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

VAPOR PHASE PHOTOCHEMICAL BROMINATION OF 2,3-DIMETHYLBUTANE AND 2,2,4,4-TETRAMETHYLPENTANE*

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INTRODUCTION

A careful study of the products formed in the vapor phase photochemical bromination of alkyl halides was made by Kharasch, Zimmt, and Nudenberg (1). A specially designed apparatus (see Fig. 1 in that paper) was used for this purpose. The same apparatus was used in the study of the products formed in the vapor phase photochemical bromination of 2,3-dimethylbutane and 2,2,4,4-tetramethylpentane.

The liquid phase photochemical bromination of 2,3-dimethylbutane was studied by Grosse and Ipatieff (2). If liquid bromine is added slowly to the hydrocarbon, the bromination proceeds very rapidly at room temperature. The reaction product is 2,3-dibromo-2,3-dimethylbutane. The authors suggest that the monobromo derivative of 2,3-dimethylbutane, if first formed, would be converted to the 2,3-dibromo-2,3-dimethylbutane, since the rate of bromination of the monobromo compound is many times faster than that of the hydrocarbon.

Insofar as we have been able to find, the bromination of 2,2,4,4-tetramethylpentane in either the liquid or the vapor phase has not been investigated.

Vapor phase photochemical bromination of 2,3-dimethylbutane and 2,2,4,4-tetramethylpentane. The bromination of 2,3-dimethylbutane was carried out at 100° and atmospheric pressure in the apparatus shown in Fig. 1 of Ref. 1. The bromine was introduced very slowly, so that a very large excess of hydrocarbon was always present. Since only a small quantity of the 2,2,4,4-tetramethylpentane was available, the apparatus used was similar to the one shown in Fig. 1, but smaller (see exp. part). The bromination was carried out at reduced pressure, and the bromine was introduced as a vapor into the reaction chamber, heated to 200°, since little or no bromination took place at 100°.

The products formed in the bromination of the two hydrocarbons are indicated in Diagrams 1 and 2.

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* The authors are fully aware that the reactions here described (like so many other so-called vapor phase reactions) are not really vapor phase reactions in the "true" sense of that term. They may be "wall reactions", and there may be fine droplets (mist) in the reaction chamber, in spite of the fact that this chamber was heated to a temperature considerably above the boiling point of either reactant.

[1] The authors wish to acknowledge their indebtedness to the U. S. Rubber Company for generous financial support and to Dr. P. O. Tawney and R. Snyder (of the same organization) for furnishing them with the 2,2,4,4-tetramethylpentane used in this investigation.

DIAGRAM 1

Photochemical Vapor Phase Bromination of 2,3-Dimethylbutane at 100°[2]

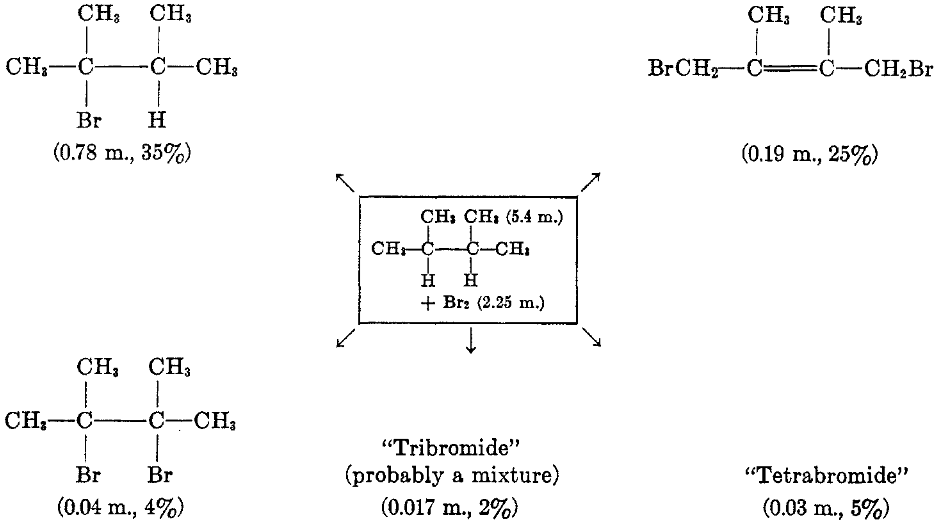
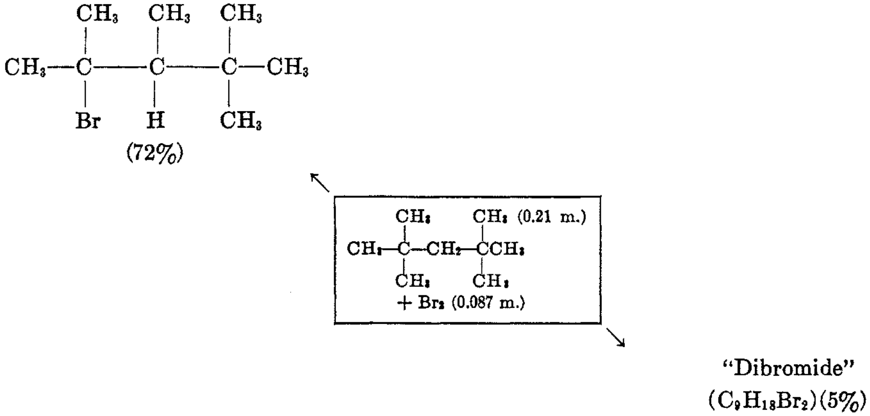


