate (IIIb).**—*cis*-1,5-Dichloro-9,10-dihydro-9,10-anthradiol (8 mg., 0.03 mmole) in 0.2 ml. of pyridine containing 0.05 ml. (0.43 mmole) of benzoyl chloride was allowed to stand in an ice-box for one day. The benzoate was precipitated with 1 ml. of water and recrystallized from 4 ml. of acetone in 10-ml. centrifuge tubes. Colorless crystals were obtained (11.2 mg., 76%) which melted at 242–246°. Recrystallization from acetone again raised the m.p. to 250–251° (without decomposition). This was distinguished from the *trans* compound by its melting without decomposition and by the fact that a mixture of the two melted at 238–253° dec.

*Anal.* Calcd. for C<sub>28</sub>H<sub>18</sub>Cl<sub>2</sub>O<sub>4</sub>: C, 68.72; H, 3.71. Found: C, 68.61; H, 3.88.

***cis*- and *trans*-1,5-Dichloro-9,10-dihydro-9,10-anthradiol Dibenzoates from 1,5-Dichloroanthracene Dihalides.**—1,5,9,10-Tetrachloro-9,10-dihydroanthracene<sup>5</sup> (2.1 g., 6.6 mmoles) was stirred in dry dioxane at room temperature for two days with 5 g. (22 mmoles) of silver benzoate. The solid obtained by precipitation with water was extracted with 80 ml. of hot acetone and then with hot dioxane until no precipitation was noted when the extract was diluted with water. An orange oil was precipitated from the acetone washes with water, and washing this with 25 ml. of acetone left 380 mg. (12%) of the crude *cis*-dibenzoate, m.p. 227–232°. Recrystallization of this from acetone gave 230 mg. (7.2%) of the *cis* isomer melting at 243–245° and from the extracts from the oil was obtained 300 mg. (19%) of crude dichloroanthracene, m.p. 175–186°. The dioxane extracts yielded 1.34 g. (42%) of the *trans*-dibenzoate, m.p. 248–250° dec.

When this reaction was carried out using the 1,5-dichloroanthracene 9,10-dibromide with stirring for one day, there was more decomposition to form dichloroanthracene and difficulty was encountered in the separation of it from the *cis*-dibenzoate. Crude dichloroanthracene (m.p. 140–160°), crude *cis*-dibenzoate (m.p. 185–210°) and *trans*-dibenzoate (m.p. 250–251°) were obtained in 24, 4 and 30% yields, respectively.

**1,5-Dichloro-9,10-dihydro-9,10-anthradiol Monobenzoate (VIb).**—*trans*-1,5-Dichloro-9,10-dihydro-9,10-anthradiol (VIII) (560 mg., 2 mmoles) was allowed to stand in an ice-box for 12 hours with 0.45 ml. (3.9 mmoles) of benzoyl chloride in 7 ml. of pyridine. Water was then added and 755 mg. of white solid, melting over a range from 155 to 200° was collected. Fractional crystallization of this from dioxane gave first 150 mg. (15%) of dibenzoate, m.p. 246–249° (no depression with authentic material), then 120 mg. of mixed products (m.p. 200–215°) and finally 118 mg. (15%) of the desired monobenzoate melting at 178–180°. Two recrystallizations from toluene and one from dioxane brought the melting point to 180–181°.

*Anal.* Calcd. for C<sub>21</sub>H<sub>14</sub>Cl<sub>2</sub>O<sub>3</sub>: C, 65.46; H, 3.66. Found: C, 65.47; H, 3.75.

The above was the fifth attempt to prepare the compound from the diol. The other reactions were run in the same manner, but with varying molar ratios of benzoyl chloride to diol, and gave poorer results.

**1,5-Dichloro-9-anthryl Acetate (IXa).**—A solution of 400 mg. (1.5 mmoles) of 1,5-dichloroanthrone (XI)<sup>28</sup> and 0.5 ml. (5 mmoles) of acetic anhydride in 5 ml. of dry pyridine was heated on a steam-bath for two hours. Addition of water to the reaction mixture precipitated 460 mg. (100%) of crude acetate, m.p. 170–175°. Recrystallization from acetone gave feathery yellow needles, m.p. 177.5–178°.<sup>29</sup>

This same material was obtained by heating *trans*-1,5-dichloro-9,10-dihydro-9,10-anthradiol diacetate (IVa) above its melting point.

