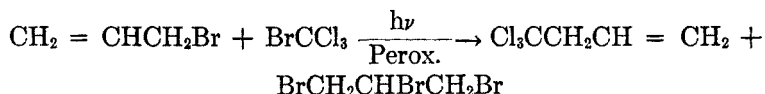


REACTIONS OF ATOMS AND FREE RADICALS IN SOLUTION. XVII.  
DECOMPOSITION OF DIACETYL PEROXIDE IN ALLYL  
BROMIDE<sup>1</sup>

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The unusual behavior of allyl bromide with bromotrichloromethane (1) to give (as the main reaction products) 4,4,4-trichloro-1-butene and 1,2,3-tribromopropane,



prompted us to investigate the decomposition of diacetyl peroxide in allyl bromide.

RESULTS

When diacetyl peroxide dissolved in allyl bromide is added dropwise to excess boiling allyl bromide, a slow decomposition ensues. About one mole of carbon dioxide is formed per mole of peroxide. It is most interesting, however, that no methane and very little methyl bromide are formed in this reaction. The following products were isolated in the amounts indicated per mole of diacetyl peroxide:

1. 1-Butene (25.7 g., 0.459 mole; 46% of the calculated amount, on the basis of equation 2);
2. Methyl bromide (5.2 g., 0.055 mole);
3. 1,3-Dibromopropane (4.5 g., 0.22 mole);
4. An unidentified strongly lachrymatory material containing bromine; apparent molecular weight 166 (2.2 g.);
5. A dimer of allyl bromide (4-bromomethyl-5-bromo-1-pentene) (44 g., 0.182 mole);
6. 1,5-Dibromo-2-bromomethylpentane (?) (5.6 g., 0.017 mole);
7. A polymer of the consistency and color of pitch (72 g.).

DISCUSSION

The formation of compounds 1 to 7 may be accounted for on the basis of the following series of reactions:

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1.  $(\text{CH}_3\text{COO})_2 \xrightarrow{\Delta} \text{CH}_3\cdot + \text{CO}_2 + \text{CH}_3\text{COO}\cdot$
2.  $\text{CH}_2=\text{CHCH}_2\text{Br} + \text{CH}_3\cdot \rightarrow \text{CH}_3\text{CH}_2-\dot{\text{C}}\text{HCH}_2\text{Br} \rightarrow \text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2 + \text{Br}\cdot$   

$\swarrow$   
 (A)  
 $\text{CH}_2=\text{CHCH}_2\text{CH}_3 + \text{Br}\cdot$
- 2A.  $\text{A} + \text{CH}_2=\text{CHCH}_2\text{Br} \rightarrow \text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2 + \text{BrCH}_2\dot{\text{C}}\text{HCH}_2\text{Br}$
3.  $\text{CH}_2=\text{CHCH}_2\text{Br} + \text{Br}\cdot \rightarrow \text{BrCH}_2\dot{\text{C}}\text{HCH}_2\text{Br}$   
 (B)
4.  $\text{BrCH}_2\dot{\text{C}}\text{HCH}_2\text{Br} + \text{CH}_2=\text{CHCH}_2\text{Br} \rightarrow \text{BrCH}_2\text{CHCH}_2\text{Br}$   

$\swarrow$   
 B  
 $\text{BrCH}_2\text{CHCH}_2\text{Br}$   
 $\quad |$   
 $\quad \text{CH}_2$   
 $\quad |$   
 $\quad \text{HC}=\text{CH}_2 + \text{Br}\cdot$

