

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OHIO UNIVERSITY]

Some Dehalogenation Reactions of 1,4-Dibromobutane¹

WILLIAM B. SMITH

Received October 3, 1957

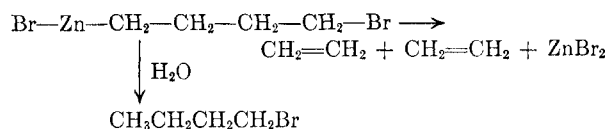
The dehalogenation of 1,4-dibromobutane under a variety of conditions has been found to lead to a mixture of ethylene, butane, 1-butene, *trans* and *cis* 2-butenes, 1,3-butadiene, and cyclobutane. A free radical mechanism accounting for the formation of each of the above is proposed.

A literature survey of the metal dehalogenation reactions of 1,4-dibromobutane reveals a wide divergence of reported products. While it does not follow that all metal dehalogenations must proceed *via* a common mechanism, it is only through a thorough study of the reaction products that such a question can really be answered. Such a study is reported here.

The reaction of sodium vapor with 1,4-dibromobutane at 300° has been reported by Bawn and Milstead² to give ethylene (41%) and butylene (51%). The mechanism proposed by these authors involves the formation of a 1,4-butyl diradical and its subsequent reactions to give the observed products. Cason and Way³ carried out essentially the same reaction in refluxing toluene and observed butane and cyclobutane (12%) as products. While they suggested no reaction mechanism, the further observation that cyclobutane formation was less in boiling benzene was interpreted as meaning that this was a process of relatively high activation energy.

Demjanow⁴ reported the treatment of 1,4-dibromobutane with zinc in ethanol to give butyl bromide; while Hamonet⁵ obtained butane under the same conditions. When the dehalogenation was carried out with zinc and refluxing dioxane, Grob and

Bauman⁶ identified ethylene, butylene, and butyl bromide as reaction products. They proposed the initial formation of an organozinc halide which then decomposed by an ionic process.



In this laboratory the treatment of 1,4-dibromobutane with a variety of metals in refluxing xylene and in butyl ether has been found to produce the same gaseous products in each case (Table I); ethylene, butane, 1-butene, *trans*- and *cis*-2-butene, 1,3-butadiene, and cyclobutane. Analysis of the complex reaction products was carried out by means of gas chromatography (Fig. 1). Direct comparison of yields between reactions conducted in xylene and in butyl ether is complicated by the fact that butyl ether itself undergoes some cleavage when heated with the metals used in this study. The treatment of boiling butyl ether with sodium produced a large amount of propane and small amounts of C-2 and C-4 hydrocarbons. With the less active metals listed in Table I, the production of propane was negligible.

While the distribution among the products observed on metallic dehalogenation of 1,4-dibromobutane varied considerably with the reaction conditions, the over-all consistency of products strongly supports the supposition of a common mechanism for all of these reactions. In order to

(1) Presented in part before the April 19, 1957, meeting of the Ohio Academy of Sciences, Bowling Green, Ohio.

(2) C. E. H. Bawn and J. Milstead, *Trans. Faraday Soc.*, **35**, 889 (1939).

(3) J. Cason and R. L. Way, *J. Org. Chem.*, **14**, 31 (1949).

(4) N. J. Demjanow, *Ber.*, **28**, 22 (1895).

(5) J. Hamonet, *Compt. rend.*, **132**, 789 (1901).

(6) C. A. Grob and W. Bauman, *Helv. Chim. Acta*, **38**, 594 (1955).

TABLE I
DEHALOGENATION REACTIONS OF 1,4-DIBROMOBUTANE (0.01 MOLE)

