

dioxide was used instead of sesquioxide. Crude nitrosoisodurene was obtained, m. p. 123°; yield, 4.5 g. (72%).

C. Preparation of Nitrodurene and Nitroisodurene

Oxidation of Nitrosodurene.—A mixture of 2 g. of nitrosodurene and 40 cc. of nitric acid (sp. gr. 1.26) was heated to 70° and shaken for ten minutes. The material was dissolved and nitrogen oxides were evolved. The solution was cooled immediately, poured into 100 cc. of ice and water, and filtered. The product was crystallized from 14 cc. of alcohol; pale yellow prisms, m. p. 112–113°; yield, 0.87 g. (40%). Reduction of nitrodurene formed aminodurene, m. p. 71°.

Acetoxymercuridurene and Nitric Acid.—The mercury compound (11.8 g.) was heated and shaken with 120 cc. of nitric acid (sp. gr. 1.26); the substance was changed to material which floated (probably nitrosodurene). Nitrogen oxides were evolved. At 70°, the material was dissolved within five minutes; the solution was kept warm two minutes longer, then it was poured into ice and water, and filtered. The precipitate was triturated and washed with water, and dried for one day over sulfuric acid. The crude nitrodurene weighed 4.8 g. (89%); m. p. 100–105°.

Oxidation of Nitrosoisodurene.—The substance was oxidized with nitric acid at 70–80°; the oxidation was stopped by dilution with ice and water as soon as the material had dissolved. The diluted mixture was extracted with ether; the ether was washed and evaporated. The residual oil was steam distilled; the yellow oil was removed from the distillate by extraction with ether; the residue from evaporation of the ether was crystallized from methanol at the temperature of liquid air. The

product was dried for three days in a desiccator. The melting point of nitroisodurene was 38–39°.

Nitrosoisodurene was oxidized also by nitrogen dioxide. The solvent, absolute chloroform, was heated nearly to the boiling point by the heat of reaction. After action had subsided the chloroform was washed with water and evaporated. The residual oil was steam distilled; the distillate was extracted with ether, the ether was evaporated and the residue crystallized from low boiling petroleum ether. The melting point of nitroisodurene was 39°.

Acetoxymercuriisodurene and Nitric Acid.—The procedure was the same as for the reaction between nitric acid and acetoxymercuridurene. From 4 g. of the mercury compound, there was obtained 1.5 g. (82%) of crude (liquid) nitroisodurene. Further oxidation of nitroisodurene occurred when the reactions were continued too long, or were allowed to proceed at higher temperatures.

Reduction of nitroisodurene formed a liquid amine. The melting point of acetaminoisodurene was 215°.

Summary

1. A method was developed for synthesis of nitroso compounds by the action of nitrosyl chloride upon organomercury derivatives of polymethylbenzenes. Four new nitroso and two new nitro compounds were prepared.

2. The action of nitrogen sesquioxide upon arylmercury compounds, like that of the dioxide, formed nitroso compounds as the primary products.

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[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

The Peroxide Effect in the Addition of Reagents to Unsaturated Compounds. X. The Addition of Hydrogen Bromide to Methylacetylene (Allylene)

BY M. S. KHARASCH, J. G. MCNAB¹ AND M. C. MCNAB

Introduction

In previous communications from this Laboratory Kharasch and his collaborators² have demonstrated the importance of peroxides in directing the addition of hydrogen bromide to olefinic hydrocarbons, in which the double bond is at the end of the chain. It seemed desirable to extend the investigation to the acetylene series, and so the addition of hydrogen bromide to methylacetylene was studied in some detail.

The experiments of Réboul³ have previously

(1) The authors wish to express here their appreciation to the Eli Lilly Company of Indianapolis for support which made this work possible.

(2) Kharasch and co-workers, *THIS JOURNAL*, **55**, 2468, 2521, 2531 (1933); **56**, 1642 (1934).

(3) Réboul, *Ann. chim.*, [5] **14**, 365 (1878).

shown that hydrogen bromide in aqueous solution adds to methylacetylene to yield 2,2-dibromopropane.

Addition of Hydrogen Bromide to Methylacetylene.—We found it expedient, after a few preliminary experiments, to limit our investigation to a study of the final product formed by the addition of two moles of hydrogen bromide to methylacetylene. These experiments were carried out in the presence of peroxides and also *in vacuo* under peroxide-free conditions.

