

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Investigations on the Stereoisomerism of Unsaturated Compounds. VII. Further Studies on Diastereomeric Dibromides<sup>1</sup>

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**Introduction.**—In the work of Young, Jasaitis and Levanas<sup>2</sup> on the preparation of the diastereomeric 4,5-dibromoöctanes and the *cis*- and *trans*-4-octenes related to them, as well as in the later expansion to similar compounds reported by Young, Pressman, and Coryell,<sup>3</sup> it was necessary to assume that removal of bromine from a dibromide with zinc and consequent re-addition of bromine did not result in diastereomer formation. This seemed warranted by the fact that such regenerations of dibromobutanes<sup>4</sup> did not cause any formation of diastereomer.

However, it was shown later by Lucas, Schlatter and Jones<sup>5</sup> that, in the case of the *threo*- and *erythro*-2,3-dibromopentanes, debromination with zinc and readdition of bromine caused diastereomer formation to the extent of 2–3%. As the four-carbon systems did not involve isomerization and the five-carbon system did, it seemed possible to us that the six- and eight-carbon systems might be increasingly unsatisfactory. This prediction seemed likely in view of the fact that the ratio of the reported rates of reaction with potassium iodide of *meso*- and *dl*-4,5-dibromoöctane was extremely low (*ca.* 1.3) as compared with the corresponding dibromobutanes and dibromohexanes (2–3).<sup>3</sup>

It was also necessary to assume in the earlier syntheses that treatment with fuming hydrobromic acid of sterically pure  $\alpha$ -diacetates resulted in the formation of sterically pure dibromides with an odd number of Walden inversions.<sup>6</sup>

These considerations led us to a detailed investigation of the steps involved in these syntheses. It is the purpose of this paper to describe the synthesis of several pairs of diastereomeric dibromides from pure diastereomeric glycols through the diacetates and the purification of these products by low temperature recrystallization, and to report the kinetic constants of these dibromides in their reaction with potassium iodide in 99% methanol. A comparison is also made of the physical properties and rate constants of the dibromides obtained by debromination of some of these purified dibromides with zinc and re-bromination of the resulting olefins with those of the original pure dibromides.

**Reaction Rate Constants for Pure Dibromides**

The preparation of the dibromides is described in the later experimental section. The measure-

(1) For previous papers on this subject, see references 2, 3, 4, 11, and 17.

(2) Young, Jasaitis and Levanas, *THIS JOURNAL*, **59**, 403 (1937).

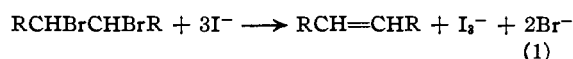
(3) Young, Pressman and Coryell, *ibid.*, **61**, 1640 (1939).

(4) Young and Winstein, *ibid.*, **58**, 102 (1936).

(5) Lucas, Schlatter and Jones, *ibid.*, **63**, 22 (1941).

(6) Wilson and Lucas, *ibid.*, **58**, 2396 (1936).

ments of reaction rates with potassium iodide in 99% methanol were made as described previously<sup>3</sup> by titration of the triiodide ion liberated with standard sodium thiosulfate solution. The reaction involved is



for which the rate is first order with respect to both the dibromide and iodide concentrations.<sup>7</sup>

An analysis of equation (1) for the reaction first order with respect to both dibromide and iodide concentrations leads to the following equation connecting initial iodide concentration  $a$ , initial dibromide concentration  $b$ , fraction  $\varphi$  of the dibromide consumed, and  $t$ , time in hours

$$d \log_{10} \frac{1 - 3b\varphi/a}{1 - \varphi} / dt = \frac{a - 3b}{2.303} k_{\text{obsd.}} \quad (2)$$

Values of  $\log_{10} (1 - 3b\varphi/a / 1 - \varphi)$  corresponding to the various samples of a run were plotted against corresponding values of  $t$ , and the best straight line drawn through the points. The slope of this line was multiplied by the value of  $2.303/a - 3b$  for the run to give  $k_{\text{obsd.}}$ . Column 2 of Table I lists the values of  $k_{\text{obsd.}}$  for the compounds studied in this report.

**Correction of Rate Constants.**—These values of  $k_{\text{obsd.}}$  were corrected to exactly 60.00 or 75.00°, and for solvent expansion from the temperature of mixing the solution to 60 or 75°, as well as for small salt corrections where necessary, by methods described previously.<sup>3</sup> These corrected constants are listed in column 4 of Table I as  $k_{\text{cor.}}$

It has been shown that different solvent preparations of 99% methanol exhibit slightly different rates for the same compound.<sup>3,4</sup> The solvent used in these measurements was prepared from synthetic methanol and gave rate constants 5.7% higher than those in natural methanol<sup>8</sup> for 1,2-dibromobutane and mixtures of the 2,3-dibromobutanes.