*Anal.* Calcd. for C<sub>16</sub>H<sub>10</sub>O<sub>2</sub>Cl<sub>2</sub>: C, 62.97; H, 3.30. Found: C, 62.92; H, 3.44.

**1,5-Dichloro-9-anthryl Benzoate (IXb).**—1,5-Dichloroanthrone (XI) (800 mg., 3 mmoles) was heated on a steam-bath for two hours in 10 ml. of pyridine containing 0.6 ml. (5 mmoles) of benzoyl chloride. After cooling, water was added and the yellow product collected. This weighed 1.2 g. and melted at 170–175°. Recrystallization from acetone gave 1.02 g. (93%) of bright yellow needles melting at 178–

(28) E. d. B. Barnett and M. A. Mathews, *J. Chem. Soc.*, 2549 (1923).

(29) E. d. B. Barnett, J. W. Cook and M. A. Mathews, *Ber.*, 58, 976 (1925), report an m.p. of 178°.

179°. A second recrystallization from acetone gave a product melting at the same temperature.

*Anal.* Calcd. for  $C_{21}H_{12}Cl_2O_2$ : C, 68.68; H, 3.30. Found: C, 68.73; H, 3.30.

Sixteen milligrams (45%) of the same material was obtained by heating 50 mg. of *trans*-1,5-dichloro-9,10-dihydro-9,10-anthradiol dibenzoate (IVb) just above its melting point.

Thirty milligrams (0.06 mmole) of IVb was heated in a sealed tube for 30 minutes at 240–275°. The tube was cooled and opened, and the contents were taken up in water. The liberated acid was titrated with 0.01 *N* sodium hydroxide; 0.06 meq. of base was required.

**1,8-Dichloroanthracene** was prepared by reduction of 1,8-dichloro-9,10-anthraquinone, following the procedure of Bergmann and Weizmann<sup>7</sup> and was converted by chlorine in carbon tetrachloride to 1,8,9,10-tetrachloro-9,10-dihydroanthracene, m.p. 183–186° dec., as described previously.<sup>5,7</sup> The products of the decomposition at the m.p. of the tetrachloro compound was 1,8,10-trichloroanthracene,<sup>12</sup> m.p. 191°. Liebermann and Beudet<sup>5</sup> and Barnett, Cook and Mathews<sup>6f</sup> have shown that this same trichloro compound is produced by the action of alkali.

**Isolation of Products in the Reaction of *cis*-1,5-Dichloro-9,10-dihydro-9,10-anthradiol Dibenzoate with Alkali.**—*cis*-1,5-Dichloro-9,10-dihydro-9,10-anthradiol dibenzoate (22.4 mg., 0.046 mmole) was dissolved in 45 ml. of 75% ethanolic dioxane, brought to temperature (62.3°), and base was then added to make the solution 0.00640 *N* in sodium hydroxide when brought to 50-ml. volume. After one hour at this temperature 0.4 millimole of acetic acid in alcohol was added and the solvent was removed *in vacuo* at 40–50°. The white residue was washed with a total of 4 ml. of water and 1 ml. of 2% sodium carbonate solution, and taken up in 2 ml. of acetone. The volume of acetone was reduced to 0.5 ml. and water was added to the hot solution until cloudy. The solid obtained on cooling was centrifuged, the acetone decanted and the precipitate washed with 0.1 ml. of acetone. The acetone fractions were thereafter lost when a tube containing them was crushed during centrifuging. The solid melted at 200–210° and was recrystallized from toluene to give 8.2 mg. (64%) of the *cis*-diol, melting at 216–217°. This was reconverted to the dibenzoate (m.p. 245–246.5 with no dec.; mixed m.p. with authentic *cis*-dibenzoate, 244–246°) in 39% yield.

The solutions remaining from the two rate runs with the *cis*-dibenzoate at 22° (see Table I) were combined after three days and the base was neutralized with dilute acetic acid. Evaporation to dryness *in vacuo* yielded a white residue which was taken up in 9 ml. of acetone. The acetone solution was separated by centrifuging or was evaporated from the filtrate leaving 10.5 mg. of white solid melting at 195–210°. This was recrystallized from toluene to give 8.9 mg. (98%) of the *cis*-diol melting at 216–217° without decomposition. Mixed with authentic *cis*-diol (m.p. 215–216°) this melted without depression.