$\downarrow$   
 (C)  
 $\text{CH}_2$   
 $|$   
 $\text{HC}\cdot$   
 $|$   
 $\text{CH}_2\text{Br}$   
 $\downarrow$   
 $\text{BrCH}_2\text{CHCH}_2\text{Br}$   
 $\quad |$   
 $\quad \text{CH}_2$   
 $\quad |$   
 $\quad \text{HC}=\text{CH}_2 + \text{Br}\cdot$   
 (D)
5.  $(\text{C}) + \text{CH}_2=\text{CHCH}_2\text{Br} \rightarrow (\text{D}) + (\text{B})$
6.  $\text{BrCH}_2\dot{\text{C}}\text{HCH}_2\text{Br} + \text{Hydrogen donor} \rightarrow \text{BrCH}_2\text{CH}_2\text{CH}_2\text{Br}$   
 (B) (E)
7.  $(\text{C}) + \text{Hydrogen donor} \rightarrow \text{BrCH}_2\text{CHCH}_2\text{CH}_2\text{CH}_2\text{Br}$   

$\quad |$   
 $\quad \text{CH}_2\text{Br}$   
 (F)
8.  $(\text{C}) + \text{CH}_2=\text{CHCH}_2\text{Br} + \xrightarrow{(\text{CH}_3\text{COO})_2} \text{Polymer}$
9.  $(\text{D}) + \text{CH}_2=\text{CHCH}_2\text{Br} \xrightarrow{(\text{CH}_3\text{COO})_2} \text{Polymer}$
10.  $\cdot\text{CH}_3 + \text{Bromine donor} \rightarrow \text{CH}_3\text{Br}$

It is rather uncertain whether in step 2 the free methyl radical first adds to the allyl bromide molecule, with decomposition of the newly formed free radical to 1-butene and a bromine atom, or whether the free methyl radical attacks the allyl bromide molecule displacing a bromine atom and forming 1-butene. The fact that methyl radicals attack butyl chloride and crotyl chloride (2) to give pentane and 2-pentene would indicate that such a displacement reaction is possible, whereas we have not had any evidence as yet of an addition of a free methyl radical to a double bond of an aliphatic olefin. An alternative suggestion for the formation of 1-butene and (B) is offered in 2A. Similarly, there is uncertainty concerning the mechanism of formation of (D). This substance could

be formed by a displacement mechanism (step 4) or an addition mechanism followed either by disproportionation (step 4), or interaction with a molecule of allyl bromide (step 5) to give (D) + (B).

The products (E) and (F) probably result from abstraction of hydrogen atoms from some molecules by the free radicals (B) and (C), respectively. The free radical (B), is obviously the precursor of all of the brominated substances isolated in this reaction.

#### PROOF OF STRUCTURE OF REACTION PRODUCTS

The 1-butene and the 1,3-dibromopropane were identified by the usual methods (see experimental part). The structure of the dimer of allyl bromide (D) (4-bromomethyl-5-bromo-1-pentene) was established by degradation and synthesis (Fig. 1).