Reagent	Solvent	Yield, ML.	Products, Mole %					Cyclo C ₄ H ₈
			C ₂ H ₄	C ₄ H ₁₀	1-C ₄ H ₈	2-C ₄ H ₈	1,3-C ₄ H ₆	
Na	Xylene	80	63	16	5	2	3	11
Li	Xylene	80	16	46	15	5	5	13
Mg	Xylene	90	14	51	12	4	6	13
Na	Bu ₂ O ^a	200	High	s.a.	s.a.	s.a.	s.a.	0
Mg	Bu ₂ O ^a	190	31	24	19	6	2	9
Zn	Bu ₂ O ^a	260	34	28	16	11	1	0
Zn	dioxane	60	27	47	13	13	0	0
Mg + CoBr ₂	Bu ₂ O ^a	200	8	24	46	13	3	1
Mg + CoBr ₂	Et ₂ O	70	8	33	42	17	0	0
CH ₃ MgBr + CoBr ₂	Xylene ^b	.. ^c	21	3	8	5	4	2
CH ₃ MgBr + CoBr ₂	Bu ₂ O	.. ^c	23	17	15	30	0	8
CH ₃ MgBr + CoBr ₂	Et ₂ O	.. ^c	6	3	51	17	0	0

^a The high yields in butyl ether were due to the secondary reaction of the metal with the solvent; the other product being propane. Small amount is abbreviated s.a. ^b In addition, 53% ethane and 4% propane were found. ^c No yield of reaction products was measured here due to the large dilution by methane.

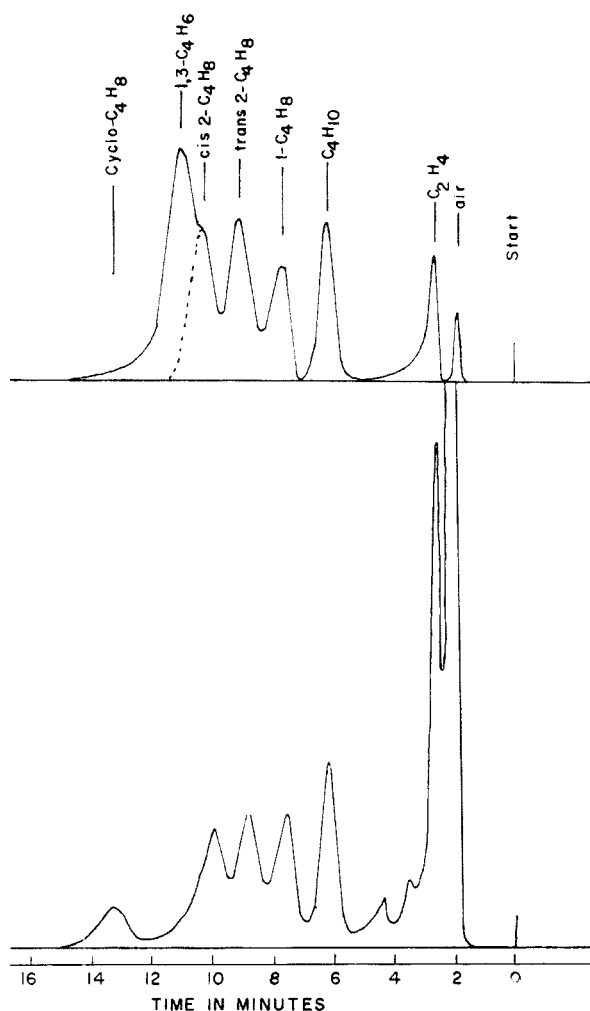
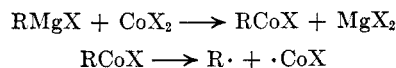


Fig. 1. Gas chromatography tracings for a standard mixture of hydrocarbons (upper curve) and the reaction product of 1,4-dibromobutane with methylmagnesium bromide and cobaltous bromide in butyl ether (lower curve)

further clarify the question of whether the dehalogenations are free radical or ionic in nature, the re-

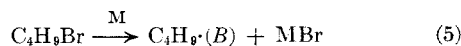
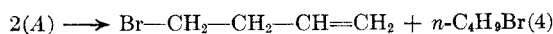
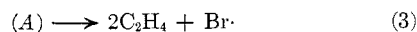
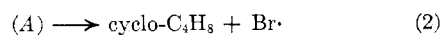
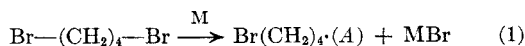
action was carried out under conditions which would favor radical formation.

Kharasch and co-workers⁷ have carried out a number of reactions using a Grignard reagent and cobaltous halides as a source of free radicals in solution. It was proposed that radical formation takes place according to the following scheme.



