[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF NORTHWESTERN UNIVERSITY]

Elimination Reactions in Cyclic Systems. VI. Reaction of Iodide Ion with Cyclic *trans*-Dibromides

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The relative reactivity of 4-, 5-, 6-, 7- and 8-membered ring *trans*-1,2-dibromocycloalkanes toward elimination of bromine as initiated by iodide ion was found to be $C_7 > C_8 \cong C_5 > C_6 \gg C_4$. The activation energies for the elimination reactions of C_5, C_6 and C_7 dibromides were of comparable magnitude and were an average of 4.8 kcal. lower than those for *dl*- and *meso*-2,3-dibromobutanes, the open-chain analogs. This is interpreted as evidence that the C_5, C_6 and C_7 cyclic systems can all arrive readily at conformations favorable for elimination. The relative rates for the C_5, C_6, C_7 and C_8 dibromides are correlated with the relative stability of the cycloalkane *vs.* cycloalkene as revealed by heats of hydrogenation and heats of bromination. When zinc was used as the reagent, the rates of debromination of the C_4 and C_5 cyclic dibromides and *dl*-2,3-dibromobutane were all of the same order of magnitude. It is suggested that the rates may be controlled by the rate of adsorption on the zinc surface, or the high reactivity of zinc as compared to iodide ion may minimize the importance of stereochemical factors.

The large differences in the rate (10^4–10^6) for *trans vs. cis* eliminations demonstrated by Cristol to exist among benzene hexachloride isomers (as initiated by hydroxide ion),[1] and the large differences in rates for *axial vs. equatorial trans* debromination eliminations (initiated by iodine ion) revealed by the work of Barton[2] have led to the view that eliminations in which the leaving groups are coplanar and *trans* are greatly favored over eliminations in which other stereo relationships between the leaving groups exist.

On the other hand, previous papers in this series[3] have shown that in cyclic systems where the leaving groups are sufficiently activated, steric and electrostatic interactions rather than changes in mechanism[1] or the necessity of a four-centered planar transition state geometry[2] may become the most important rate-controlling factors in elimination reactions. It was also established that eliminations from five-membered ring compounds occur more readily than in six-membered ring analogs.

It seemed probable that an investigation of the relative rates of elimination of bromine from *trans*-cyclic 1,2-dibromides might help to elucidate further the relative importance of various factors controlling the rates of elimination reactions. With this in mind a study of the rates of iodide ion initiated debrominations of cyclic *trans* C_4, C_5, C_6, C_7 and C_8 1,2-dibromides was undertaken.

The preparation of the dibromides followed methods described in the literature. With the exception of 1,2-dibromocyclooctane it is believed that the compounds are of reasonably high purity.

The rates were determined in 99% methanol according to the method of Young, Pressman and Coryell.[4] Except for *trans*-1,2-dibromocyclobutane, the rate of which was too slow to measure accurately, and 1,2-dibromocyclooctane, which was of doubtful purity, the rates were determined at three temperatures. The rate data are summarized in Table I.

For the C_4, C_5 and C_6 dibromides a plot of the log of the rates *vs.* the reciprocal of the absolute temperature gave straight lines from which the activation energies were determined. Activation entropies were calculated in the usual manner.[5]

TABLE I

REACTION OF CYCLIC *trans*-DIBROMIDES WITH IODIDE ION IN 99% METHANOL

Dibromide	t, °C.	10^5k_2[f, g]	10^5k_2[f, h]	Relative rates at 110°
trans-1,2-Dibromocyclobutane	110	0.045[a]		0.0027[a]
trans-1,2-Dibromocyclopentane	75	2.67 2.75	2.88	
	95	17.95 18.05	19.7	
	110	63.3 64.7	71.8	3.88
trans-1,2-Dibromocyclohexane	75	0.600 0.582	0.627[b]	
	95	3.96 3.93	4.32	
	110	16.55 16.45	18.55	1.0
trans-1,2-Dibromocycloheptane	75	12.9 12.5	13.5	
	95	70.8 71.4	77.9	
	110	258 256	288	15.6
trans-1,2-Dibromocyclooöctane	75	2.48 2.59		
	110	52.5		3.2[c]
meso-2,3-Dibromobutane[d]	75		1.80[d]	
	110		73.4[e]	4.45[e]
dl-2,3-Dibromobutane[d]	75		0.579[d]	
	110		25.5[e]	1.55[e]

[a] It is possible that this represents the rate of displacement of bromide ion rather than the rate of elimination of bromine (see Discussion). [b] H. L. Goering and H. H. Espy, THIS JOURNAL, **77**, 5023 (1955), report similar rates for this reaction. [c] This value is only approximate since the dibromide was not of high purity. [d] Ref. 4. [e] Calculated using the activation energies given in ref. 4. [f] $M.^{-1}$ sec.$^{-1}$. [g] Observed. [h] Corrected for solvent expansion.

