

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 696, AND THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

## Investigations on the Stereoisomerism of Unsaturated Compounds. V. A Mechanism for the Formation of Butenes from 2,3-Dibromobutanes by the Action of Iodide Ion

BY SAUL WINSTEIN, DAVID PRESSMAN AND WILLIAM G. YOUNG

The reaction of 1,2-dihalides with inorganic iodides to yield unsaturated compounds has been studied from a kinetic standpoint<sup>1</sup> and has been recommended as a method for synthesis of ethylenic compounds.<sup>2</sup> In spite of the considerable attention paid the reaction, the steric result of the elimination of halogen by iodide ion has remained uncertain<sup>1d</sup> until the present time. The question as to whether bromine is eliminated *trans* or *cis* to give pure products or by both of these processes to give a mixed product is of importance from the theoretical standpoint in formulating a mechanism for the reaction and from a practical standpoint for deciding the applicability of the reaction to syntheses of stereoisomeric olefin derivatives. It is the purpose of this paper to show that the removal of bromine from 2,3-dibromobutanes by iodide ion involves almost entirely *trans* elimination at moderate temperatures and that at a higher temperature considerable rearrangement accompanies the reaction. The mechanism of the reaction is discussed on the basis of the experiments presented here and of the previous kinetic results.

The nature of the elimination of bromine from 2,3-dibromobutanes by iodide was investigated by treating pure 2,3-dibromobutanes or a mixture of them with iodide ion either in aqueous propanol at approximately 95° or in diethylene glycol at approximately 200°. The generated butenes were converted to dibromobutanes and analyzed by measuring the rate of reaction of the final dibromide with potassium iodide in methyl alcohol.<sup>1e,3</sup> Table I summarizes the results obtained. Inspection of the table discloses that in propyl alcohol at the lower temperature *meso*-2,3-dibromobutane gives rise to a butene which is 96% *trans*, and *dl*-2,3-dibromobutane

gives a butene which is 91% *cis*. Also the ratio of isomers in a mixed dibromide is essentially unchanged by the successive elimination and addition of bromine. These results show that *trans* elimination is by far the predominating reaction. However, in diethylene glycol at the higher temperature *dl*-2,3-dibromobutane gives a butene mixture showing that considerable rearrangement occurs, but even here the elimination is largely *trans*. The small changes in composition of the dibromides at the lower temperature and the considerable change at the higher temperature may be due to the isomerizing effect of the iodine on the butenes<sup>4</sup> or possibly the participation of a mechanism other than the predominating one.

**The Mechanism of the Reaction.**—The facts that: (a) the elimination of halogen from 1,2-diiodoethane, 1-bromo-2-iodoethane, and 1,2-dibromides, in general, is first order with respect to the dihalide and iodide ion concentrations<sup>1</sup>; (b) elimination of halogen is induced by reducing agents such as iodide ion or zinc; and (c) the elimination of bromine by iodide ion is *trans* suggest a general mechanism (equations (1), (2) and (3)) for the elimination of iodide ion which is in part the reverse of Ogg's<sup>5</sup> negative mechanism for the addition of halogen to the ethylenic linkage.

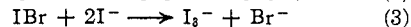
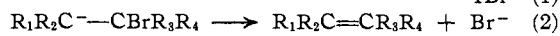
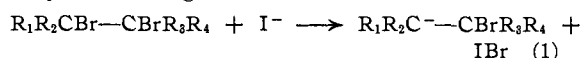


Figure 1 shows graphically the mechanism we propose. Iodide ion attacks and donates elec-

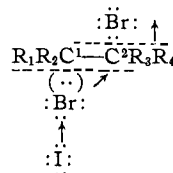


Fig. 1.

(1) (a) Slator, *J. Chem. Soc.*, 1697 (1904); (b) Billmann, *Rec. trav. chim.*, **36**, 319 (1917); (c) Van Duin, *ibid.*, **43**, 341 (1924); **45**, 345 (1926); (d) **47**, 734 (1928); (e) Dillon, Young and Lucas, *THIS JOURNAL*, **52**, 1953 (1930); (f) Dillon, *ibid.*, **54**, 952 (1932); (g) Davis and Heggie, *J. Org. Chem.*, **2**, 470 (1938); (h) Young, Pressman and Coryell, *THIS JOURNAL*, **61**, 1640 (1939).

(2) Hickinbottom, "Reactions of Organic Compounds," Longmans, Green and Co., New York, N. Y., 1936, p. 369.

(3) Young and Winstein, *THIS JOURNAL*, **58**, 102 (1936).

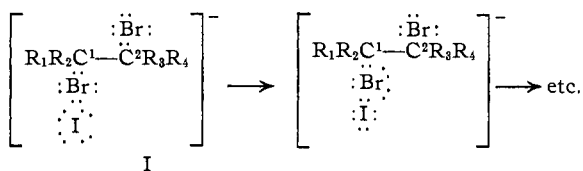
(4) Gilman, "Organic Chemistry," John Wiley and Sons, Inc., New York, 1938, p. 376.

(5) Ogg, *THIS JOURNAL*, **57**, 2727 (1935).