**Discussion of Results.**—The specific reaction rate constants and the Arrhenius heats of activation for the reaction of several pairs of diastereomeric dibromides with potassium iodide in 99% methanol are listed in columns 5 and 7 of Table I. In the earlier paper of Young, Pressman and Coryell,<sup>3</sup> the generalization was made that the *meso* (or *dl-erythro*) isomer, that is, the one related to the *trans* parent hydrocarbon by *trans* addition of bromine, always had a greater rate constant and a lower activation energy than the *dl* (or *dl-threo*) isomer. These rules were suggested as a means for distinguishing *cis-trans* isomers by for-

(7) Dillon, *ibid.*, **54**, 952 (1932).

(8) Dillon, Young and Lucas, *ibid.*, **52**, 1953 (1930).

TABLE I  
 DATA AND CALCULATED VALUES FOR REACTION RATE CONSTANTS AND HEATS OF ACTIVATION

Dibromide	$k_{\text{obsd.}}$	Temp., °C.	$k_{\text{cor.}}^a$	Av. $k_{\text{cor.}}^a$	% Deviation	Heat of activation
<i>dl</i> -threo-2,3-Dibromopentane <sup>b</sup>	0.0330	74.88	0.0357	0.0358	0.3	25.71
	.03345	74.88	.0359			
	.00637	60.01	.00668	.00671	.5	
	.00644	60.01	.00675			
<i>dl</i> -erythro-2,3-Dibromopentane <sup>b</sup>	.0889	74.93	.0949	.0949 <sup>c</sup>	...	
	.0877	74.88	.0942			25.66
	.01717	60.00	.01791	.01785	.7	
	.01706	60.00	.01779			
<i>dl</i> -3,4-Dibromohexane <sup>b</sup>	.04084	74.93	.04398	.04435	.8	
	.04152	74.93	.04472			
	.007423	59.92	.007850	.007849	.2	26.60
	.007420	59.92	.007847			
<i>meso</i> -3,4-Dibromohexane	.1435	74.92	.1540 <sup>d</sup>	.1543	.2	
	.1440	74.94	.1540 <sup>d</sup>			
	.1436	74.91	.1549 <sup>b</sup>	.03005	.2	25.10
	.02885	59.98	.03009 <sup>d</sup>			
	.02875	59.98	.03000 <sup>d</sup>			
<i>dl</i> -3,4-Dibromoöctane <sup>b</sup>	.0566	74.93	.0603	.0604	.2	
	.0562	74.91	.0605			
	.01183	59.98	....	.01234	...	24.40
<i>meso</i> -3,4-Dibromoöctane <sup>b</sup>	.1699	74.93	.1811	.1828	.9	
	.1712	74.91	.1845			
	.0339	59.98	....	.0353	...	25.25

<sup>a</sup> These results have been corrected for solvent expansion, salt effect and to the temperatures 75.00 or 60.00°. <sup>b</sup> Purified by recrystallization. <sup>c</sup> This value has been chosen as it agrees with values obtained previously.<sup>8</sup> <sup>d</sup> This compound was not purified by recrystallization, but was not resolvable with brucine.<sup>15</sup>

mation of the dibromides. The data herein reported indicate that, in the case of the *meso*- and *dl*-4,5-dibromooctanes, the generalization regarding the heat of activation is no longer true. However, it still seems correct to assume that rate constants alone are sufficient for identifying the dibromides from *cis-trans* isomers of the type herein discussed.

#### Extent of Diastereomer Formation in Dibromide Syntheses

The dibromohexanes and octanes were prepared through the steps glycol  $\rightarrow$  diacetate  $\rightarrow$  dibromide. The conversion of glycol to diacetate does not involve the configuration of the asymmetric carbon atoms. The second step, which involves the net replacement of two acetoxy groups by bromines with hydrobromic acid, has been shown<sup>6,9</sup> to occur with an odd number of Walden inversions. We have measured the reaction rate at 75° of the *meso*-3,4-dibromohexane obtained from *dl*-3,4-diacetoxyhexane and purified simply by washing and distillation. This has a  $k_{\text{cor.}}$  of 0.1540 as compared with 0.1549 for the dibromide recrystallized several times from methanol at -80°. <sup>10</sup> As this deviation is well within experimental error, it may be assumed that this synthesis method causes no measurable diastereomer formation.

(9) Winstein and Lucas, *THIS JOURNAL*, **61**, 1576, 1581 (1939).