The activation energies and activation entropies are summarized in Table II, which also includes the

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(1) S. J. Cristol, N. L. Hause and J. S. Meek, THIS JOURNAL, **73**, 674 (1951); see also E. D. Hughes, C. K. Ingold and R. Pasternak, *J. Chem. Soc.*, 3832 (1953).

(2) D. H. R. Barton and E. Miller, THIS JOURNAL, **72**, 1066 (1950).

(3) See J. Weinstock, R. G. Pearson and F. G. Bordwell, *ibid.*, **78**, 3473 (1956), and papers cited therein.

(4) W. G. Young, D. Pressman and C. D. Coryell, *ibid.*, **61**, 1640 (1939).

(5) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 96.

heats of hydrogenation[6] and heats of bromination[7] of the corresponding cycloalkenes.

TABLE II

ACTIVATION ENERGIES AND ENTROPIES FOR THE REACTION OF IODIDE ION WITH CYCLIC *trans*-DIBROMIDES

Ring size	$-\Delta H$ (H_2)[a]	$-\Delta H$ (Br_2)[b]	E_a[c]	$\Delta S^{\ddagger}$[c]
C_4	..	..	High (?)	....
C_5	26.9	28.6	23.2	−14.7
C_6	28.6	33.6	24.8	−13.3
C_7	26.5	30.4	22.5	−13.8
C_8	23.5	29.3	..	....
meso-2,3-Dibromobutane	27.6	..	28.0[4]	− 1.9
dl-2,3-Dibromobutane	28.6	..	28.6[4]	− 2.5

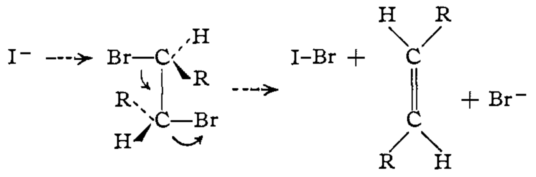
[a] Heat of hydrogenation of the olefin (see ref. 6). [b] Heat of bromine addition to the olefin (see ref. 7). [c] Corrected for solvent expansion.

In calculating the rate constants and therefore the activation energies and entropies, the approximate volume increase at 75, 95 and 110° was calculated using a table of orthobaric densities[8] for methanol. At 75° the observed rate constant was increased by 6.2%, at 95° by 9.5%, and at 110° by 11.2%.

In sharp contrast to the inertness of *trans*-1,2-dibromocyclobutane in the reaction with iodide ion, elimination of bromine by zinc to form cyclobutene was almost as rapid as a comparable elimination with *trans*-1,2-dibromocyclopentane. The reactions were essentially quantitative and the time for completion of elimination of bromine by zinc from these two dibromides and from *dl*-2,3-dibromobutane were all of the same order of magnitude.

Discussion

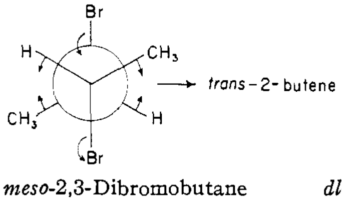
The work of Young and co-workers[4,9] has clearly demonstrated that a *trans* elimination of bromine occurs preferentially in the iodide initiated reaction, *meso*-dibromides giving *trans*-olefins and *dl*-dibromides giving *cis*-olefins selectively. These authors[9] were the first to suggest the presently accepted mechanism for the reaction in which the two bromine atoms and two carbon atoms participating in the reaction are represented as being coplanar, with the bromine atoms *trans* to one another.[10]



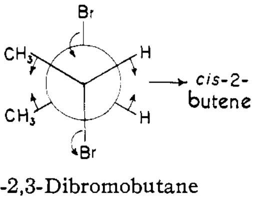
meso-dibromide *trans*-olefin

The demonstration by Barton and Miller[2] that bromine is eliminated readily from "ordinary" cholesterol dibromide in which the bromine atoms are axial-*trans*, whereas the reaction is very slow with the isomeric dibromide where the bromine atoms are equatorial-*trans*, has emphasized the importance of the planar four-centered geometry for the transition state of this reaction.