**Isolation of Products in the Reaction of *trans*-1,5-Dichloro-9,10-dihydro-9,10-anthradiol Monobenzoate with Alkali.**—The reaction between *trans*-1,5-dichloro-9,10-dihydro-9,10-anthradiol monobenzoate (0.00077 *M*) and sodium hydroxide (0.0025 *M*) in 75% alcoholic dioxane (100 ml.) was allowed to proceed for 44 minutes at 22.4° before stopping with dilute acetic acid solution. The calculated fraction reacted at this time was 0.81 without a correction for further saponification of the anthryl benzoate. The solvent was removed *in vacuo* on a steam-bath and the yellow residue was taken up in 20 ml. of acetone. Evaporation of the acetone gave 27.5 mg. of yellow, toluene-soluble material. Recrystallization from toluene gave material melting at 172–176°, and, after another recrystallization from acetone, 13.3 mg. (58% of expected) of 1,5-dichloro-9-anthryl benzoate melting at 173.5–175°, was obtained. Mixed with authentic benzoate, m.p. 178–179°, it melted at 174–176°, while when mixed with dichloroanthrone it melted at 154–169°.

**Relative Stability of *cis*-1,5-Dichloro-9,10-dihydro-9,10-anthradiol Diacetate with Alkali.**—A 411-mg. sample of *cis*-1,5-dichloro-9,10-diacetoxy-9,10-dihydroanthracene was dissolved in 75 ml. of dioxane at 50.0°, 10 ml. of 0.36 *M* ethanolic sodium hydroxide solution was added, and the system brought to a volume of 100 ml. with 92.6% aqueous ethanol. The concentration of the acetate was 0.0112 *M* and that of the base 0.036 *M*.

After five minutes at 50°, 50 ml. of the solution was poured into 100 ml. of dilute hydrochloric acid (0.03 *M*) containing 5 g. of sodium acetate, and cooled on ice for ten minutes. A white precipitate appeared at the moment of addition to the aqueous acid. To determine the loss of diacetate inherent in the method, a second experiment was performed, where 200 mg. of the diacetate was dissolved in 50 ml. of solvent and immediately poured into 100 ml. of dilute hydrochloric acid containing 5 g. of sodium acetate. The loss of the solvent was 27 mg. This number was added to the milligrams of precipitate recovered in the first experiment (157, m.p. 238–243°; a mixture with authentic starting material melted at 238–243°).

**Absorption Spectra.**—Absorption spectra of many of the compounds prepared in the course of this work were measured in the near ultraviolet and/or visible range in 95% ethanol solutions by means of a Beckman model DU spectrophotometer. The *meso*-dihydro compounds, represented by the 1,5-dichloro-9,10-dihydro-9,10-anthradiols (VII and VIII), their diacetates and dibenzoates (III and IV) and the *trans*-monobenzoate (VIb) all had no significant absorption of light at wave lengths above 300  $m\mu$ . The spectra of the anthryl acetate IXa, the benzoate IXb, the anthrone XI, the anthraquinone XII and the sodium anthroxide (salt of X), were of use in following the reactions and their maxima and minima are as follows: ( $\lambda$  is wave length in  $m\mu$  and  $\epsilon$  is the molar extinction coefficient,  $^{\circ}$  shoulder).

IXa, maxima:  $\lambda$  399,  $\epsilon$  9420;  $\lambda$  378,  $\epsilon$  9950;  $\lambda$  358,  $\epsilon$  6560;  $\lambda$  342,  $\epsilon$  3150;  $\lambda$  255,  $\epsilon$  134000. Minima:  $\lambda$  390,  $\epsilon$  3690;  $\lambda$  365,  $\epsilon$  4220;  $\lambda$  345,  $\epsilon$  2890;  $\lambda$  300,  $\epsilon$  510;  $\lambda$  230,  $\epsilon$  7450.

IXb, maxima:  $\lambda$  400,  $\epsilon$  10400;  $\lambda$  379,  $\epsilon$  10900;  $\lambda$  359,  $\epsilon$  7160;  $\lambda$  342,  $\epsilon$  3420;  $\lambda$  255,  $\epsilon$  120000. Minima:  $\lambda$  390,  $\epsilon$  3830;  $\lambda$  365,  $\epsilon$  4800;  $\lambda$  345,  $\epsilon$  3240;  $\lambda$ , 300,  $\epsilon$  490.

XI, maxima:  $\lambda$  300–315,  $\epsilon$  3350;  $\lambda$  257,  $\epsilon$  19000. Minimum:  $\lambda$  244,  $\epsilon$  8500.

