TABLE II

RADIOACTIVITY EXCHANGE BETWEEN Mg^*Br_2 AND Et_2Mg AND $(C_6H_5)_2Mg$

System	Specific activity,[a] c./min.-mg. Mg Mg*Br	R_2Mg	Contact time, hr.	Activity ratio	Migration, %
$Et_2Mg + Mg^*Br_2$	715	32	36	22/1	4.5
$(C_6H_5)_2Mg + Mg^*Br_2$	715	53	36	14/1	7.0

[a] Corrected to the same time of counting.

complete exchange between the Mg^*Br_2 and R_2Mg was noted in all cases. This exchange is not due to impurities in the "Grignard grade" magnesium used for dilution since deliberate dilution of the tagged magnesium in one of the Mg^{28} runs with the same "Grignard grade" magnesium did not affect the final results. The impurity that caused the exchange apparently lies in the Mg^{25} metal supplied by the Stable Isotopes Division. No attempt was made to find whether one of the major impurities, Ca, Mo, Si, Na or Cu was the agent responsible, since trace impurities of other elements may have been responsible.

Discussion

Fundamentally, the present work indicates that "ethylmagnesium bromide" and probably "phenylmagnesium bromide" contain two different types of magnesium. This is evident from the exchange reactions. The comparison of the Mg^{28} and Mg^{25} runs indicates that when sufficient impurities are present the Mg of the two species exchanges. These impurities are apparently not present in "Grignard grade" magnesium, and we may therefore conclude that the Grignard reagent prepared in the normal manner from RX and Mg also contains two types of Mg, and therefore might be best represented as $R_2Mg \cdot MgX_2$.

The mass balance in the electrolysis cell supports the findings of Evans for the butylmagnesium bromide system. Although the middle compartment is not too good it is much better than Evans, and the general result indicates that for ethyl Grignard: 1. The net migration of magnesium to the anode indicates it is present in the anion as well as the cation. 2. The cathode compartment appears to lose Et in preference to Br, while the anode compartment appears to gain Et in preference to Br. 3. The large amount of material transported in comparison to the amount of Mg plated out indicates that the ions are actually large aggregates, probably involving 2 or 3 molecules.

The radioactivity balance in the cell indicates even more surprising features: 1. The magnesium which plates out at the cathode has its origin in the Et_2Mg. 2. The largest portion of the magnesium which migrates to the anode compartment has its origin in the $MgBr_2$. 3. The gain of activity in the anode compartment is at the expense of both the middle and cathode compartments.

The results indicate that process 3b cannot be responsible for the cathodic discharge, and that therefore ionization 2e is not involved. The discharge does arise from a process similar to 3a, which is related to ionization 2b, regardless of what associations take place after this step. The basic ion is therefore $RMg^{\oplus}$.

The negative ion is not as easy to unravel. It is hoped that work on the conductivity of mixtures of Et_2Mg and $MgBr_2$ now in process will shed some light on the problem of the origin and structure of the negative ion.

Acknowledgments.—The authors wish to acknowledge the support of this work by a Frederick Gardner Cottrell grant from the Research Corporation. They also wish to acknowledge the aid of Mr. Earl Pantier, Westinghouse Research Laboratories; and Dr. R. B. Sutton and the staff of the Carnegie Institute of Technology Synchrocyclotron.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Organic Peroxides. XXI. A Study of the Decomposition of 2,5-Dimethyl-3-hexyn-2,5-Dihydroperoxide[1]

BY NICHOLAS A. MILAS AND JOHN T. NOLAN, JR.[2]

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The thermal, ferrous ion-catalyzed and acid-catalyzed decomposition of 2,5-dimethyl-3-hexyn-2,5-dihydroperoxide has been studied, and in every case an attempt has been made to isolate and identify all the products formed. Tentative-mechanisms have been proposed to account for the products formed in the various decompositions.

The thermal, ferrous ion-catalyzed and acid-catalyzed decomposition of alkyl hydroperoxides containing a single tertiary hydroperoxy group is well known.[3a-d] However, the decomposition of hydroperoxides containing two tertiary hydroperoxy groups separated by an acetylenic linkage[4] is not known. One may raise two questions regarding the decomposition of these peroxides. Would the two hydroperoxy groups decompose simultaneously or consecutively? If free radicals or ions are formed during the decomposition would they react with the acetylenic linkage or would they decompose to form other products? In the hope of contributing to an answer of these questions a study of the decomposition of 2,5-dimethyl-3-hexyn-2,5-dihydroperoxide was undertaken and the results will be described in the present communication.