Young[9b] has suggested that the almost threefold greater rate of elimination of bromine from *meso*-2,3-dibromobutane than from *dl*-2,3-dibromobutane can be explained by the smaller repulsions existing in the *trans* (with respect to bromine atoms) conformation of the *meso*-dibromide. This may be visualized with the aid of the conformation diagrams shown. The *trans* conformation for the *meso* isomer is seen to be more stable, and, what is more important, the relative stability will be reflected by a lower energy in the transition state, since a methyl group and hydrogen atom are being compressed, whereas in the *dl*-isomer two methyl groups must be compressed.[11]



meso-2,3-Dibromobutane
(*trans* conformation)



dl-2,3-Dibromobutane
(*trans* conformation)

If ease of arriving at a favorable conformation in the transition state were decisive in controlling the rates of debromination with iodide ion, it would be anticipated that the *trans*-C_6-dibromide would react more readily than the other cyclic dibromides, since the conformation with the bromine atoms axial-*trans* is favored in the ground states of *trans*-1,2-dibromocyclohexane.[12] Examination of molecular models indicates that the C_8, C_7 and C_5 *trans*-dibromides can assume conformations with the bromine atoms axial-*trans*, but some distortion of the ring is required. It is necessary that the five-membered ring become non-planar to arrive at this conformation, but this need not require much strain since cyclopentane itself is non-planar.[13,14]

The relative order of rates of elimination of these dibromides with iodide ion, $C_7 > C_5 \cong C_8 > C_6$, indicates that either (1) the C_8, C_7 and C_5 dibromides can acquire the necessary conformation with axial-*trans* bromine atoms with little or no expenditure of energy, or (2) a *precise trans* relationship for the elimination is not required. A comparison of activation energies of the cyclic and open-chain dibromides favors the first assumption (see below).

The more rapid elimination of bromine from

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[6] G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941, p. 275.

[7] M. W. Lister, THIS JOURNAL, **63**, 144 (1941).

[8] N. A. Lange, "Handbook of Chemistry," Handbook Publishers, Inc., Sandusky, Ohio, 1946, p. 1432.

[9] (a) S. Winstein, D. Pressman and W. G. Young, THIS JOURNAL, **61**, 1645 (1939); (b) W. G. Young, Abstracts of the 8th National Organic Symposium at St. Louis, Missouri, Dec. 28–30, 1939, p. 90.

[10] For recent supporting evidence for this mechanism, see J. Hine and W. H. Brader, Jr., *ibid.*, **78**, 598 (1956); S. J. Cristol, J. Q. Weber and M. C. Brindell, *ibid.*, **78**, 598 (1956).

[11] This is referred to by D. Y. Curtin as the *cis* effect; see Abstracts of the 13th National Organic Symposium of the American Chemical Society, Ann Arbor, Michigan, June, 1953. The magnitude of the effect is indicated by 1 kcal. greater heat of hydrogenation of *cis*-2-butene as compared to *trans*-2-butene.

[12] P. L. Bender, D. L. Flowers and H. L. Goering, *ibid.*, **77**, 3463 (1955), conclude that an axial conformation for *trans*-1,2-dibromocyclohexane is favored by 70 cal. per mole in benzene solution and 400 cal. per mole in carbon tetrachloride solution.

[13] K. S. Pitzer, *Science*, **101**, 672 (1945); J. G. Aston, H. L. Fink and S. C. Schumann, THIS JOURNAL, **65**, 341 (1943); J. E. Kilpatrick, K. S. Pitzer and R. Spitzer, *ibid.*, **69**, 2483 (1947).

[14] F. V. Brutscher, T. Roberts, S. J. Barr and N. Pearson, *ibid.*, **78**, 1507 (1956), recently have obtained evidence which suggests that two adjacent *trans* groups in a cyclopentane derivative can assume a geometry similar to that of diaxial cyclohexane substituents.

trans-1,2-dibromocyclopentane than from *trans*-1,2-dibromocyclohexane can be rationalized by assuming that some of the oppositions which lead to strain in the cyclopentane derivative are relieved by the transformation to cyclopentene. A similar argument may be used to account for the greater reactivity of the C_7 and C_8 dibromides as compared to the C_6 dibromide.[15] The lower heats of hydrogenation and heats of bromination of C_5, C_7 and C_8 alkenes as compared to cyclohexene are consistent with the greater ease of introducing a double bond into these rings. The latter data do not allow an ordering of the relative strains in the C_5, C_7 and C_8 rings, however.