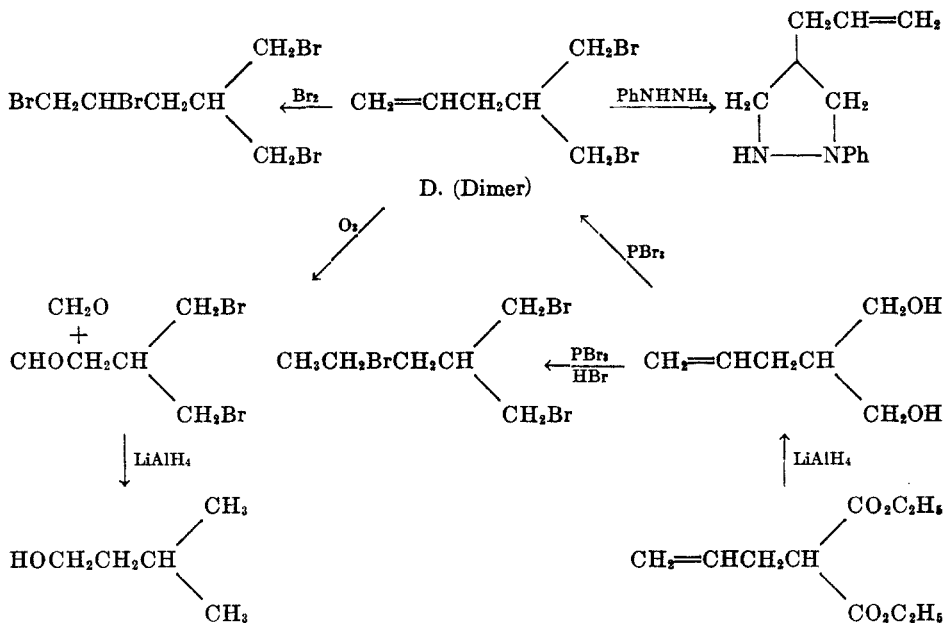


FIG. 1

Establishment of Identity of Dimer (4-Bromomethyl-5-bromo-1-pentene)

The structure of compound (F) (1,5-dibromo-2-bromomethylpentane) was not definitely established. The analytical data agree well with this structure. Furthermore, because of formation of 1,3-dibromopropane (step 6), there is strong presumptive evidence that the free radical (C) can also abstract a hydrogen atom to give 1,5-dibromo-2-bromoethylpentane (step 7).

#### EXPERIMENTAL

Allyl bromide, Eastman's pure grade, was distilled through a Vigreux column (b. 71.3°) and was free of peroxides.

*Decomposition of diacetyl peroxide in allyl bromide.* A solution of diacetyl peroxide (33.5

g., 0.284 mole) in allyl bromide (50 g.) was added dropwise (through a capillary tube which projected below the surface of the liquid) to allyl bromide (183 g.) contained in a 500-cc. flask, which was immersed in an oil-bath held at 90°. The gaseous products of the reaction were passed through an efficient reflux condenser, attached directly to the reaction flask, and into a gas-absorption train, consisting of a trap cooled with ice-salt mixture, a second trap immersed in a Dry Ice-acetone bath, three U-tubes filled with soda-lime, and a fourth with calcium chloride. The gases not absorbed by the soda-lime were collected over water in a special gas-collection apparatus.

The addition of the diacetyl peroxide required 6 hours. Carbon dioxide (10.9 g.; 0.25 mole) was the only non-condensable gas formed in the reaction. The contents of the first trap (14 g.) were distilled at normal pressure through a Vigreux column; 13.6 g. of allyl bromide was obtained. The residue (about 0.9 g.) was mostly acetic acid, which was confirmed by the fact that the residue gave a lanthanum nitrate test. The material which had collected in the Dry Ice-acetone cold-trap was allowed to distill at room temperature and again condensed in a cold-trap. The material was thus separated into two fractions: allyl bromide and the material (8.7 g.) which collected in the cold-trap. To ascertain the butene content of this material three grams of it was mixed with 20 cc. of chloroform and cooled with a Dry Ice-acetone mixture. A solution of bromine in chloroform which contained 211.3 mg. of bromine per cc. was then added dropwise. When 7170 mg. of bromine (34 cc.) had been taken up the solution turned yellow, indicating that the mixture contained 84% of butene. The other material in the butene was shown to be methyl bromide by absorbing the butene in sulfuric acid and determining the molecular weight of the unabsorbed gas. The value obtained was in excellent agreement with that calculated for methyl bromide. The total amount of methyl bromide formed is, however, small (1.5 g.).

Further to identify the butene formed in the reaction, the dibromide prepared as described above was carefully purified by distillation at reduced pressure. A colorless material boiling at 55°/15 mm. was thus obtained ( $d_4^{20}$  1.7984;  $n_D^{20}$  1.5152). These values agree well with those of a synthetic sample of 1,2-dibromobutane: b.p. 55°/15 mm.;  $d_4^{20}$  1.7951;  $n_D^{20}$  1.5149. The yield of butene (on the basis of equation 2) was 46%.