Thermal Decomposition.—When 2,5-dimethyl-3-hexyn-2,5-dihydroperoxide was heated above its melting point it was found to decompose explo-

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[1] Paper XX, THIS JOURNAL, **77**, 2536 (1955).

[2] From the Ph.D. Thesis of John T. Nolan, Jr., M.I.T., May, 1955.

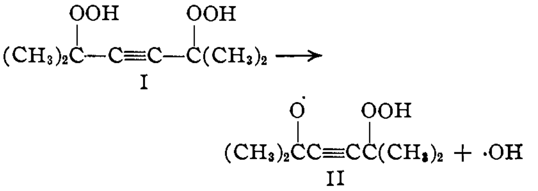
[3] (a) N. A. Milas and D. M. Surgenor, THIS JOURNAL, **68**, 205 (1946); (b) M. S. Kharasch, A. Fono and W. Nudenberg, *J. Org. Chem.*, **16**, 106, 113 (1951); (c) R. J. Orr and H. L. Williams, *Can. J. Chem.*, **30**, 985 (1952); (d) W. S. Wise and G. H. Twigg, *J. Chem. Soc.*, 2172 (1953).

[4] N. A. Milas and O. L. Mageli, THIS JOURNAL, **74**, 1471 (1952).

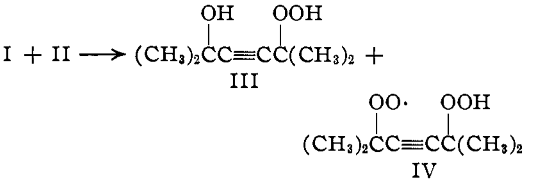
sively liberating a variety of gases and a complex liquid. Analysis of the gaseous products showed the presence of carbon dioxide, carbon monoxide, oxygen, acetylene, ethane and methane. The first two probably were formed through a secondary combustion of the reaction products at elevated temperatures and were not necessarily primary decomposition products. Oxygen is a usual product of the thermal decomposition of tertiary alkyl hydroperoxides.[3a] Acetylene was identified by infrared spectra, combustion analysis and by hydrolysis to acetaldehyde. Methane and ethane were also identified by infrared spectra and by combustion analysis.

Among the non-gaseous products of decomposition were found water, acetone, 2,5-dimethyl-3-hexyn-2,5-diol (VII), 5-methyl-2-keto-3-hexyn-5-ol (VIII) and 2-ketopentyne-3 (XII). The absence of 2,5-diketohexyne-3 as well as the presence of the above products constitutes a strong indication that the two hydroperoxy groups undergo decomposition consecutively rather than simultaneously. Furthermore, the presence in the decomposition products of acetylene and certain of its derivatives shows that the free radicals formed during the decomposition failed to react with the acetylene bonds.

To account for the various compounds produced by the thermal decomposition of 2,5-dimethyl-3-hexyn-2,5-dihydroperoxide these equations are proposed

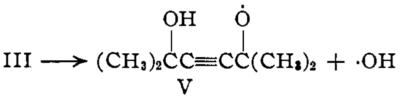


$$\underset{\text{I}}{(CH_3)_2\overset{OOH}{C}-C\equiv C-\overset{OOH}{C}(CH_3)_2} \longrightarrow \underset{\text{II}}{(CH_3)_2\overset{\dot{O}}{C}C\equiv C\overset{OOH}{C}(CH_3)_2} + \cdot OH \qquad (1)$$

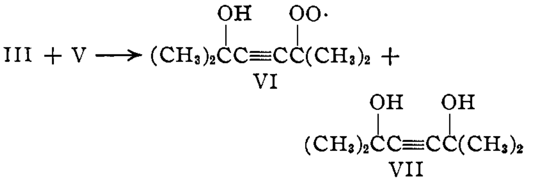


$$\text{I} + \text{II} \longrightarrow \underset{\text{III}}{(CH_3)_2\overset{OH}{C}C\equiv C\overset{OOH}{C}(CH_3)_2} + \underset{\text{IV}}{(CH_3)_2\overset{OO\cdot}{C}C\equiv C\overset{OOH}{C}(CH_3)_2} \qquad (2)$$

$$\text{IV} + \cdot OH \longrightarrow \text{III} + O_2 \qquad (3)$$

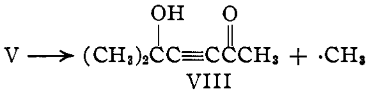


$$\text{III} \longrightarrow \underset{\text{V}}{(CH_3)_2\overset{OH}{C}C\equiv C\overset{\dot{O}}{C}(CH_3)_2} + \cdot OH \qquad (4)$$