The rates of elimination in the C_5, C_6, C_7 and C_8 cyclic systems are of the same order of magnitude as in open-chain analogs (Table I), but the activation energies for the cyclic dibromides are on an average about 4.8 kcal. lower than for the open-chain dibromides. This indicates the operation of a substantial geometric factor favoring elimination in the cyclic systems.[1,2]

The similarities in activation energies and entropies for the C_5–C_8 cyclic dibromides and the appreciable differences between these data and those for *meso*- and *dl*-2,3-dibromobutanes suggests a similarity in mechanism for elimination in the C_5–C_8 cyclic dibromides. This in turn points to a similarity in the geometry of the transition states which would imply that favorable conformations for elimination are easily arrived at.[14]

The much more positive entropy of activation for the eliminations in open-chain systems is surprising, since one would expect that the constraining effect would be greater in going from the ground state to transition state in the open-chain compounds. One interpretation might be that, while a precise four-centered planar geometry is energetically favored for eliminations,[1,2] this ordering results in considerable rigidity of the system and a low entropy of activation. This may be the situation in C_5–C_8 cyclic systems. Perhaps in open-chain systems a compromise between a highly ordered transition state and one with less constraint is effected, and the activation energy and activation entropy are more positive.

As shown in Table I, *trans*-1,2-dibromocyclobutane reacts with iodide ion at a rate less than 0.0025th the rate of the other cyclic dibromides. Since the product from the reaction of the C_4 dibromide was not determined, it is possible that the rate given represents that of displacement of bromine rather than elimination of bromine, or both. The rate given in Table I, therefore, is a maximum value.

The inertness of *trans*-1,2-dibromocyclobutane to the action of iodide ion is reminiscent of the nonreactivity observed by Barton and Miller[2] for the cholesterol dibromide where the bromine atoms are equatorial-*trans*. Berson and Swidler[16] have observed a similar failure to react for a dibromide in a bicyclic system (dimethyl *trans*-4,5-dibromo-*exo-cis*-3,6-endoxohexahydrophthalate) where the bromine atoms cannot approach an axial-*trans* relationship. The inertness of these dibromides to reaction with iodide ion, as the previous investigators suggest,[2,16] must in part be due to an unfavorable geometry for reaction. The iodide ion must remove a bromine with a sextet of electrons in the face of the repulsive forces exerted by a developing negative charge on the other bromine atom. An equally important effect in these systems may be the low entropy of activation. In effect, the transition state may be constrained in an unfavorable geometry. Still another factor for cyclobutane dibromide in making it less reactive than, say cyclopentane dibromide, may be the relatively high ratio of energies $C_4H_6/C_4H_6Br_2$ as compared to $C_5H_8/C_5H_8Br_2$. Data on heats of bromination and hydrogenation of cyclobutene are not available to assess the magnitude of this factor.

Zinc promoted eliminations of halogen from open-chain 1,2-dihalides lead to a stereoselectivity of olefin production comparable to iodide initiated reactions, and a similar mechanism has been proposed.[17,18] It might be anticipated, therefore, that the geometry of the Br–C–C–Br system would also be important for determining the rates of these reactions. However, it was observed that the rates of elimination of bromine by zinc were comparable for the C_4, C_5 dibromides and *dl*-2,3-dibromobutane. Similarly, Berson and Swidler[16] reported a facile reaction with zinc for their dibromide, and Cristol and Hause[19] have observed similar results in a system (*cis*- and *trans*-11,12-dichloro-9,10-dihydro-9,10-ethanoanthracene) where the halogens are fixed in non-coplanar relationships by a rigid system. Evidently, a favorable geometry for *trans* elimination is not nearly so important for reactions initiated by zinc as for those initiated by iodide ion.

Several explanations are possible. It may be that the zinc reactions occur on the surface of the zinc, and that the rate of adsorption is the rate-determining factor. This view is supported by the fact that in our work the rate of gas evolution (2-butene, cyclobutene or cyclopentene) was found to be essentially constant throughout the reactions. This corresponds to a zero-order reaction, and can be accounted for if the reaction rate is independent of the dibromide concentration but depends instead on the rate at which the compound diffuses to the zinc surface and becomes properly oriented there. The diffusion rates should not vary much for different dibromides. The small differences in reaction rates observed would be explicable on the basis that the adsorption may be reversible, and the rates of adsorption and deadsorption will vary somewhat depending on the structure of the dibromide.