When a mixture of 1,4-dibromobutane and cobaltous bromide was treated with methylmagnesium bromide in a high boiling solvent, it was found that the same group of gaseous reaction products was observed as in the metal dehalogenation reactions. The results of this series of reactions are also listed in Table I. At the lower temperature of refluxing ethyl ether, no cyclobutane was formed; a not unexpected result in view of the observations of Cason and Way.³

The experimental results of this study support the view that the metal dehalogenation reactions of 1,4-dibromobutane are free radical in nature. However, it should be born in mind that in any reactions as complex as these there is no difficulty in finding explanations of the experimental facts, but only in defending a preferred explanation selected from many. One reasonable reaction scheme which will accommodate the above observations is as follows:

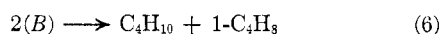


(7) M. S. Kharasch, R. D. Mulley, and W. Nudenberg, *J. Org. Chem.*, **19**, 1477 (1954).

TABLE II
REACTIONS OF *n*-BUTYL BROMIDE AND 4-PHENOXYBUTYL BROMIDE

Reagents	Solvent	Yield, Ml.	Product, Mole %					Cyclo C ₄ H ₈
			C ₂ H ₄	C ₄ H ₁₀	1-C ₄ H ₈	2-C ₄ H ₈	1,3-C ₄ H ₆	
<i>n</i> -Butyl bromide, 0.02 mole								
Mg + CoBr ₂	Et ₂ O	490	0	55	21	24
CH ₃ MgBr + CoBr ₂	Et ₂ O	... ^a	6	11	20
4-Phenoxybutyl bromide, .0052 mole								
Mg + CoBr ₂	Xylene	25	5	3	79	10	1	2

^a No yield of reaction products was measured due to the high dilution with methane. The other major product (63%) was pentane.

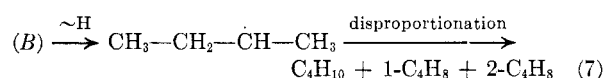


In the same fashion the 4-bromo-1-butene (Equation 4) may decompose to form 1,3-butadiene and 1-butene. The 4-bromo-1-butyl radical (*A*) may be generated either by the direct abstraction of the halogen by the metal or by the thermal decomposition of a metal alkyl intermediate.⁸

The formation of cyclobutane as envisioned in Equation 2 above is a displacement of bromine atom from carbon by an attacking radical. The experimental evidence regarding radical displacement reactions has been summarized by Steacie.⁹ The formation of a 1,4-butyl diradical as suggested by Bawn and Milstead² is also a possibility. In order to test the proposal of the 4-bromo-1-butyl radical (*A*) as a reaction intermediate, the decomposition of 4-phenoxybutyl bromide with magnesium and cobaltous bromide in refluxing xylene was carried out. Again a complex mixture of gaseous products was formed (Table II). Analysis of this mixture showed the same products as observed in the reactions of 1,4-dibromobutane. Cyclobutane was formed to the extent of 2 mole percent. Kharasch, Stampa, and Nudenburg¹⁰ have reported that treatment of 4-phenoxybutyl bromide with phenylmagnesium bromide and cobaltous bromide in ether gave predominantly butyl phenyl ether and butenyl phenyl ether.

Both *trans* and *cis* 2-butene (the ratio *trans/cis* varied from two to five) were formed in each of the reactions studied. Kharasch, Lambert, and Urry¹¹ noted the formation of 2-butene when 1-chloro-3-phenylpropane was treated with butylmagnesium bromide and cobaltous bromide. Their suggestion of the rearrangement of a *n*-butyl radical to a *sec*-butyl radical *via* a hydrogen atom migration has not received further experimental support. However,

should such a migration occur then the formation of 2-butene may be postulated as follows:



When butylbromide is allowed to react with magnesium and cobaltous bromide in ether, the yields of 1-butene and 2-butene were essentially the same (Table II). In another experiment butyl bromide and cobaltous bromide were allowed to react with methylmagnesium bromide. There was no observable yield in 2-butene under these conditions (Table II) and the high yield of pentane suggests that the recombination of methyl and butyl radicals is a faster reaction than any process leading to 2-butene formation.