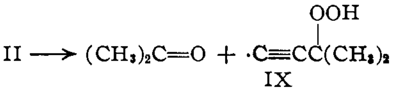


$$\text{III} + \text{V} \longrightarrow \underset{\text{VI}}{(CH_3)_2\overset{OH}{C}C\equiv C\overset{OO\cdot}{C}(CH_3)_2} + \underset{\text{VII}}{(CH_3)_2\overset{OH}{C}C\equiv C\overset{OH}{C}(CH_3)_2} \qquad (5)$$

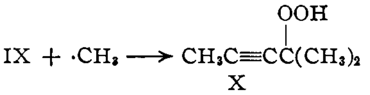
$$\text{VI} + \cdot OH \longrightarrow \text{VII} + O_2 \qquad (6)$$



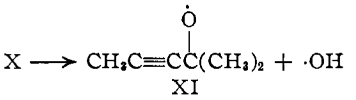
$$\text{V} \longrightarrow \underset{\text{VIII}}{(CH_3)_2\overset{OH}{C}C\equiv C\overset{O}{\overset{\|}{C}}CH_3} + \cdot CH_3 \qquad (7)$$



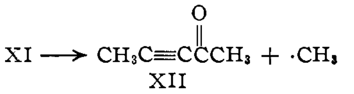
$$\text{II} \longrightarrow (CH_3)_2C{=}O + \underset{\text{IX}}{\cdot C\equiv C\overset{OOH}{C}(CH_3)_2} \qquad (8)$$



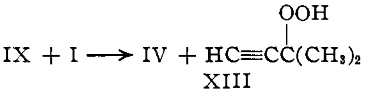
$$\text{IX} + \cdot CH_3 \longrightarrow \underset{\text{X}}{CH_3C\equiv C\overset{OOH}{C}(CH_3)_2} \qquad (9)$$



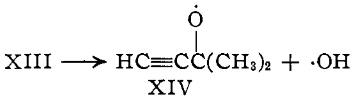
$$\text{X} \longrightarrow \underset{\text{XI}}{CH_3C\equiv C\overset{\dot{O}}{C}(CH_3)_2} + \cdot OH \qquad (10)$$



$$\text{XI} \longrightarrow \underset{\text{XII}}{CH_3C\equiv C\overset{O}{\overset{\|}{C}}CH_3} + \cdot CH_3 \qquad (11)$$



$$\text{IX} + \text{I} \longrightarrow \text{IV} + \underset{\text{XIII}}{HC\equiv C\overset{OOH}{C}(CH_3)_2} \qquad (12)$$



$$\text{XIII} \longrightarrow \underset{\text{XIV}}{HC\equiv C\overset{\dot{O}}{C}(CH_3)_2} + \cdot OH \qquad (13)$$

$$\text{XIV} \longrightarrow \underset{\text{XV}}{HC\equiv C\cdot} + (CH_3)_2C{=}O \qquad (14)$$

$$\text{XV} + \text{I} \longrightarrow \text{IV} + HC\equiv CH \qquad (15)$$

$$\cdot CH_3 + \cdot CH_3 \longrightarrow CH_3CH_3 \qquad (16)$$

Methyl radicals are known to dimerize and form ethane. Methane probably was formed by the abstraction of hydrogen atoms by methyl radicals from either I or III.

Ferrous Ion-catalyzed Decomposition.—Ferrous ions are known to catalyze the decomposition of tertiary alkyl hydroperoxides by a free radical mechanism.[3c,d,5] It also has been found that the products coming from this type of decomposition are somewhat the same as those frequently observed in thermal decompositions. However, experience has shown that the more drastic thermal treatment leads often to more complex mixtures.

When 2,5-dimethyl-3-hexyn-2,5-dihydroperoxide was allowed to decompose in the presence of ferrous ions, a gas was liberated which proved by infrared spectra and by other analytical methods to be a mixture of methane, ethane and oxygen. Neither carbon dioxide nor carbon monoxide was detected in the gaseous mixture indicating that these gases were not the primary products in the thermal decomposition. Acetylene also was absent in the gaseous products.