Alternatively, the nearly equivalent rates of zinc debromination of 4- and 5-membered ring dibromides and *dl*-2,3-dibromobutane may be the result of a leveling effect of the zinc, which is a much more powerful reagent than iodide ion. The situation

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(15) H. C. Brown, R. S. Fletcher and R. B. Johannesen, *ibid.*, **73**, 212 (1951), refer to the strains in saturated C_5, C_7 and C_8 as I-strains.

(16) J. A. Berson and R. Swidler, *ibid.*, **76**, 4057 (1954).

(17) (a) W. G. Young, Z. Jasaitis and L. Levanas, *ibid.*, **59**, 403 (1937); (b) W. G. Young, S. J. Cristol and T. Skei, *ibid.*, **65**, 2099 (1943).

(18) W. M. Schubert, B. S. Rabinovitch, N. R. Larson and V. A. Sims, *ibid.*, **74**, 4590 (1952), have shown that zinc in water leads to *trans* elimination without isomerization of the butenes formed.

(19) S. J. Cristol and N. L. Hause, *ibid.*, **74**, 2193 (1952).

might be comparable in this respect to that in activated systems wherein structural features become of less importance as the system becomes more prone to react. For example, it has been found that the high ratio of rates of *trans/cis* elimination in some cyclic systems may be markedly decreased by the introduction of an activating group.[3]

Experimental

Materials.—*trans*-1,2-Dibromocyclobutane was prepared by a modification of the method of Willstätter and Bruce.[20] Cyclobutanecarboxylic acid[21] was converted to cyclobutylamine by a modified Curtius rearrangement.[22] This was methylated with formic acid–formaldehyde[23] to the dimethylamine and then with methyl iodide to the quaternary ammonium iodide. This was converted to the hydroxide by means of the ion-exchange resin,[24] Amberlite IRA-400-OH, and then pyrolyzed by the method of Roberts and Sauer[25] to give cyclobutene. The cyclobutene was brominated in chloroform at −70° and the dibromide purified by shaking with alkali according to the method of Snyder and Brooks.[26] Distillation gave the dibromide as a colorless liquid, b.p. 74–75° at 26.5 mm., n^{25}D 1.5352. On standing in a 2° cold room, the oil crystallized; reported[20] m.p. 1–4°, b.p. 62° at 13 mm.

trans-1,2-Dibromocyclopentane was prepared by the bromination of cyclopentene at −8° in carbon tetrachloride containing 5% absolute ethanol. It was purified by treatment with ethanolic 20% potassium hydroxide and two distillations. The final product had b.p. 83° at 16 mm., n^{25}D 1.5444; reported,[7] n^{24}D 1.5444.

trans-1,2-Dibromocyclohexane was prepared by the method of Snyder and Brooks[26] and recrystallized three times from pentane. Redistillation from an all glass apparatus gave a colorless liquid, b.p. 140° at 68 mm., n^{25}D 1.5493; reported[27] b.p. 90.1–92.3° at 8 to 9 mm., n^{25}D 1.5507.

trans-1,2-Dibromocycloheptane was obtained by bromination of cycloheptene at −5° in carbon tetrachloride. Treatment with alcoholic potassium hydroxide followed by distillation gave a colorless liquid, b.p. 137–138° at 30 mm., n^{25}D 1.5528. On standing in a 2° cold room it crystallized to a white solid, m.p. 11°; reported[7] n^{24}D 1.5544.

trans-1,2-Dibromocyclooctane was obtained by bromination of *cis*-cyclooctene prepared by the catalytic reduction of cyclooctatetraene.[28] After several distillations it was obtained as a colorless liquid, b.p. 96.5° at 1.5 mm., n^{25}D 1.5532; reported[29] b.p. 89–91° at 0.5 mm., n^{25}D 1.5522.

dl-2,3-Dibromobutane was prepared by the method of Young, Dillon and Lucas[30] from "Pure Grade 99% Minimum Purity" *cis*-2-butene obtained from Phillips Petroleum Company. The product obtained was a colorless liquid, b.p. 76–77° at 50 mm., n^{25}D 1.5120; reported[30] b.p. 75.6–75.8° at 50 mm., n^{25}D 1.5125.