DIAGRAM 2

Photochemical Vapor Phase Bromination of 2,2,4,4-Tetramethylpentane at 200°



DISCUSSION

(*a*). *Formation of monobromides.* The monobrominated product (Diagram 2) formed in the vapor phase photochemical bromination of 2,2,4,4-tetramethylpentane is readily accounted for upon the following basis[3]:

1. $Br_2 \xrightarrow{h\nu} 2Br\bullet$
2. $(CH_3)_3C{-}CH_2{-}C(CH_3)_3 + Br\bullet \rightarrow (CH_3)_3C\underset{\bullet}{C}HC(CH_3)_3$ (A)

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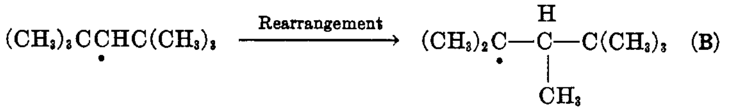
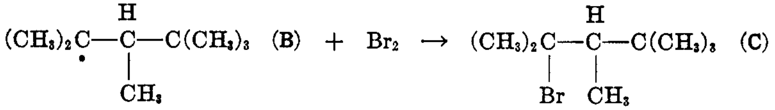
[2] The yields given in Diagrams 1 and 2 are calculated on the basis of the bromine used.

[3] With the data at hand, it is idle to speculate whether the free radical A has an independent existence, or whether it rearranges to B at the moment the hydrogen atom is being abstracted by the bromine atom.

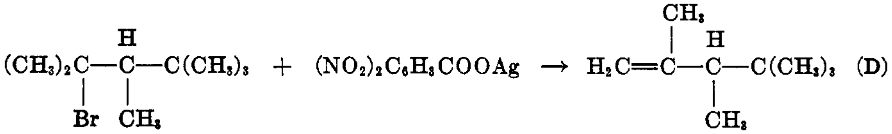
3. 

$$(CH_3)_3C\underset{\bullet}{C}HC(CH_3)_3 \xrightarrow{\text{Rearrangement}} (CH_3)_2\underset{\bullet}{C}-\overset{H}{\underset{CH_3}{C}}-C(CH_3)_3 \quad (\mathbf{B})$$

4. 

$$(CH_3)_2\underset{\bullet}{C}-\overset{H}{\underset{CH_3}{C}}-C(CH_3)_3 \ (\mathbf{B}) + Br_2 \rightarrow (CH_3)_2\underset{Br}{C}-\overset{H}{\underset{CH_3}{C}}-C(CH_3)_3 \quad (\mathbf{C})$$

The structure of compound **C** was surmised from the fact that it reacted instantly with silver salts. Furthermore, when **C** was dissolved in anhydrous ether and shaken with the silver salt of 3,5-dinitrobenzoic acid, an olefin **D**, silver bromide, and 3,5-dinitrobenzoic acid were formed.