The main reaction mixture was dark brown. It was distilled at reduced pressure. The following fractions were collected: Fraction 1, unchanged allyl bromide; Fraction 2, b.p. 58–95°/23 mm., 9.5 g.; Fraction 3, b.p. 95–108°/23 mm., 12.5 g.; Residue, black solid resembling heavy tar, 20.5 g.

Fraction 2 was purified by distillation through a Vigreux column. Two fractions were obtained. The fraction boiling at 43–45°/15 mm. (1.3 g.) was identified as 1,3-dibromopropane ( $n_D^{20}$  1.5237).

*Anal.* Calc'd for  $C_3H_6Br_2$ : Br, 79.2. Found: Br, 78.9.

The fraction boiling at 55–60°/20 mm.,  $n_D^{20}$  1.4760, (2.2 g.) is probably a mixture. The apparent molecular weight of the material was 166. Because the analyses for carbon, hydrogen, and bromine were inconsistent (C, 24.76 and 26.89; H, 3.05 and 3.47; Br, 57.73 and 51.95); and because it decomposed violently when heated, the study of this mixture was not pursued further. The substance when first isolated liberated iodine from potassium iodide solution.

Fraction 3 was distilled through a Vigreux column, and the fraction (12.5 g.) which boiled at 93–95°/15 mm. was collected ( $n_D^{20}$  1.5256). This fraction was shown to be a dimer of allyl bromide, namely, 4-bromomethyl-5-bromo-1-pentene.

*Anal.* Calc'd for  $C_6H_{10}Br_2$ : C, 29.8; H, 4.14; Br, 66.19; mol. wt., 242.

Found: C, 29.4; H, 3.91; Br, 66.3; mol. wt., 244.

The black residue was ground in a mortar and extracted with chloroform. The chloroform was removed, and the remainder was distilled in a Hickman flask at 0.01 mm. pressure (temperature of bath 85–90°). The material had the index of refraction 1.5672 at 20°. This substance is probably 2-bromomethyl-1,5-dibromopentane [compound (F) in the theoretical part of the paper].

*Anal.* Calc'd for  $C_6H_{11}Br_3$ : Br, 74.3; mol. wt., 323.

Found: Br, 74.2; mol. wt., 321.

The residue remaining in the Soxhlet apparatus was dried *in vacuo* at 80° and analyzed. Found: C, 51.7; H, 3.89; Br, 40.8.

It was insoluble in all common organic solvents.

*Proof of structure of dimer of allyl bromide—4-bromomethyl-5-bromo-pentene-1.* (a) *Presence of a double bond.* The dimer (1.9858 g.) was dissolved in 10 cc. of carbon tetrachloride and treated with a solution of bromine in carbon tetrachloride (1 cc. of CCl<sub>4</sub> sol. contained 36.8 mg. of Br<sub>2</sub>). After the addition of 36 cc. of the bromine solution, the reaction mixture turned yellow. The calculated amount of bromine solution for one double bond is 35 cc. To isolate the adduct, the volatile solvents were first removed, and the residue was distilled in a Hickman flask at 0.02 mm. pressure and a bath temperature of 150°. The index of refraction of the material thus obtained was 1.5909 at 20°.

*Anal.* Calc'd for C<sub>6</sub>H<sub>10</sub>Br<sub>4</sub>: C, 17.9; H, 2.5; Br, 79.6; mol. wt., 402.

Found: C, 17.6; H, 2.2; Br, 79.8; mol. wt., 404.