The structure of the molecule first formed, under peroxide-free conditions, by the addition of one mole of hydrogen bromide to methylacetylene, can be inferred readily from a consideration of the products isolated in this investigation, together

TABLE I

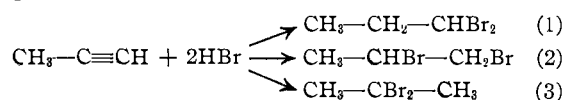
ADDITION OF HYDROGEN BROMIDE TO METHYLACETYLENE

In all experiments 15 g. of methylacetylene and 91 g. of hydrogen bromide were used. The reaction mixture was allowed to stand for four days. The experiments recorded were checked many times. The yields were quantitative (95-100%).

Conditions	B. p., °C.	n_D^{20}	% 1,2-dibromopropane	% 2,2-dibromopropane
No agent added. Vacuum technique	112-115	1.4977	0	100
0.4 g. diphenylamine added to the methylacetylene. Vacuum technique	112-115	1.4977	0	100
0.2 g. thiocresol added to methylacetylene. Vacuum technique	112-115	1.4977	0	100
0.8 g. ascaridole added to methylacetylene, HBr passed in at -33°	139-142	1.5192	100	0
Same as above except vacuum technique used	139-142	1.5193	100	0

with the work on the addition of hydrogen bromide to various bromopropylenes under way in this Laboratory.

From structural considerations, it is obvious that methylacetylene can add two moles of hydrogen bromide to yield three dibromopropanes.



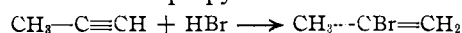
In all of our experiments, however, the reaction product proved to be the 2,2-dibromopropane, the 1,2-dibromopropane or a mixture of these two compounds. The possibility of obtaining the 1,1-dibromopropane was not disregarded, but careful analysis of the reaction products (experimental part) revealed none of this compound.

Some of our experimental results are given in Table I. A consideration of these data leaves little doubt regarding the striking effect peroxides exert in governing the direction of the addition. The 2,2-dibromopropane is formed when the reaction is allowed to take place *in vacuo*, and in the absence of any appreciable amounts of peroxides; on the other hand, 1,2-dibromopropane is formed exclusively in the presence of peroxides.

It should be mentioned here that although it is possible to obtain the "abnormal" product (1,2-) in the presence of added peroxides, the system as a whole is not particularly sensitive to traces of peroxides. This of course readily can be predicted from the fact that freshly prepared methylacetylene, or even material three to four days old, does not give a peroxide test, even though no precautions are used to exclude oxygen. Further corroboration of the low susceptibility of the system to the "peroxide effect" is found in the fact that the same product (2,2-dibromopropane) was formed whether the addition was carried out in air, or *in vacuo* or with antioxidants *in vacuo*. In this respect methylacetylene is similar to propylene,² and markedly different from halogen ethyl-

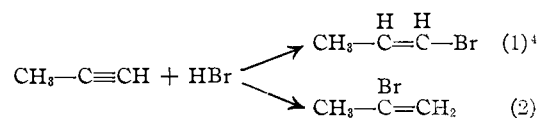
enes, which are extremely sensitive even to traces of oxygen and (or) peroxides.

A critical consideration of this addition, in the light of our knowledge of the effect of peroxides on the direction of addition, points to the conclusion that the product of the non-catalyzed first addition of hydrogen bromide to methylacetylene should be 2-bromopropylene.



If the probability of a rearrangement is ignored (and there is not the slightest reason to assume it) then only 2-bromopropylene can yield the 2,2-dibromopropane under peroxide-free conditions. It is to be noted that from the standpoint of the theory developed in our earlier papers,² the methyl group and the bromine atom in 2-bromopropylene reinforce each other in their directive effect, an interpretation in strict agreement with the exclusive formation of 2,2-dibromopropane under peroxide-free conditions.

The structure of the bromopropylene formed in the addition of hydrogen bromide to methylacetylene under peroxide conditions, is not deducible from a consideration of our data.



In the light of our experience, the 1,2-dibromopropane should be the product formed by addition of hydrogen bromide to either (1) or (2) in the presence of peroxides. To check this prediction, the addition of hydrogen bromide to the isomeric bromopropylenes is now under way in our laboratory. However, it is clear that the information thus obtained may not give an unequivocal

(4) We have purposely omitted in this discussion the probability of formation of the *cis-trans* isomers of 1-bromopropylene, and the possibility of formation of different products due to a difference in the addition to the two stereoisomers. The justification for this omission rests upon our demonstration of the identity of the products formed in the addition of hydrogen bromide to many *cis-trans* isomers [McNab, Doctorate Dissertation, University of Chicago, 1935].

answer regarding the nature of the product when methylacetylene reacts with one mole of hydrogen bromide under peroxide conditions.