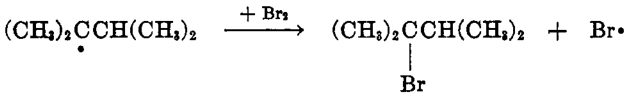
5. 

$$(CH_3)_2\underset{Br}{C}-\overset{H}{\underset{CH_3}{C}}-C(CH_3)_3 + (NO_2)_2C_6H_3COOAg \rightarrow H_2C=\overset{CH_3}{C}-\overset{H}{\underset{CH_3}{C}}-C(CH_3)_3 \quad (\mathbf{D})$$

The olefin **D** upon ozonolysis gave formaldehyde (identified as the methone derivative), and 3,4,4-trimethylpentan-2-one (identified as the 2,4-dinitrophenylhydrazone). A careful but unsuccessful search was made for acetone. The observations suggest that little, if any, of an isomer of **D** (containing a non-terminal double bond) is formed in reaction 5.

We know of no way of accounting for the formation of compound **C**, except by rearrangement of a methyl group either in the free radical as indicated in equation 3, or rearrangement of the compound $(CH_3)_3CHBrC(CH_3)_3$ (formed from the radical **A** and bromine) by some ionic mechanism. Because rearrangement of a methyl group in the free radical **A** has been demonstrated (3), the free radical mechanism of formation of **C** appears to us more reasonable.

The formation of 2-bromo-2,3-dimethylbutane, in the vapor phase photochemical bromination of 2,3-dimethylbutane may be explained (Diagram 1) in a similar manner except that here the free radical $(CH_3)_2\underset{\bullet}{C}CH(CH_3)_2$ does not rearrange, but reacts with bromine to give 2-bromo-2,3-dimethylbutane.

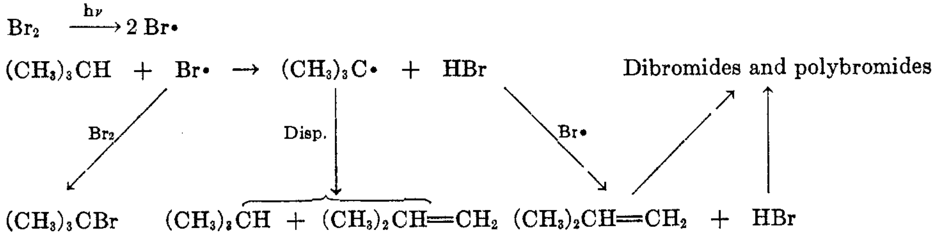
6. 

$$(CH_3)_2\underset{\bullet}{C}CH(CH_3)_2 \xrightarrow{+Br_2} (CH_3)_2\underset{Br}{C}CH(CH_3)_2 + Br\cdot$$

(*b*). *Formation of di- and poly-bromides.* The formation of di- and poly-bromides in the vapor phase photochemical bromination of the 2,3-dimethylbutane and 2,2,4,4-tetramethylpentane must be explained as part of the general explanation dealing with the mechanism of the formation of such bromides under all conditions. Because of the variation (under varying conditions) in the concentration of free organic radicals, bromine atoms and bromine molecules, present at any one time in the reaction mixture, the vapor phase reaction and the liquid phase reaction (unless carried out at very high dilutions) may be expected to differ considerably in the nature of their reaction products, even though both are initiated in the same manner and proceed by a free radical mechanism. When viewed from this standpoint, the liquid phase bromination of hydrocarbons presents a very complicated picture, and the products formed are largely dependent on the bromine concentration, on temperature, the intensity of the light, and the presence or absence of even traces of oxygen, metallic halides, or peroxidic materials.

It cannot be denied that the dibromides produced in the liquid and vapor phase bromination of some hydrocarbons might be due to the further bromination of the monobromides first formed. It would, however, be naive to assume that all di- and poly-bromides are formed exclusively in this manner, particularly in those instances when very dilute solutions of bromine in the hydrocarbon are used, or when the reaction is carried out in the vapor phase, where the concentration of the bromine with respect to the hydrocarbon is very low.

The formation of dibromides from the olefins (formed by elimination of hydrogen bromide from tertiary bromides) was suggested by us some years ago (4). We still believe that di- and poly-bromides are formed from olefins, but no longer believe that formation of the olefins by breakdown of the tertiary halide is usually a matter of much importance. A more attractive hypothesis is that olefins are formed during the bromination step. Thus, for example, the bromination of isobutane may be supposed to proceed as follows:



It should be emphasized that disproportionation of the free *tert*-butyl radical with a bromine atom is in all respects similar to the disproportionation of two alike free alkyl radicals to give an olefin and a saturated compound. As a matter of fact, work in this laboratory indicates that it is possible to disproportionate two unlike free radicals, such as a free octyl and a free methyl radical. The end products in the latter case are methane and a mixture of isomeric octenes.[4]