One referee has suggested that the metal salts present in the reaction mixture may serve as Lewis acids catalyzing the rearrangement of 1-butene to 2-butene. While there is a real possibility of such an isomerization occurring in the reactions at lower temperatures, it would be dubious that 1-butene would have a sufficiently long residence time in the reaction vessel at the temperatures of refluxing butyl ether and xylene for such a rearrangement to occur.

Finally, with regard to the balance of product yields predicted by the above proposed mechanistic scheme, it should be born in mind that no mention has been made of the interactions of the various radicals proposed with each other or with the solvents employed. Such factors undoubtedly play an important role in determining the yields of reaction products. Thus, it is not to be expected that the above scheme should account quantitatively for the products but rather for the spectrum of products observed.

(8) A. A. Morton and E. J. Lanpher, *J. Org. Chem.*, **21**, 93 (1956).

(9) E. W. R. Steacie, *Atomic and Free Radical Reactions*, Reinhold Publishing Corp., New York, N. Y., Vol. II, p. 743; Vol. I, p. 269.

(10) M. S. Kharasch, G. Stampa, W. Nudenburg, *J. Org. Chem.*, **18**, 575 (1953)

(11) M. S. Kharasch, F. L. Lambert, W. H. Urry, *J. Org. Chem.*, **10**, 298 (1945).

EXPERIMENTAL

Reagents. Eastman Kodak White Label 1,4-dibromobutane was carefully distilled through a Widmer column. After a slight forerun, the major fraction was taken; b.p. 74.5°/11 mm.

Butyl ether was washed with dilute potassium hydroxide and water. While still wet it was treated with an excess of

calcium hydride and then distilled from the excess hydride; b.p. 141°.

n-Butyl bromide was Eastman Kodak White Label carefully distilled through a Todd column; b.p. 106.6°.

The magnesium used in this study was Fisher Grignard Reagent magnesium.

Method of gas analysis. The gases produced in the following reactions were analyzed by means of a Fisher Gulf Partitioner using the standard column provided with the instrument (tricresyl phosphate on firebrick). The eluting gas was helium. The peaks produced by an unknown sample were identified by comparison with those produced by a standard known mixture of light hydrocarbon gases (Fig. 1). The cyclobutane band was identified by inference from the products formed by the treatment of 1,4-dibromobutane with sodium in refluxing toluene.³

The mole percent of each component was calculated by the expression:

$$\text{mole } \% \text{ A} = \frac{\text{area under A}}{\text{total area}} \times 100$$

Apparatus. The apparatus consisted of a 100-ml., three-necked flask fitted with a dropping funnel and a condenser. All reactions were stirred by means of a magnetic stirrer. All gases were collected, after passing through the condenser, in a gas collection bottle filled either with mercury or a saturated salt solution.

Reaction of 1,4-dibromobutane with various metals. To a refluxing mixture of 2 g. of the appropriate metal and 20 ml. of solvent was slowly added 2.16 g. (0.01 mole) of 1,4-dibromobutane. The mixture was usually allowed to reflux overnight. The evolved gases were then measured and analyzed according to the above procedure. The metals, solvents, and reaction products are tabulated in Table I.

Reaction of 1,4-dibromobutane with methylmagnesium bromide and cobaltous bromide in various solvents. To a re-

fluxing mixture of 2.16 g. (0.01 mole) of 1,4-dibromobutane and 2 g. of cobaltous bromide in 20 ml. of solvent, was added ca. 0.03 mole of methylmagnesium bromide in the same solvent. The solvents used were ethyl ether, butyl ether, and xylene. In the latter two solvents, the addition reagent was formed by mixing the solvent with the appropriate amount of methylmagnesium bromide in ethyl ether and then removing as much of the ethyl ether as possible by evacuating to water pump pressure. In xylene and butyl ether, the Grignard reagent was added in the form of a slurry. The gases produced were collected and analyzed as described previously.

Reactions of n-butyl bromide. (a) A mixture of 2.74 g. of *n*-butyl bromide (0.02 mole), 4.36 g. of cobaltous bromide (0.02 mole), and 1 g. of magnesium was refluxed in 15 ml. of ethyl ether for three hours. The reaction gas was collected and analyzed as before. The results are recorded in Table II.