(10) Low temperature recrystallization has been found useful in separation of dibromides by Kharasch, Walling and Mayo, *ibid.*, **61**, 1559 (1939); see also ref. 5.

An attempt was made to make a similar comparison of *dl*-4,5-dibromooctane. In this case recrystallization of the crude dibromide caused an increase in rate constant from 0.0545 to 0.0613 and in refractive index from 1.4921 to 1.4982. However, the impurities removed by the recrystallization process must have been reaction intermediates such as bromoglycol or bromoacetate<sup>9</sup> rather than the diastereomer since the changes in rate constant and refractive index were in the opposite direction to those expected if appreciable amounts of diastereomer were present.

**The Dibromide-Olefin-Dibromide Cycle.**—Purified recrystallized samples of *dl*-3,4-dibromohexane and *dl*-4,5-dibromooctane were dropped onto zinc-copper couple in boiling 95% ethanol and the resulting olefins were removed by co-distillation with the solvent simultaneous with the addition. To the olefins, which were washed and distilled, were added the theoretical amounts of bromine. The regenerated dibromides, after washing and distillation, had the rate constants listed in Table II. In this table are also listed the

 TABLE II  
 DIASTEREOMER FORMATION IN DIBROMIDE-OLEFIN-DIBROMIDE CYCLE

Dibromide	Original	Av. $k_{\text{cor.}}$ (75°) After treatment	% diastereomer after treatment
<i>dl</i> -3,4-Dibromohexane	0.0444	0.0514	6.4
<i>dl</i> -4,5-Dibromoöctane	.0614	.0843	19.5

compositions of the resulting mixtures, assuming the only contaminants were the diastereomeric dibromides.

These data indicate the serious error which may be involved in the use of this treatment in the synthesis and purification of diastereomeric dibromides or in the synthesis of *cis-trans* olefins corresponding to them.

The exact step or steps in the procedure where diastereomer formation occurs has not been determined. The removal of bromine by zinc from dibromobutanes has been suggested to occur with the donation of two electrons by zinc to one bromine atom rapidly followed by or simultaneous with the inversion of the other carbon by the liberated electrons from the carbon-bromine bond and the resultant formation of olefin and bromide ion in order to explain the completely *trans* elimination in this reaction.<sup>11</sup> In the case of the higher molecular weight products, it is possible that the life of the carbanion fragment from which positive bromine has been removed is sufficiently long to allow for racemization.

The addition of bromine to the olefin, which is assumed to occur with the donation of positive bromine to the olefinic linkage to form the positive three-membered ring bromonium ion,<sup>12</sup> may involve stereomutation by a process involving a preliminary opening of the ring to form a carbonium ion which may reclose after the carbon-carbon bond has rotated half a revolution or may react directly with bromide ion.

Perhaps a more likely mechanism for racemization involves *cis-trans* rearrangement of the olefin in the zinc treatment of the dibromide. In the treatment, the strong acid zinc bromide is formed which may catalyze the rearrangement. The increase in rearrangement with increasing molecular weight may be a result of increased contact time with the catalyst,<sup>13</sup> as the higher molecular weight olefins were removed from the zinc bromide solution more slowly.

The rearrangement of *trans*-2-butene to a mixture of *cis*- and *trans*-2-butene with phosphoric acid, as well as the rearrangement of 1-butene to 2-butene with various acid catalysts including aqueous zinc chloride has been reported.<sup>13</sup> Here the rearrangement of the olefins includes not only *cis-trans* isomerization, but also double-bond migration. Further work on this postulated zinc salt rearrangement of olefins is planned in view of these results, since bromine addition and removal with zinc, as well as removal of bromine and alkoxy, has been a common tool in the synthesis of olefins.<sup>2,3,14,15,16</sup>

(11) Winstein, Pressman and Young, *THIS JOURNAL*, **61**, 1645 (1939).

(12) Roberts and Kimball, *ibid.*, **59**, 947 (1937).

(13) Ipatieff, Pines and Schaad, *ibid.*, **56**, 2697 (1934).

(14) Gladstone and Tribe, *Ber.*, **7**, 364 (1874); *J. Chem. Soc.*, **21**, 306 (1878).

(15) Wilkinson, *J. Chem. Soc.*, 3057 (1931).

(16) Boord, *et al.*, *THIS JOURNAL*, **53**, 3398 (1930); **54**, 751 (1932); **55**, 3293 (1933).

The authors are indebted to Professor H. J. Lucas for his generosity in furnishing samples of some of the dibromides.

### Preparation of Materials

**2,3-Dibromopentanes.**—These compounds were kindly supplied by Professor H. J. Lucas<sup>4</sup> of the California Institute of Technology.