The formation of tri- and higher bromides from monobromides can be readily accounted for on this basis.[5]

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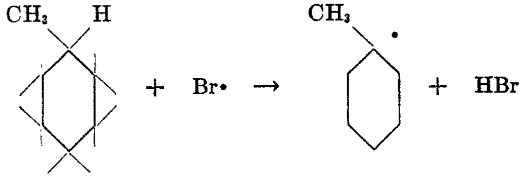
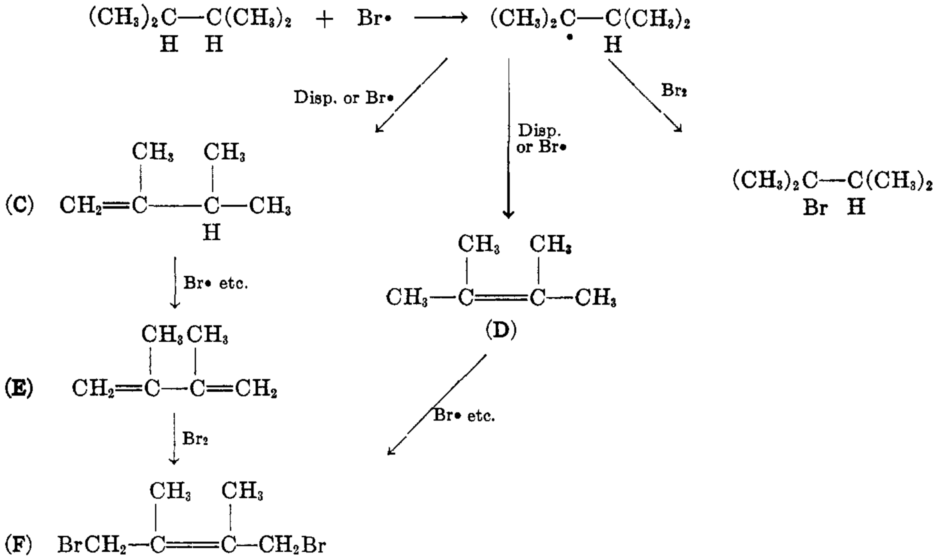
[4] This phase of the work will be treated in a paper now being prepared for publication by Kharasch, Liu, Mathur, and Nudenberg.

[5] The dibromides formed in the bromination of methylcyclohexane need not necessarily be the 1,2-dibromo derivatives, since either an isomeric olefin or a bicyclic compound may be formed:

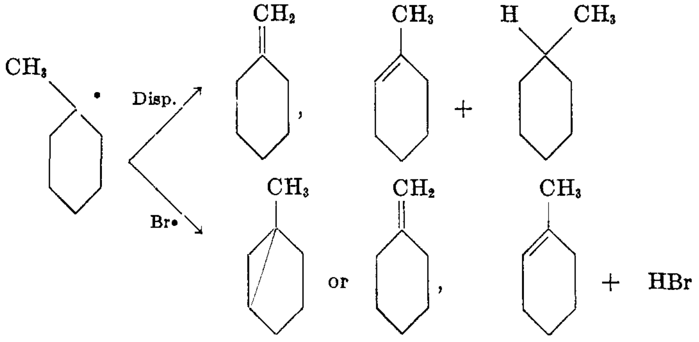


The formation of 1,4-dibromo-2,3-dimethylbut-2-ene (see Diagram 1) in the bromination of 2,3-dimethylbutane may therefore be illustrated in the following scheme:



The data at hand do not permit an unequivocal choice between the two schemes suggested above. Both give rise to intermediates (**C** and **D**) which should react much more rapidly with bromine atoms than does 2,3-dimethylbutane. Presumably they would therefore react with bromine atoms even in the presence of a large amount of the hydrocarbon.

It is noteworthy that the tetrabromide (see Diagram 1) isolated in the above reaction (m.p. 149–152°) differs from the tetrabromide formed by the addition of bromine to compound **F**. The latter substance melts at 137–138°; it is identical with the tetrabromide obtained by the addition of bromine to 2,3-dimethylbutadiene.



These would in turn give rise to isomeric dibromides. Unfortunately, at the time this work (4) was done, our major concern was with the factors which influence bromination (light, oxygen, concentration of bromine, effect of inhibitors, etc.). Hence no investigation was made of the dibromides formed. We hope to rectify this omission in the near future.