(b) *Position of the double bond in the dimer, and its skeletal structure.* The position of the double bond was determined by ozonolysis. The substance (1 g.) was dissolved in 20 cc. of carbon tetrachloride and cooled to 0°, and a stream of ozone (4.5% O<sub>3</sub>) was passed through the mixture for 20 minutes. The volatile materials were collected in two test tubes each containing 20 cc. of water. The water solutions were combined and treated with 5 cc. of saturated water solution of methone. Within a few minutes a crystalline material had separated. This was collected and dried, m.p. 189°, which was not depressed by admixture with a very pure synthetic sample of the formaldehyde methone compound (m.p. 191°). The yield of formaldehyde was 32% of the calculated amount. In an investigation of this method, it has been shown (3) that the optimum yield of formaldehyde by this process is about 35% of the calculated value.

The carbon tetrachloride was removed from the "ozonized" sample at reduced pressure. The ozonide which remained was a colorless oil. In order to decompose it, it was treated with 20 cc. of water, and the whole was heated on a steam-bath for one hour. The reaction mixture was extracted four times with small amounts of ether; the ether extracts were combined, washed with a cold solution of sodium bicarbonate, dried with sodium sulfate, and filtered. The ether was removed from the filtrate, and the residue distilled in a Hickman flask at 15 mm. pressure. The material which boiled at 130° (temperature of the oil-bath) was collected. The material gave the characteristic reactions of an aldehyde. Thus, it gave a 2,4-dinitrophenylhydrazone (m.p. 158°), a positive test with C<sub>6</sub>H<sub>5</sub>SO<sub>2</sub>NHOH and with Tollens' reagent.

The skeletal structure of this presumably dibromo aldehyde was determined in the following manner.

The dibromo aldehyde (500 mg.) was diluted with 10 cc. of dry ether, and the solution was added dropwise to a mixture of lithium-aluminum hydride (1 g.) (4) and lithium hydride (1 g.) in 10 cc. of anhydrous ether, maintained at its boiling point. The mixture was heated for a total of 2 hours. At the end of that time, ice-water was added to destroy the residual hydrides, and the solution was carefully neutralized with dilute hydrochloric acid. The ether layer was washed twice with a saturated solution of ammonium chloride, dried with sodium sulfate, and the ether was distilled. The residue was distilled in a Hickman flask and 80 mg. of colorless liquid was collected. The 3,5-dinitrobenzoate of this material melted at 62°, and it did not change the melting point of the 3,5-dinitrobenzoate prepared from a pure authentic sample of isoamyl alcohol.

(c) *Proof that the bromine atoms in the dimer are situated beta to each other.* To the dimer (500 mg.), dissolved in 10 cc. of benzene, was added the sodium derivative of phenylhydrazine (5) (1 g.). The mixture was heated to boiling for 10 hours. At the end of that time a good deal of sodium bromide had separated. The reaction mixture was then diluted with water, additional ether was added, the layers were separated, and the ether solution was washed repeatedly with water to remove the phenylhydrazine. The ether was then extracted with hydrochloric acid (2 N), the ether was rejected, the acid solution was made

alkaline and extracted with ether. The ether solution was removed, and the residue was distilled in a Hickman flask. The distillate was 1-phenyl-4-allylpyrazolidine (b.p. 130°/0.01 mm.;  $n_D^{20}$  1.5860).

*Anal.* Calc'd for  $C_{12}H_{16}N_2$ : N, 14.9. Found: N, 14.8.

The picrate of the 1-phenyl-4-allylpyrazolidine was too soluble for crystallization. The picrolonate of this material, however, was readily obtained.

*Anal.* Calc'd for  $C_{22}H_{24}N_6O_6$ : N, 18.5. Found: N, 18.0.

The picrolonate crystallizes in yellow needles from ethyl alcohol. It melted at 186–187°, and its melting point was not depressed by admixture with a picrolonate of synthetic 1-phenyl-4-allylpyrazolidine prepared by a conventional method (5).