**3,4-Dibromohexanes.**—Samples of pure *meso*- and *dl*-3,4-hexanediol were prepared by separation of the diastereomers in the mixture resulting from the catalytic hydrogenation of the product from the pinacolic reduction of acrolein with zinc-copper couple.<sup>17</sup> Each of the glycols was acetylated with a 20% excess of acetic anhydride, using a few drops of concentrated sulfuric acid as catalyst. The reaction flask was cooled in water in order to control the violent reaction. After a few hours at room temperature, anhydrous calcium carbonate was added to neutralize the acid catalyst. The liquid was decanted from the inorganic solid and distilled through a small glass helices-filled column. The yield of crude diacetate at this stage was 89% for both isomers. The diacetates were then redistilled in a 3-foot adiabatic metal spiral column at high reflux. The physical properties of the diacetates were: *dl*, b. p. 88.0–88.4° (5.5 mm.),  $n_D^{20}$  1.4239,  $d_4^{25}$  0.9953, equiv. wt., calcd., 101.1, found, 101.6, 100.9; and *meso*, b. p. 83.3–83.7° (5.5 mm.),  $n_D^{20}$  1.4193,  $d_4^{25}$  0.9843, equiv. wt., found, 100.1, 100.6.

The diacetates were converted to dibromides with the aid of 65% aqueous hydrogen bromide, using 200 ml. of the reagent to 0.3 mol of the diacetate. The reactants were mixed in a glass-stoppered bottle, sealed against pressure, and allowed to stand for about a week in the dark with intermittent shaking. The crude dibromide layers were washed with water, potassium carbonate solution, water, and then filtered to clarify. The yield of crude *dl* dibromide (from the *meso* diacetate) was 90%, of *meso*, 98%. The dibromides were dried over anhydrous potassium carbonate and distilled in a Weston column.

The dibromides were recrystallized several times from methanol at "dry-ice" temperature. The *meso* dibromide was crystallized twice from 4 volumes of methanol (recovery 76%). The *dl* dibromide was recrystallized 4 times from 4 volumes of methanol. This isomer did not form as clean crystals as the *meso* isomer, as a large fraction of the solvent seemed to be tied up with the solid in the earlier recrystallizations (recovery 50%). The recrystallized dibromides were washed with water, dried with anhydrous potassium carbonate, and distilled with anhydrous potassium carbonate, and distilled in a Weston column. The physical properties of the dibromides were: *dl*, b. p. 72.1–72.5° (9 mm.),  $n_D^{20}$  1.5050 and  $d_4^{25}$  1.5897; *meso*, b. p. 70.1–70.3° (9 mm.),  $n_D^{20}$  1.5078 and  $d_4^{25}$  1.5946.

11.9 g. of the *dl*-dibromide was added dropwise to a copper-zinc couple, prepared by adding 170 ml. of 10% copper sulfate solution to 14.5 g. of granular 80-mesh zinc and washing with water and 95% alcohol, covered completely with boiling 95% ethanol in a distilling flask. The rate of addition was such as to approximate the rate of removal of olefin by co-distillation with aqueous alcohol. After the addition was completed and the distillate had become miscible with water, heating was stopped. The distillate was diluted with ice and water; the oil phase was removed, washed several times with water and dried with calcium chloride. The hexene distilled in a small Claisen flask at 65.4–66.4°; yield, 2.6 g. (64%). The equivalent amount of bromine was added to the hexene cooled to –2°. The crude dibromide was washed with sodium bisulfite and sodium bicarbonate solutions, then dried over anhydrous potassium carbonate. Distillation in a modified Claisen flask gave 4.7 g. boiling at 71.0–72.5° (9 mm.). The purity of this material has been discussed above.

A sample of the unrecrystallized but non-resolvable *meso* isomer was obtained from Professor H. J. Lucas.<sup>18</sup>

(17) Young, Cristol and Weiss, *ibid.*, **65**, 1245 (1943).

(18) Lucas and Gould, *ibid.*, **64**, 601 (1942).

**4,5-Dibromoöctanes.**—Samples of the *dl* and *meso* isomers which were obtained from Professor Lucas<sup>18</sup> were used as the pure compounds in the rate determinations.

A large sample of the *dl*-dibromide was prepared from the *meso*-diacetate as described by Lucas and Gould.<sup>18</sup> The crude product (yield 85%) upon distillation through a Weston column had a rate constant  $k_{cor.}$  of 0.0545 (pure compound 0.0604), indicating contaminants of relatively unreactive bromohydrins and/or bromoacetates (confirmed by lower refractive index,  $n_D^{20}$  1.4921, 1.4982 for pure *dl*-dibromide). Upon four recrystallizations, the  $k_{cor.}$  was 0.0613.