XII, maxima:  $\lambda$  344,  $\epsilon$  26800;  $\lambda$  254,  $\epsilon$  175000. Minimum:  $\lambda$  295,  $\epsilon$  7300.

Salt of X, maxima:  $\lambda$  396,  $\epsilon$  6200;  $\lambda$  378,  $\epsilon$  6600;  $\lambda$  360,  $\epsilon$  5400;  $\lambda$  340,  $\epsilon$  4200. Minimum:  $\lambda$  390,  $\epsilon$  5600. (This compound was not studied below 320  $m\mu$ .)

#### Measurements of Reaction Rates

**General Procedure for Elimination Reactions.**—Rate measurements were made in 50- or 100-ml. volumetric flasks using 75 volume % of dry dioxane<sup>30</sup> in ordinary commercial ethanol (92.6 weight %). The base solutions were prepared by dilution from a saturated solution of sodium hydroxide in ethanol (treated with silver oxide and distilled<sup>31</sup>), the final dilution being made to result in a 75% alcoholic dioxane solution. The substrate was weighed into the volumetric flask, dissolved in the dioxane-ethanol solvent, and brought to temperature. An aliquot of standard base solution, whose titer was determined just prior to use by titration with 0.1 *N* hydrochloric acid and phenolphthalein indicator, was added, the reaction mixture was brought to volume with the mixed solvent and the flask was shaken at zero reaction time. Five-milliliter samples were removed at suitable time intervals and the reaction stopped by quenching in 1 ml. of 0.2 *M* acetic acid in ethanol.

The reactions were followed spectrophotometrically as the starting *meso*-dihydroanthracene did not absorb above 300  $m\mu$ . With the *trans*-dibenzoate IVb and diacetate IVa and with the *trans*-monobenzoate VIb the formation of 1,5-dichloroanthryl benzoate (IXb) or acetate IXa was followed by measuring the extent of light absorption at the maximum at 378–379  $m\mu$ .

The formation of the anthryl benzoate was noted in the first samples taken in the elimination reaction of the *cis*-dibenzoate IIIb, but the rate of elimination was so slow that saponification of this intermediate occurred more rapidly than its production. Since this saponification yielded the anthrolate which in turn on acidification gave the anthrone XI, it was found necessary, in order to follow the reaction, to oxidize the anthrone, which had no suitable peak for a spectrophotometric concentration determination, to the anthraquinone XII with hydrogen peroxide-sodium carbonate solution. The rate samples were added to 1 ml. of 3% hydrogen peroxide, and then 1 ml. of 1% sodium car-

(30) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., New York, N. Y., 1941, p. 369.

(31) I. M. Kolthoff and V. A. Stenger, "Volumetric Analysis," Interscience Publishers, Inc., New York, N. Y., 1947, p. 72.

bonate solution was added. The loss of water from the *trans*-diol VIII gave the anthrolate directly and these rate samples were treated in the same manner as with the *cis*-dibenzoate. The reaction samples taken of the other compounds were transferred into dilute alcoholic acetic acid to neutralize the base, and the optical density at the appropriate wave length was determined in the acidic solution.

The rate calculations were all made on the basis of the reactions being first order in base and first order in the compound studied. No base was assumed to be used up in the loss of water from the *trans*-hydroxy benzoate, and one equivalent of base was assumed to be consumed in the eliminations from the *trans*-dibenzoate and from the *trans*-diol by the formation of the anthrolate ion.

The rates with the *cis*-dibenzoate were complicated by the fact that the major product with base was the diol given by saponification. At 22 and 62° the reaction was followed until anthraquinone production appeared to cease. This was found to be at 3.3 and 7% reaction, respectively. The *cis*-diol was isolated from the reaction mixtures at both temperatures. Rate constants for the elimination reactions were calculated by multiplying the fraction of the reaction observed to be elimination by the appropriate factor (30 in the 22° case) to convert to total fraction reaction and plotting the usual logarithmic function of this, assuming two equivalents of base consumed per mole of dibenzoate, against time (Fig. 2). The rate constant thus obtained when divided by the same conversion factor gave the rate constant for elimination. The 4% deviation between the two runs at 22° seems surprisingly good in view of the very minor extent of the elimination reaction and the consequential small optical densities to be determined (less than 0.1).

The unexpected loss of water, and not benzoic acid, from the *trans*-hydroxy benzoate was shown to take place both from the spectra of the rate samples being identical to that of 1,5-dichloroanthryl benzoate and the isolation of the pure product from the reaction mixture.