EXPERIMENTAL PART

Bromination of 2,3-dimethylbutane. The hydrocarbon (700 ml.) was placed in the flask A (see Fig. 1 of ref. 1), attached to the fractionating column, and heated to boiling under vigorous refluxing. The water in flask K was boiled to heat the bromination tube H which was covered with a sheet of aluminum foil and wrapped with glass wool. The stopcock D then was opened to let the condensate from the fractionating column run into the bromination tube at a fairly fast rate. After the lights placed under the inner wall of the tube I were turned on, bromine (120 ml., 360 g.) was introduced dropwise from the dropping-funnel into the reaction chamber. Under these conditions the reaction between bromine and 2,3-dimethylbutane appeared to be quite fast, and the rate of the addition of bromine was so adjusted that the liquid running back through the U-tube remained colorless. The hydrogen bromide produced was absorbed in water. The addition of the bromine took ten hours.

Isolation of the products. The bromination products, collected in flask A, were stripped of hydrogen bromide with dry nitrogen and fractionated to remove the unreacted starting material. The recovered 2,3-dimethylbutane showed no unsaturation. The residue was distilled under reduced pressure to yield a fraction which boiled at 41–41.5°/27.5 mm., n_{D}^{20} 1.4541. This product (128 g.) was 2-bromo-2,3-dimethylbutane (35% on the basis of the bromine used).

Anal. Calc'd for $C_6H_{13}Br$: Br, 48.46. Found: Br, 48.24.

The residue on cooling deposited a crystalline material. Some crystals also formed on the wall of the flask through sublimation. These were collected and the combined material (6 g.) was crystallized from ether. The material sublimed without melting at 170–175°. This sublimation point corresponds to that of 2,3-dibromo-2,3-dimethylbutane obtained by Grosse and Ipatieff (2).

Residue. The high-boiling residue was distilled *in vacuo.* After a small amount of low-boiling material (presumably the monobromo compound) distilled over more crystalline material sublimed and formed a deposit in the condenser. This was rinsed off with ether and crystallized from this solvent as needles (3.2 g.) which sublimed at 165–175°, thus making the total yield of 2,3-dimethylbutane 9.2 g. (4% on the basis of the bromine used). Continued distillation gave the following fractions: fraction 1, b.p. 44–46°/0.2 mm., 46 g.; fraction 2, b.p. 67–70°/0.2 mm., 5.4 g.; fraction 3, b.p. 96–100°/0.4 mm., 10.1 g. A small amount of tarry residue remained in the flask.

Fraction 1 was a strong lachrymator. On distillation *in vacuo* it boiled at 40°/0.1 mm. The distillate was a faintly yellowish liquid which partially crystallized on cooling; the crystals (colorless needles) melted at 57–57.5°. The fraction consisted of a mixture of the *cis-* and *trans-*isomers of 1,4-dibromo-2,3-dimethylbut-2-ene.[6] The analysis was performed on the mixture of the two isomers.

Anal. Calc'd for $C_6H_{10}Br_2$: Br, 66.05; Mol. wt., 242.

Found: Br, 66.19; Mol. wt., 250.

Fraction 3 was a heavy oil which partly solidified on cooling. On crystallization from ether it formed colorless needles, m.p. 149–152°.

Anal. Calc'd for $C_6H_{10}Br_4$ (or $C_6H_8Br_4$): Br, 79.56; Mol. wt., 402.

Found: Br, 79.10; Mol. wt., 391.

The analysis indicated that the fraction was a tetrabromide the structure of which was undetermined.

Fraction 2 gave the following analysis: Br, 78.14; Mol. wt., 310. It was probably a mix-

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[6] Sweeting and Johnson [*J. Am. Chem. Soc.*, **68,** 1057 (1946)] report that the isomers, formed by the addition of bromine to 2,3-dimethyl-1,3-butadiene, can be separated by fractional distillation. The *cis*-isomer boils at 77.5–79.5°/5 mm.; and the *trans*-isomer (m.p. 47–47.5°) at 88.5–91.0°/5 mm. Macallum and Whitby [*Trans. Roy. Soc. Canada*, **22,** III, 33 (1928)], however, give the same b.p. 105–110°/18.5 mm. for both isomers. See also Kondakov, *J. prakt. Chem.*, **62,** 166 (1900); Farmer, Lawrence, and Scott, *J. Chem. Soc.*, 510 (1930).

ture of the tetrabromo compound and some lower-boiling material, and was not further investigated.