15.6 g. of this material was treated with a zinc-copper couple as described above for the *dl*-dibromohexane. The recovered olefin, b. p. 121–123.5° (yield 72%), was treated with bromine as above, and the dibromide product was distilled to give 7.9 g. of material boiling at 97.5–100° (9 mm.). The purity of this material has been discussed above.

### Summary

Pure samples of the *meso*- and *dl*-dibromohexanes and octanes have been prepared from the pure diastereomeric glycols through their corresponding diacetates. A comparison of physical properties and rates of reaction with potassium iodide in 99% methanol before and after recrystallization indicates that little or no diastereomer formation is involved in the change glycol  $\rightarrow$  diacetate  $\rightarrow$  dibromide. A comparison of pure recrystallized dibromides with samples obtained by debromination with zinc followed by bromination of the resulting olefin indicates an increasing tendency toward stereomutation as the number of carbon atoms is increased from four to eight.

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## The $\gamma$ Bands in Absorption Spectra

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It was first pointed out by Lewis and Calvin<sup>1</sup> that in a planar or nearly planar molecule there should be two types of absorption bands. In the one case, the  $\alpha$  bands, the electronic oscillations characterizing the excited state have a certain direction in the molecule, and this direction may be called the main optical axis. In the other case, the  $\gamma$  bands, the electronic vibrations of the excited state are in that direction in the plane perpendicular to that main axis.

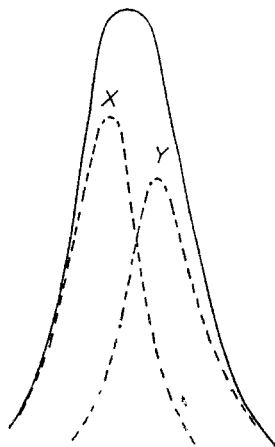


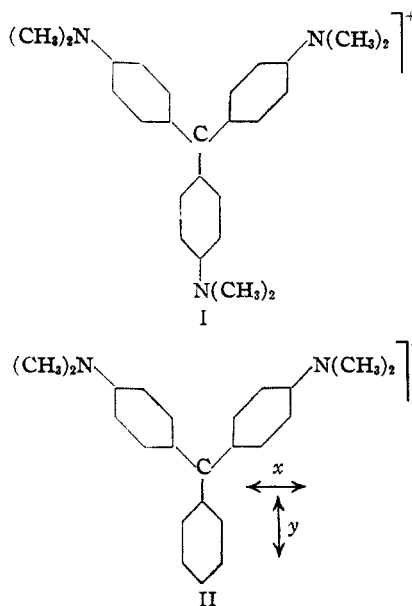
Fig. 1.—Hypothetical resolution of the band of a radially symmetrical molecule into an  $\alpha$  and  $\gamma$  band, when a slight dissymmetry is introduced.

If we could measure the polarizability of such a planar molecule in different directions, we should find a direction of maximum polarizability and, at right angles thereto, a direction of minimum polarizability. These two directions may be identified with the  $x$  and  $y$  axes of absorption. In a symmetrical molecule such as that of crystal violet (I) we have a degenerate case, in which the polarizability (except perhaps at very great field strength) is the same in all directions of the plane.<sup>2</sup> In such a case the  $\alpha$  and  $\gamma$  bands coincide.

If, in a symmetrical molecule, such as the A isomer of crystal violet, we make some minor chemi-

(1) Lewis and Calvin, *Chem. Rev.*, **25**, 273 (1939).

(2) This would not be quite true of the B isomer found by Lewis, Magel and Lipkin, *THIS JOURNAL*, **64**, 1774 (1942).



cal substitution so as to produce a slight dissymmetry, we should expect the absorption curve to be resolved into two neighboring  $\alpha$  and  $\gamma$  bands as indicated schematically in Fig. 1. If the dissymmetry is great, as in malachite green (II), where one of the auxochromes has been entirely removed, we may expect a wide separation and indeed, as was first shown by Hantzsch,<sup>3</sup> there are two bands<sup>4</sup> in the visible, one at 6250 Å. and another at 4230 Å.

(3) Hantzsch, *Ber.*, **52**, 509 (1919).

(4) Foerster, *Z. Elektrochem.*, **45**, 548 (1939), quoting also the earlier work of Eistert, "Tautomerie und Mesomerie," Ferdinand Enke, Stuttgart, 1938, concluded that malachite green should have two bands for the one of crystal violet. However, these authors considered only the energy and not the orientation of the excitations.