Kinetic Procedure.—For each run one hundred ml. of a 99% methanol (prepared by adding 10 ml. of water to each 990 ml. of commercial absolute methanol) solution approximately 0.25 molar in iodate-free potassium iodide and 0.025 molar in dibromide was prepared by dissolving weighed amounts of the reactants. Ten-ml. aliquots were placed in Pyrex ampules and sealed. At zero time a basket of ampules was placed in a constant temperature bath and individual ampules were withdrawn at appropriate times for analysis. Each ampule as it was withdrawn was chilled in an ice-bath and then carefully cleaned with acetone and distilled water. The tube was then scratched and broken with a heavy glass rod in a 1-liter heavy-walled Pyrex flask containing about 20 ml. of water and 10 ml. of glacial acetic acid. The contents of the flask was then titrated with 0.01 *N* thiosulfate. The observed reaction rate was then calculated for each run by the method of Young, Pressman and Coryell.[4]

In the runs on dibromocyclobutane the prolonged reaction time (14 days) and high temperature (110°) could have allowed solvolysis to occur. However, the reaction mixture was found to be neutral.

Reaction of Zinc and Dibromocycloalkanes.—The apparatus used[31] consisted essentially of a magnetically stirred reaction flask connected to a brine filled gas buret which in turn led to a small vacuum line. The vacuum line had provisions for freezing out the gas sample with liquid nitrogen, filling an infrared gas cell, and measuring the pressure in the system.

(a) ***trans*-1,2-Dibromocyclobutane.**—The reaction flask was charged with 1.0 g. (0.0047 mole) of the dibromide, 1.5 g. (0.023 gram atom) of zinc dust and 20 ml. of water. The flask was kept at room temperature by an air jet. It took 4.5 hours to collect 115 ml. (97% of theory) of gas. The infrared spectra of this gas agreed with that of Roberts and Sauer.[32] Willstätter and Bruce[20] reported a 95% yield of cyclobutene from 1,2-dibromocyclobutane by the action of zinc in ethanol at 80–100°.

In a run at 68° on the same scale it took 25 minutes to collect 115 ml. of gas.

(b) ***trans*-1,2-Dibromocyclopentane.**—A mixture of 1.07 g. (0.0047 mole) of the dibromide and 1.5 g. (0.023 gram atom) of zinc in 20 ml. of water required 18 min. at 68° to release 112 ml. (91% of theory) of cyclopentene. The less than theoretical yield of cyclopentene may be due to a small amount of liquefaction in the apparatus.

(c) ***dl*-2,3-Dibromobutane.**—A mixture of 1.0 g. (0.0047 mole) of the dibromide, 1.5 g. (0.023 gram atom) of zinc dust and 20 ml. of water required 12 minutes at 68° to release 111 ml. of gas.

The rate of gas evolution was found to depend on the particular sample of zinc dust used. All of the runs above were done with Baker and Adamson "90% zinc metal dust." With "technical zinc dust" at 68° the reaction of *dl*-2,3-dibromobutane took 37 minutes and with a sample labeled "zinc metal dust, 90% reagent" at 68° the same reaction required only 8 minutes.

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(20) R. Willstätter and J. Bruce, *Ber.*, **40**, 3979 (1907).

(21) J. Cason and C. F. Allen, *J. Org. Chem.*, **14**, 1036 (1949).

(22) G. B. Heisig, THIS JOURNAL, **63**, 1698 (1941).

(23) H. T. Clarke, H. B. Gillespie and S. Z. Weisshaus, *ibid.*, **55**, 4576 (1933).

(24) J. Weinstock and V. Boekelheide, *ibid.*, **75**, 2546 (1953).

(25) J. D. Roberts and C. W. Sauer, *ibid.*, **71**, 3925 (1950).

(26) H. R. Snyder and L. A. Brooks, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., p. 171.

(27) H. L. Goering and L. L. Sims, THIS JOURNAL, **77**, 3465 (1955).

(28) A. C. Cope and L. L. Estes, Jr., *ibid.*, **72**, 1128 (1950).

(29) A. C. Cope, R. A. Pike and C. F. Spencer, *ibid.*, **75**, 3214 (1953).

(30) W. G. Young, R. T. Dillon and H. J. Lucas, *ibid.*, **51**, 2528 (1929).

(31) We wish to thank Mr. Norman Neureiter for aid in these experiments and for the use of his apparatus.

(32) J. D. Roberts and C. W. Sauer, THIS JOURNAL, **74**, 3193 (1952).