The main product of the ferrous ion-catalyzed decomposition was found to be 2,5-dimethyl-3-hexyn-2,5-diol (VII). This probably was formed by the same sequence of reactions as in the case of thermal decomposition. The second most abundant product was found to be 5-methyl-2-keto-3-hexyn-5-ol (VIII), the formation of which also accounts for the presence of methane and ethane in the gaseous mixture. Neither 2-keto-pentyne-3 (XII) nor acetylene was found among the decomposition products, thereby eliminating equations 9 to 15 inclusive from consideration in this decomposition. However, since acetone was found among the products of decomposition one of the primary steps must proceed according to equation 8. In addition, a solid product was isolated which analyzed for $C_{11}H_{12}O_3$. It is therefore quite pos-

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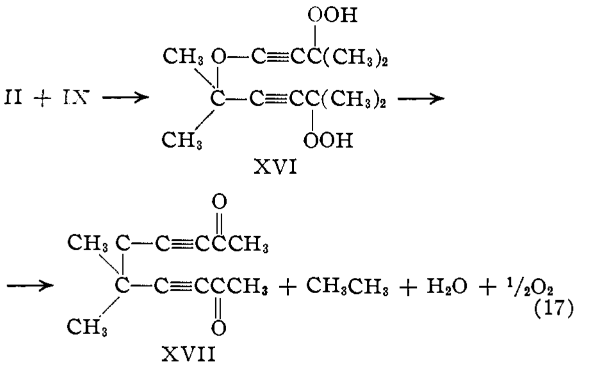
[5] N. A. Milas, R. L. Peeler, Jr., and C. W. Mageli, THIS JOURNAL, 76, 2322 (1954).

sible that the free radical IX could have reacted with the initial decomposition product II in accordance with equation 17.



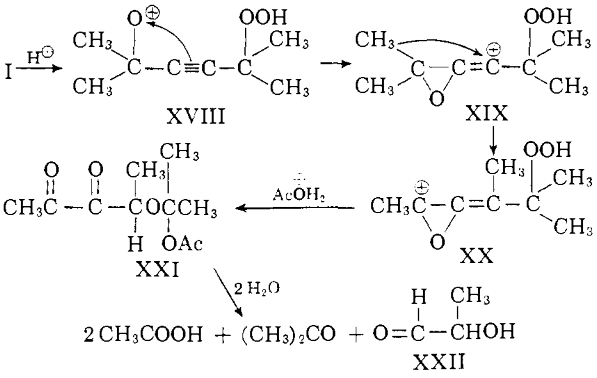
XVI

XVII

(17)

Structure XVII is therefore tentatively suggested for the solid product analyzing for $C_{11}H_{12}O_3$.

Acid-catalyzed Decomposition.—Mineral acids have often been used as catalysts in the study of the decomposition of hydroperoxides by an ionic mechanism. The mechanism proposed by Criegee for a reaction of this type involves the abstraction by the acid of a negative hydroxyl from the hydroperoxy group leaving a positively charged oxygen atom.[6] Such a decomposition usually leads to intramolecular rearrangements and is best illustrated by the decomposition of α-cumyl hydroperoxide[7] in acetic acid using perchloric acid as the catalyst.



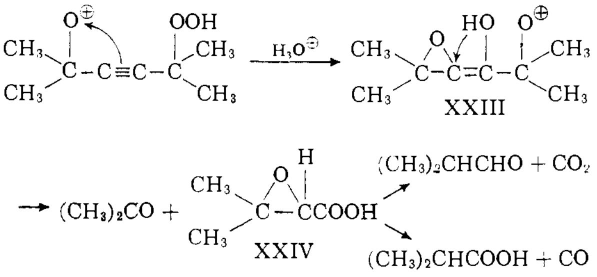
XVIII XIX XX XXI XXII

When 2,5-dimethyl-3-hexyn-2,5-dihydroperoxide was allowed to decompose at 100° in a mixture of glacial acetic and sulfuric acids no glyoxal was isolated indicating that the two hydroperoxy groups did not decompose simultaneously but consecutively. The main identifiable products were methylglyoxal (as bis-2,4-dinitrophenylhydrazone derived from α-hydroxypropionaldehyde), acetone and 4-methyl-4-hydroxypentanone-2, and no gases were evolved during the decomposition. However, when this dihydroperoxide was allowed to decompose at 95–100° in 10% aqueous sulfuric acid, a gas was evolved which was shown to be a 50–50 mixture of carbon monoxide and dioxide. Other products identified in this case were acetone, methylglyoxal (derived from α-hydroxypropionaldehyde), isobutyraldehyde and isobutyric acid. The decomposition in water solution was slow and even after 24 hr. there were still small amounts of peroxide remaining undecomposed. Small amounts of polymeric resinous products were also formed in water as well as in glacial acetic acid.