Proof of the structure of 1,4-dibromo-2,3-dimethylbutene. Fraction 1 (2 g.) was dissolved in 25 ml. of carbon tetrachloride and treated with 1.5 g. of bromine. The solution was allowed to stand for 40 minutes at room temperature under moderate illumination. The bromine completely disappeared after this time. The solvent was removed by distillation and the residue cooled. The crystals were collected (1.8 g.) and recrystallized three times from absolute alcohol furnishing faintly yellow needles, m.p. 137–138°. This is the m.p. of 2,3-dimethyl-1,2,3,4-tetrabromobutane reported in the literature (5).

Bromination of 2,2,4,4-tetramethylpentane at 200°. The 2,2,4,4-tetramethylpentane was furnished us through the courtesy of the Research and Development Division of the United States Rubber Company (b.p. 121–122°; n_D^{20} 1.4065). The bromine was distilled prior to use.

Apparatus. Due to the availability of only a limited amount of the starting material a small bromination apparatus, which had a design similar to the one used for the bromination of 2,3-dimethylbutane, was constructed. The reaction vessel was a double-walled tube, 140 mm. long and 10 mm. in diameter, and a 200-watt lamp was used as the source of illumination. Since the bromination was carried out under reduced pressure, bromine was introduced as vapor from a vial carrying a bent side-tube fitted to the top of the reaction vessel.

The same procedure was used in the bromination of this hydrocarbon as previously described except that it was operated under reduced pressure (155 mm.). A Dry Ice-acetone trap was placed between the exit tube and the water pump to collect the volatile products. The reaction tube was heated to 200° by refluxing ethylene glycol in the flask attached at the bottom of the heating jacket. While 2,2,4,4-tetramethylpentane (27 g., 0.21 mole) was refluxing vigorously, bromine (14 g., 0.087 mole) vapor was allowed to vaporize into the reaction tube at such a rate that the condensate at the bottom of the tube contained only traces of bromine. The bromination took place quite slowly, and it required 7.5 hours to complete the addition of bromine. The reaction mixture was then cooled and the apparatus filled with nitrogen.

Isolation of the products. The dissolved hydrogen bromide and traces of bromine were removed by passing nitrogen through the mixture. The whole was then distilled under reduced pressure and the following fractions were collected: fraction 1, b.p. 51°/5 mm., n_D^{20} 1.4690, 0.7 g.; fraction 2, b.p. 51–52°/5 mm., n_D^{20} 1.4695, 1.1 g.; fraction 3, b.p. 52°/5 mm., n_D^{20} 1.4719, 11.2 g. All fractions gave a positive test for halogen.

Anal. (fraction 3) Calc'd for $C_9H_{19}Br$: C, 52.18; H, 9.24; Br, 38.58; Mol. wt., 207.
Found: C, 52.24; H, 9.29; Br, 38.90; Mol. wt., 206.

The combined yield of the three fractions was 13.0 g. (72.2% on the basis of bromine used). It was shown to be 2-bromo-2,3,4,4-tetramethylpentane (see below).

The residue deposited a colorless crystalline solid (0.6 g.) on cooling. This was collected, washed with a little ether, and dried [m.p. 122–132° (sintered above 114°)].

Anal. Calc'd for $C_9H_{18}Br_2$: Br, 55.87; Mol. wt., 286.
Found: Br, 56.26; Mol. wt., 288.

The analysis indicated that the solid was a dibromide. The structure of this dibromide was not determined.

The lower-boiling material, which condensed in the cold trap during the distillation, and the liquid collected from the Dry Ice trap used in the bromination were combined and stripped of hydrogen bromide with nitrogen. The residue (9.0 g.) was distilled in a Claisen flask to give 6.7 g. of material, b.p. 120–123°; n_D^{20} 1.4091, which contained no unsaturation. A Beilstein test showed the presence of some halogen indicating that it was the starting material contaminated with traces of the bromide.

Proof of the structure of the monobromide. (a). Hydrolysis. A solution of 0.1104 g. of the monobromide in 45 ml. of 75% alcohol was treated with an excess of 0.1 *N* silver nitrate solution, and the mixture was allowed to stand at room temperature for 30 minutes with constant swirling. The precipitate was collected, washed with dilute nitric acid, and the filtrate was titrated according to Volhard's method. The titrations indicated that 92.5% of the bromide had been hydrolyzed during the 30 minutes shaking with silver nitrate.