*Synthesis of 4-bromomethyl-5-bromo-1-pentene.* (a) *Preparation of 2-hydroxymethyl-4-penten-1-ol.* Lithium-aluminum hydride (5 g.) was suspended in 50 cc. of ether contained in a three-necked flask equipped with an efficient reflux condenser, a mechanical stirrer, and a dropping-funnel. To this mixture was added dropwise a solution of diethyl allylmalonate (b.p. 120°/18 mm.;  $n_D^{20}$  1.4319) in 20 cc. of anhydrous ether. Upon completion of the addition, the mixture was refluxed for 30 minutes and cooled in an ice-salt mixture. Water was then added to destroy the excess of hydrides, and the solution was finally acidified with dilute sulfuric acid. Sufficient sodium sulfate to saturate the water solution was then added, and the whole was extracted with ether in a continuous extractor for 10 hours. The ether solution was then dried, and ether was removed by evaporation. The residue was distilled *in vacuo* (b.p. 136–139°/15 mm.;  $n_D^{20}$  1.4747). The yield of 4-hydroxymethyl-4-penten-1-ol was 52% of the calculated amount.

*Anal.* Calc'd for  $C_8H_{12}O_2$ : C, 62.0; H, 10.3.

Found: C, 62.2; H, 10.2.

The bis-3,5-dinitrobenzoate of the 4-hydroxymethyl-4-penten-1-ol crystallizes in white needles from ethyl acetate and melts sharply at 145–146°.

*Anal.* Calc'd for  $C_{20}H_{16}N_4O_{12}$ : N, 11.1. Found: N, 10.6.

(b) *Preparation of 4-bromomethyl-5-bromo-1-pentene.* To 2-hydroxymethyl-4-penten-1-ol (6 g.) dissolved in 10 cc. of dry benzene was added dry pyridine (0.5 cc.), and the whole was cooled to 0°. To this mixture was added a solution of phosphorus tribromide (12 g.) in 10 cc. of dry benzene. Upon completion of the addition, the mixture was kept for 10 hours at room temperature, and then heated for 8 hours at 80°. Water was then added to destroy the excess of phosphorus tribromide, and the whole was extracted with ether. The ether extract was washed successively with a water solution of sodium bicarbonate, dilute hydrochloric acid, and water. The ether-benzene mixture was dried over sodium sulfate, and the solvents were removed by distillation. The residue was distilled through a Vigreux column and the following fractions were collected: Fraction 1, b.p. 93–95°/15 mm.,  $n_D^{20}$  1.5204; Fraction 2, b.p. 138–141°/15 mm.,  $n_D^{20}$  1.5454.

Fraction 1 is undoubtedly 4-bromomethyl-5-bromo-1-pentene and corresponds in physical constants to the dimer prepared by treating allyl bromide with diacetyl peroxide. Further to confirm the identity of these materials, the material of Fraction 1 was heated with sodium phenylhydrazine to give 1-phenyl-4-allylpyrazolidine. The picrolonate of this pyrazolidine melted at 185–187° and did not depress the melting point of the picrolonate of the 1-phenyl-4-allylpyrazolidine, prepared from the dimer of allylbromide. The identity of these materials is thus established. Furthermore, the dimer of allyl bromide formed in the decomposition of diacetyl peroxide in that solvent, is definitely established as 4-bromomethyl-5-bromo-1-pentene.

Fraction 2 (b.p. 138–141°/15 mm.;  $n_D^{20}$  1.5454) is probably formed by the addition of hydrogen bromide to 4-bromomethyl-5-bromo-1-pentene, the product is therefore 1,4-dibromo-2-bromomethylpentane.

*Anal.* Calc'd for  $C_8H_{11}Br_3$ : Br, 74.3; mol. wt., 323.

Found: Br, 74.0; mol. wt., 309.

## SUMMARY

1. The decomposition of diacetyl peroxide in allyl bromide was shown to give the following products: butene-1, methyl bromide, 1,3-dibromopropane, 4-bromomethyl-5-bromo-1-pentene, possibly 1,5-bromo-2-bromomethylpentane, and a blackresidue resembling pitch.

2. A mechanism to account for the reaction products is suggested.

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