An experimental solution of the problem, namely, the actual isolation of the bromopropylene formed under peroxide-catalyzed conditions, is not very easy, because of the number of possible isomers, and particularly because of the greater sensitivity of the bromopropylenes to peroxides, which leads to the formation of large amounts of the 1,2-dibromopropane. A few preliminary experiments have convinced us that both the theoretical and experimental objections to this approach are well justified.

Typical examples of experimental runs are recorded in Table I. It was necessary to depart slightly from the standard Kharasch-Mayo technique in order to effect complete reversal of hydrogen bromide addition through the agency of peroxides. As a rule a tube containing the unsaturated compound was immersed in a bath of carbon dioxide and acetone, ascaridole added and hydrogen bromide bubbled into the mixture. When the required amount of hydrogen bromide had been introduced, the tube was sealed and allowed to stand at room temperature until the addition was complete. However, in the case of methylacetylene, in order to reverse the addition of the halogen acid completely by peroxides, it has been found necessary to pass in the hydrogen bromide at a temperature between -33 and -40° . This is undoubtedly due to the fact that ascaridole is but very slightly soluble in methylacetylene at the temperature of the carbon dioxide-acetone mixture.

Experimental Work

I. Technique of Addition.—The usual Kharasch-Mayo² vacuum technique was employed in experiments involving the addition of hydrogen bromide under peroxide-free conditions. Quantitative yields of 2,2-dibromopropane were obtained in each case. In a few experiments using peroxides (ascaridole), the hydrogen bromide was bubbled into the mixture at -78° . Only a partial reversal in the addition was produced. However, it was observed that the ascaridole dissolved but slightly in the unsaturated hydrocarbon at the low temperature. In other experiments the ascaridole-methylacetylene mixture was allowed to stand for one hour in a bath of liquid ammonia (at which temperature the peroxide is appreciably dissolved) and hydrogen bromide introduced at a slow rate. In this case complete reversal was effected, the addition product being exclusively 1,2-dibromopropane.

II. Preparation of Methylacetylene.—Methylacetylene was prepared in 200-g. lots by the action of dimethyl sul-

fate on a solution of sodium in liquid ammonia according to the method of Meinert and Hurd.⁵ From our standpoint this was the best method, since the only impurity, acetylene, is readily removed by careful fractionation in a Davis column. Working with such relatively large quantities of materials, the experimental difficulties in this preparation (which is hard to carry out even on a small scale) were numerous. After some practice, however, we were able to obtain pure methylacetylene in yields of 70–80%. A sample of the product gave no test for peroxides.

III. Analysis and Identification of Products.—The reaction tubes were opened, allowed to stand for one hour to remove excess hydrogen bromide, the product weighed for yield and fractionally distilled three times *in vacuo*. This treatment was followed by washing with sodium bicarbonate solution and water, drying over calcium chloride and careful fractionation. The 1,2- and 2,2-dibromopropanes are distinguishable by their boiling points and can be separated to a large extent by repeated fractionations. Kharasch and Mayo⁶ have reported the refractive index, n_D^{20} of 1,2-dibromopropane as 1.5194. We have found the refractive index of 2,2-dibromopropane (not previously reported) to be 1.4977.⁷ Under peroxide-free conditions, a yield of 75 g. of product was obtained, all of which boiled in a range of 3° (112 – 115°). This product is the 2,2-dibromopropane. In the presence of peroxides we obtained 75 g. of product (100% yield) all of which distilled within the range 139 – 142° (1,2-dibromopropane). The 2,2-dibromopropane was further identified by conversion to acetone. Ten grams of the dibromide and 100 g. of water were heated at 160° for sixteen hours in a sealed tube. The acetone was distilled from the water solution and treated with 2,4-dinitrophenylhydrazine. The melting point of the product thus obtained was that given for the 2,4-dinitrophenylhydrazone of acetone (m. p. 128°). The melting of a sample was not depressed when mixed with a known synthetic sample.

Summary

1. It has been shown that the "normal" addition of hydrogen bromide to methylacetylene produces exclusively 2,2-dibromopropane.
2. Under the influence of added peroxides, hydrogen bromide adds to methylacetylene to give 1,2-dibromopropane.
3. It has been found that the hydrogen bromide must be passed into the methylacetylene, containing the added peroxide at a temperature of -33 to -40° in order to effect a complete reversal of the "normal" addition.

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(5) Meinert and Hurd, *THIS JOURNAL*, **52**, 4544 (1930).

(6) Kharasch and Mayo, *ibid.*, **55**, 2468 (1933).

(7) This substance was also prepared by us by direct bromination of isopropyl bromide. There was a perfect agreement of physical constants in the products obtained.