(*b*). *Acetolysis*. A solution of 2.1 g. (0.01 mole) of the monobromide in 30 ml. of glacial acetic acid containing 0.3 ml. of acetic anhydride was treated with 2 g. (0.012 mole) of silver acetate and the mixture was shaken for one hour. After removal of the precipitate the solution was concentrated to a small volume (under reduced pressure), some water and ether was added, and the ethereal solution washed with water, dilute sodium bicarbonate solution, and dried over sodium sulfate. The solvent then was removed under reduced pressure leaving 0.5 g. of a colorless liquid of pleasant odor, which gave a positive hydroxamic acid test for esters.

Examination of the acetic acid distilled off showed it contained unsaturation. It was neutralized with sodium carbonate in the cold and extracted with ether. The ether extract was washed with water, dried over sodium sulfate, and distilled to remove the solvent. The residue (0.6 g.), which was unsaturated, was dissolved in 80 ml. of carbon tetrachloride and ozonized for 10 minutes at 0°. The volatile products were conducted through 25 ml. of distilled water. When the aqueous solution was treated with a saturated aqueous solution of methone, a crystalline precipitate (0.05 g.) quickly formed, which melted at 191–192°, indicating that it was the methone derivative of formaldehyde (6). A careful but unsuccessful search was made for acetone.

(*c*). *Reaction with silver 3,5-dinitrobenzoate*. A solution of 2.07 g. (0.01 mole) of the monobromide in 45 ml. of anhydrous ether was treated with 7.3 g. of freshly prepared, finely pulverized silver 3,5-dinitrobenzoate, and the mixture was shaken in the dark for 36 hours to complete the reaction. The silver salts were collected and the filtrate was evaporated to dryness under reduced pressure. The ether and other volatile products were collected in a trap cooled to −80°. A crystalline residue was obtained, m.p. 205–207° (3,5-dinitrobenzoic acid). The liquid, collected in the trap, was distilled on a water-bath to remove the ether, and the residue distilled in a Hickman flask. A colorless liquid, b.p. 125–126°/754 mm.; n_D^{20} 1.4261 thus was obtained. The boiling point and refractive index agreed very closely with the observed values for 2,3,4,4-tetramethylpent-1-ene.

The identity of the olefin was further established through ozonolysis. A solution of 0.1 g. of the olefin in 100 ml. of ethyl acetate was ozonized for 2.5 minutes at −40°. After removal of the solvent under reduced pressure the ozonide was decomposed in absolute alcohol with a platinum catalyst and hydrogen. The catalyst was collected, and the filtrate was fractionated through a Vigreux column to remove the alcohol. Here again an unsuccessful search was made for acetone. The residue was treated with a methanolic solution of 2,4-dinitrophenylhydrazine, and the precipitate recrystallized three times from dilute alcohol to give orange needles, m.p. 109–110°. This was the 2,4-dinitrophenylhydrazone of 3,4,4-trimethylpentan-2-one (7).

Anal. Calc'd for $C_{14}H_{20}O_4N_4$: N, 18.17. Found: N, 18.20.

SUMMARY

1. It has been established that the vapor phase photochemical bromination of 2,3-dimethylbutane at 100° gives the following products: 2-bromo-2,3-dimethylbutane (35%); 1,4-dibromo-2,3-dimethylbut-2-ene (25%); 2,3-dibromo-2,3-dimethylbutane (4%), and small amounts of a tri- and tetra-bromo compound of unknown constitution. The yields of the products formed in the reaction are calculated on the basis of the bromine used.

2. Little or no bromination products are formed in the vapor phase photochemical bromination of 2,2,4,4-tetramethylpentane at 100°. At 200° bromination occurs, and the following products have been isolated: 2-bromo-2,3,4,4-

tetramethylpentane (72%) and a dibromide ($C_9H_{18}Br_2$) (5%) of unknown constitution.

3. It is to be noted that formation of 2-bromo-2,3,4,4-tetramethylpentane in the bromination of 2,2,4,4-tetramethylpentane involves a rearrangement of a methyl group in the bromination process.

4. Mechanisms which account for the formation of the mono- and the di-bromides in the bromination in the photochemical vapor phase bromination (at low bromine concentrations) are proposed.

CHICAGO 37, ILLINOIS.

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