TABLE I  
 THE COMPOSITION OF BUTENES RESULTING FROM THE ACTION OF IODIDE ION ON 2,3-DIBROMOBUTANES

No.	$K_2$	Original dibromide % <i>dl</i>	% <i>meso</i>	Solvent	Temp., °C.	$K_2$	Final product % <i>cis</i>	% <i>trans</i>
1	0.0564	0	100	PrOH	95	0.0554	4	96
2	.0299	100	0	PrOH	95	.0322	91	9
3	.0490	28	72	PrOH	95	.0495	26	74
4	.0298	100	0	$C_4H_{10}O_3$	200	.0394	64	36

trons<sup>6</sup> to one of the bromine atoms of the dibromide giving iodine bromide and the interme-



diolate,  $R_1R_2C^- - CBrR_3R_4$ . The unshared pair of electrons on carbon atom 1 then rapidly attacks the carbon face opposite the remaining bromine atom, freeing bromide ion with inversion of carbon atom  $C^2$ . A double bond has thus been formed between carbon atoms  $C^1$  and  $C^2$  and the whole process is then a *trans* elimination of bromine. The iodine bromide formulated as a product immediately reacts with iodide ions to give triiodide and bromide ions.

It is thought that the life of the  $R_1R_2C^- - CBrR_3R_4$  intermediate is exceedingly short, because otherwise reaction with solvent and racemization<sup>7</sup> about carbon atom  $C^1$  would be serious. The decomposition of  $R_1R_2C^- - CBrR_3R_4$  is thought to occur essentially simultaneously with the breaking of the C—Br bond of carbon atom  $C^1$ . Thus, we have here a process quite analogous to the usual bimolecular exchange leading to Walden inversion.<sup>8</sup> In the usual bimolecular exchange involving a negative ion, this ion presents a pair of electrons to an atom, another substituent being expelled with a pair of electrons previously shared. In our process an electron transfer has been brought about but through a longer chain of atoms.

Figure 1 depicts the structure of the 1,2-dibromide as being one with the two bromine atoms *trans* to each other, enabling the electron transfer discussed above to take place. The *trans* configuration with respect to the two bromine atoms is reasonable because this structure

(6) Professor Linus Pauling has suggested to one of us that perhaps a complex ion, I, is formed which then undergoes the electron transfer to be outlined.

(7) Cowdrey, Hughes, Ingold, Masterman and Scott, *J. Chem. Soc.*, 1257 (1937).

(8) (a) Olson, *J. Chem. Phys.*, **1**, 448 (1933); (b) Meer and Polauvi, *Z. physik. Chem.*, **B19**, 164 (1932).

may be essentially the normal state of affairs in dihalides<sup>9</sup> or it may tend to be assumed on the approach of the iodide ion.

One might have assumed that the first step in the reaction of iodide ion with a dihalide is a bimolecular exchange of iodide for bromide (with inversion of the carbon atom concerned) with subsequent rapid reaction of the iodobromide. But then for the reaction of the iodobromide with iodide ion only a mechanism such as that proposed by us seems plausible. Thus a total of two Walden inversions would be present in the process and *cis* elimination instead of *trans* elimination would be its result. We feel, therefore, that exchange of iodide for bromide is at most only a subsidiary reaction at low temperatures, but that it may explain part of the deviations from clean-cut *trans* elimination of bromine by iodide ion.

### Experimental

**Preparation of *meso*-2,3-Dibromobutane.**—*trans*-2-Butene was prepared by a modification of the method of Wislicenus, Talbot, Henze and Schmidt<sup>10</sup> in which tiglic acid hydrobromide instead of tiglic acid hydriodide<sup>11</sup> was used.

A solution of 70 g. (0.66 mole) of sodium carbonate in 700 ml. of water was cooled to 0° and added to 60 g. (0.33 mole) of tiglic acid hydrobromide in a flask equipped with a mercury-sealed stirrer and a gas delivery tube. The mixture was warmed slowly. At 30° a slow evolution of gas began. The gas was washed with sodium hydroxide solution, dried with anhydrous calcium chloride and condensed in an ampoule cooled with a solid carbon dioxide-alcohol bath. The temperature of the reaction mixture was raised to 70° over a period of two and one-half hours. The gas evolved at this temperature was soluble in sodium hydroxide and presumably was carbon dioxide. The yield of olefin was 80%. When the reaction was completed in one and one-half hours only 65% yield was obtained. The butene was converted to dibromide by the method previously described.<sup>11</sup>

The tiglic acid hydrobromide was prepared by Mr. Zene Jasaitis by the action of dry hydrogen bromide on a solution of tiglic acid in chloroform.

(9) (a) Beach and Stevenson, *J. Chem. Phys.*, **6**, 635 (1938); (b) Beach and Palmer, *ibid.*, **6**, 639 (1938).

(10) Wislicenus, Talbot, Henze and Schmidt, *Ann.*, **313**, 207 (1909).

(11) Young, Dillon and Lucas, *This Journal*, **51**, 2528 (1929).