(b) To a refluxing mixture of 2.74 g. of *n*-butyl bromide and 1 g. of cobaltous bromide in 15 ml. of ethyl ether was slowly added 25 ml. of ca. 1*M* methylmagnesium bromide. The yield of gas was quantitative based on the amount of methylmagnesium bromide. The analytical results are given in Table II.

Reaction of 4-phenoxybutyl bromide with magnesium and cobaltous bromide. 4-Phenoxybutyl bromide was prepared by the method of Kharasch, *et al.*;¹⁰ m.p. 40–41.5°. A mixture of 1.2 g. (5.2 mmole) of 4-phenoxybutyl bromide, 1 g. of cobaltous bromide, and 2 g. of magnesium was refluxed for three days in 25 ml. of xylene. The rather small gas yield (25 ml.) was collected and analyzed as before. The results are recorded in Table II.

Acknowledgment. The author wishes to thank Dr. W. D. Huntsman of these laboratories for his many stimulating discussions of this problem.

ATHENS, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF ORGANIC CHEMISTRY, HEBREW UNIVERSITY]

Synthesis of Tribenzocycloheptatriene and Related Compounds

ERNST D. BERGMANN AND JOSEPH KLEIN

Received July 22, 1957

From the adduct (III) of butadiene and cinnamaldehyde, 4,5-tetramethylene-2,3-benzosuberone (VI) has been prepared. Condensation of its 7-formyl derivative with the methiodide of β -diethylaminoethyl methyl ketone gave the tetracyclic hydroxyketone (X) from which by dehydration and dehydrogenation tribenzocycloheptatriene (II) has been obtained. The corresponding heptafulvene (XIV) does not differ in its physical properties from triphenylethylene; it has no "fulvenic" properties. Some other reactions of the adduct (III) and the ketone (VI) have also been explored.

The failure of the properties of the dibenzoheptafulvenes (I) to agree with those predicted by the theory, based on the linear combination of atomic orbitals (LCAO),¹⁻³ made it interesting to synthesize heptafulvenes derived from tribenzocycloheptatriene (II). The preparation of this compound started from the adduct (III) of butadiene and cinnamaldehyde, 2-phenyl-1,2,3,6-tetrahydrobenzaldehyde. The *trans*-structure of this aldehyde

follows from the configuration of cinnamaldehyde⁴ and from its oxidation to the known⁵ 2-phenyl-1,2,3,6-tetrahydrobenzoic acid, by means of silver oxide.⁶

(4) M. Bourguet, *Bull. soc. chim. France* [4], **45**, 1086 (1929); G. Gomboni, V. Thens, and H. Schmitz, *Helv. Chim. Acta*, **38**, 255 (1955); H. Schinz, *Chem. Abstr.*, **49**, 6874 (1956).

(5) J. W. Cook, C. L. Hewett, and A. M. Robinson, *J. Chem. Soc.*, 168 (1939); G. Blumenfeld, *Ber.*, **74**, 524 (1941); C. D. Gutsche, *J. Am. Chem. Soc.*, **70**, 4150 (1948); K. Alder, H. Vagt, and W. Vogt, *Ann.*, **565**, 135 (1945); N. V. Organon, Brit. Patent **674,177** [*Chem. Abstr.*, **47**, 7540 (1953)].

(6) The isomeric 2-phenyl-1,2,5,6-tetrahydrobenzaldehyde has been prepared by E. Lehmann and W. Paasche, *Ber.*, **68**, 1146 (1935), and K. Alder, H. Vagt, and W. Vogt, *ref. 5*.

(1) E. D. Bergmann, E. Fischer, D. Ginsburg, Y. Hirshberg, D. Lavie, M. Mayot, A. Pullman, and B. Pullman, *Bull. soc. chim. France*, **18**, 684 (1951).

(2) G. Berthier and B. Pullman, *Trans. Faraday Soc.*, **45**, 484 (1949).

(3) See, however, A. Julg and B. Pullman, *J. chim. phys.*, **52**, 481 (1951).