The rate constant given in Table I for the loss of water from the *cis*-diol was calculated from one point obtained 25 hours after the saponification of the *cis*-dibenzoate had

gone to completion. Correction was made for the 7% elimination from the dibenzoate and for the base used up in the initial fast reactions.

Most of the spectral measurements were obtained with a Beckman model DU spectrophotometer, but some runs were measured with a Coleman model 14 universal spectrophotometer. The latter instrument had a poorer resolving power and spectral curves of products had to be measured for comparison.

**Procedure for *trans*-1,8,9,10-Tetrachloro-9,10-dihydroanthracene.**—Solutions were prepared as described in the previous section, but the samples withdrawn from time to time were added to excess standard hydrochloric acid. The excess acid was back titrated with standard sodium hydroxide, using rosolic acid as indicator.

**Saponification of 1,5-Dichloroanthryl Benzoate (IXb) and Acetate (IXa).**—Solutions were prepared and handled as described above. The extent of reaction was estimated spectrophotometrically from the extent of disappearance of the light absorption maximum in the 370–380 m $\mu$  range.

**Calculations of Rate Constants.**—The form of the second-order rate equation used was

$$d \log \frac{1 - xa\varphi/b}{1 - \varphi} / dt = \frac{b - xa}{2.303} k$$

where  $a$  is initial substrate concentration,  $b$  is initial hydroxide concentration,  $\varphi$  is fraction of substrate reacted at time  $t$  and  $k$  is the specific reaction rate constant. The term  $x$  represents the moles of base consumed per mole of substrate reacted and was equal to 1 for the *trans*-diacetate IVa and dibenzoate IVb (formation of anthryl acetate IXa or benzoate IXb and acylate ion), for the *trans*-diol VIII (formation of the anthroxide), as well as for the tetrachloro compound, was equal to 2 for the *cis*-dibenzoate (formation of two moles of benzoate ion) and for the saponification of the anthryl acetate IXa and benzoate IXb, and was equal to 0 for elimination from the *trans*-monobenzoate VIb.

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[CONTRIBUTION NO. 1227 FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

## The Preparation of Stereoisomeric Epoxy Ketones Related to Chalcone Oxide<sup>1,2</sup>

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The usual methods for the preparation of  $\alpha$ -epoxy ketones involving reaction of  $\alpha,\beta$ -unsaturated ketones with alkaline hydrogen peroxide lead to products whose configurations are not necessarily related to those of the starting olefins. A stereo-specific method for the preparation of epoxy ketones in the present work involves reduction of the carbonyl group of the *cis* or *trans* unsaturated ketone to the alcohol, epoxidation with perbenzoic acid, and then reoxidation of the epoxy alcohol to the ketone by means of chromic anhydride-pyridine complex. In this way the hitherto unknown *cis*-chalcone oxide has been prepared. Correlations between the configuration and the ultraviolet absorption spectra of a number of *cis*- and *trans*-epoxy ketones have been made.

In connection with the determination of the configurations of *cis*- and *trans*- $\gamma$ -halo- $\alpha$ -epoxy ketones,<sup>3</sup> recently shown<sup>4-6</sup> to be the products of a Darzens-like condensation of the phenacyl halides with sodium methoxide, methods were sought for the conversion of  $\alpha,\beta$ -unsaturated ketones of known configuration to the corresponding *cis*- and *trans*-epoxides. The general method commonly employed in the formation of  $\alpha$ -epoxy ketones from

$\alpha,\beta$ -unsaturated ketones involves treatment with alkaline hydrogen peroxide, the method of Weitz and Scheffer.<sup>7</sup> This method is, however, limited by the fact that the configuration of the starting olefin is not necessarily preserved in the process of epoxide formation. Thus, as has recently been shown,<sup>8</sup> both the *cis* and *trans* isomers of chalcone<sup>9</sup> react with alkaline hydrogen peroxide to yield the same epoxy ketone, m.p. 90°, while under the same reaction conditions the known form of dypnone, which is assumed to have the *trans* configuration, reacts<sup>5</sup> to form two epoxy ketones, m.p. 94 and 164°. It has been found<sup>5</sup> furthermore that in the preparation of epoxy ketones related to dypnone oxide, the product which is formed initially, is con-

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(2) Presented, in part, at the 124th Meeting of the American Chemical Society, Chicago, Ill., Sept. 6 to 11, 1953.

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