**Preparation of *dl*-2,3-Dibromobutane.**—*dl*-2,3-Dibromobutane was prepared from *meso*-2,3-butanediol by the synthesis outlined by Wilson and Lucas.<sup>12</sup>

**Reaction of 2,3-Dibromobutanes with Sodium Iodide in Propanol.**—Seventy grams (0.46 mole) of sodium iodide was dissolved in a warm mixture of 75 ml. of *n*-propanol and 25 ml. of water. Then 20 g. (0.093 mole) of 2,3-dibromobutane was added. Two liquid phases were present initially but a homogeneous solution resulted upon further heating. The mixture was refluxed gently, the evolved gas being washed with water, dried with calcium chloride and collected in a cold ampoule at  $-78^{\circ}$ . In the reaction flask, iodine was liberated and a white precipitate of sodium bromide formed. After four hours of refluxing, the rate of butene evolution was slow and the reaction was stopped, the apparatus being flushed out with air. The crude yield of hydrocarbon was 87% of the theoretical from *meso*-2,3-dibromobutane, 80% from *dl*-2,3-dibromobutane and 81% from a mixed dibromobutane.

**Reaction of 2,3-Dibromobutane with Potassium Iodide in Diethylene Glycol.**—Forty grams (0.185 mole) of *dl*-dibromobutane was added dropwise to a hot solution of 80 g. (0.48 mole) of potassium iodide in 300 g. of diethylene glycol. The butene which was evolved continuously during the course of the reaction was washed with a dilute sodium hydroxide solution and dried over anhydrous

calcium chloride before being condensed in an ampoule. The temperature of the reaction mixture started at  $245^{\circ}$  and gradually dropped to  $165^{\circ}$  at the finish. The yield of butene was 85%.

**Analysis of Butene Mixtures.**—The butene mixtures were analyzed according to the method previously outlined.<sup>10</sup> The second order reaction rate constants of the original and final dibromobutanes with potassium iodide in 99% methanol are listed in Table I together with the corresponding compositions of butenes which they represent.

### Summary

The elimination of bromine from *dl*- and *meso*-2,3-dibromobutanes by iodide ion has been found to be an almost complete *trans* removal of halogen at moderate temperatures. A mechanism for the process has been proposed. It is thought that iodide ion removes a positive bromine atom and essentially simultaneously with this removal the electron pair which is left unshared by this removal attacks the carbon face opposite the remaining bromine atom forming a double bond and liberating bromide ion.

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(12) Wilson and Lucas, *THIS JOURNAL*, **58**, 2396 (1936).

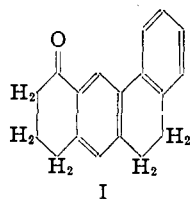
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

## Syntheses in the 1,2-Benzanthracene and Chrysene Series

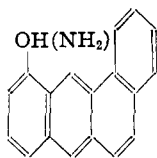
BY LOUIS F. FIESER AND WILLIAM S. JOHNSON<sup>1</sup>

Having developed a satisfactory method for the synthesis of pure 8-methyl-1,2-benzanthracene<sup>2</sup> from the keto acid resulting in nearly quantitative yield from the succinylation of 9,10-dihydrophenanthrene,<sup>3</sup> we have utilized some of the same intermediates for the synthesis of certain other compounds which seemed of interest to the problem of hydrocarbon carcinogenesis.

8-Ethyl-1,2-benzanthracene was prepared from the ketone I by a Grignard reaction followed by



I



II (III, NH<sub>2</sub>)

sulfur dehydrogenation of the low-melting but crystalline tetrahydride obtained on distillation

(1) Holder of the John Woodruff Simpson Fellowship from Amherst College.

(2) Fieser and Johnson, *THIS JOURNAL*, **61**, 168 (1939).

(3) Burger and Mosettig, *ibid.*, **59**, 1302 (1937).

of the resulting carbinol. Like the lower homolog,<sup>2</sup> the completely aromatized hydrocarbon shows a characteristic double melting point when pure. For the preparation of the phenol II, required for comparison with the weakly carcinogenic 3-isomer,<sup>4</sup> the dehydrogenation of 8-ketohexahydrophenanthrene (I) by the method of Mosettig and Duval<sup>5</sup> using Adams catalyst in naphthalene solution was tried without success. 8-Hydroxy-1,2-benzanthracene, however, can be obtained satisfactorily by dehydrogenation with sulfur,<sup>6</sup> and the phenol was converted into the amine III by the Bucherer reaction.

In view of the enhancement of carcinogenic potency noted with certain combinations of *meso*- and  $\alpha$ -methyl groups<sup>4</sup> (5,10-, 5,9-, 9,10-), it seemed important to obtain the di- $\alpha$ -substituted 5,8-dimethyl-1,2-benzanthracene (XII).

(4) For a summary of the data and literature, see Fieser, *Am. J. Cancer*, **34**, 37 (1938).

(5) Mosettig and Duval, *THIS JOURNAL*, **59**, 367 (1937).

(6) Compare the preparation of 4'-hydroxy-3,4-benzpyrene Fieser, Hershberg, Long and Newman, *ibid.*, **59**, 475 (1937).