Owing to the complexity of these reactions, only a tentative explanation may be offered. In glacial acetic acid, the following reactions seem reasonable

The 4-methyl-4-hydroxypentanone-2 is known to form by the condensation of acetone in the presence of sulfuric acid.

In addition to the above path leading to the formation of α-hydroxypropionaldehyde (XXII) which was converted to the bis-2,4-dinitrophenylhydrazone of methylglyoxal, the decomposition in aqueous sulfuric acid solution led to the formation of gaseous products as well as isobutyraldehyde and isobutyric acid. To account for the formation of these products these reactions are proposed



XXIII XXIV

It is well known that glycidic acids of the type of XXIV can, at high temperatures and in the presence of strong acids, decompose to give both carbon monoxide and dioxide.

Experimental

Thermal Decomposition of 2,5-Dimethyl-3-hexyn-2,5-dihydroperoxide (I).—The dihydroperoxide I was prepared and purified according to the procedure of Milas and Mageli.[4] The thermal decomposition of this peroxide was found to proceed with extreme violence if large portions of it were heated slightly above its m.p. (105°). Consequently, it was found necessary to carry out the decomposition with very small samples. This was accomplished by dropping 50-mg. samples into an airtight, upright tube filled with nitrogen gas and heated electrically to 150°. During the decomposition large quantities of gaseous products were liberated and were collected in a graduated buret over slightly acidic water solution. The non-gaseous products were collected in an ice-trap at the bottom of the tube. In a typical experiment 10.35 g. (0.0595 mole) of the peroxide was decomposed at 150°.

The gaseous mixture was first passed through 60% potassium hydroxide to remove the carbon dioxide then through fuming sulfuric acid to remove the acetylene and finally through ammoniacal cuprous chloride to remove the carbon monoxide. The oxygen in the gaseous mixture was determined by absorption in an alkali-pyrogallol solution. The remaining gaseous mixture was identified by infrared spectrum as methane and ethane and the ratio in which they were present by combustion experiments. The acetylene was also identified by infrared spectra as well as by hydrolysis to acetaldehyde with 80% sulfuric acid containing mercuric sulfate. The acetaldehyde was identified by preparing its 2,4-dinitrophenylhydrazone, m.p. 157°. The total volume of the gaseous products, after subtracting that due to carbon dioxide and carbon monoxide, amounted to 870 cc. Of this 167 cc. (0.0070 mole) was acetylene, 83 cc. (0.0035 mole) oxygen, 276 cc. (0.0115 mole) ethane and 344 cc. (0.0143 mole) methane.

The non-gaseous products were condensed in an ice-trap and fractionally distilled. The fraction boiling 50–60° consisted chiefly of acetone, 1 g. (0.0173 mole) identified by its 2,4-dinitrophenylhydrazone, m.p. 126°.

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(6) R. Criegee, *Ann.*, **560**, 127 (1948).

(7) M. S. Kharasch, A. Fono and W. Nudenberg, *J. Org. Chem.*, **15**, 748 (1950).

Anal. Calcd. for $C_9H_{10}N_4O_4$: N, 23.51. Found: N, 32.91.

The fraction boiling about 100° consisted of water and another product the 2,4-dinitrophenylhydrazone of which was isolated and purified by chromatography on silica gel. Analysis of this derivative proved it to be the 2,4-dinitrophenylhydrazone of 2-ketopentyne-3 (XII), m.p. 148°, lit.[8] m.p. 149°.

Anal. Calcd. for $C_{11}H_{10}N_4O_4$: C, 50.40; H, 3.82; N, 21.37. Found: C, 50.44; H, 4.40; N, 21.67.

The residue was distilled under reduced pressure and from the fraction boiling at 60–70° (2 mm.) was isolated a crystalline product (0.272 g., 0.00195 mole) which was identified as 2,5-dimethyl-3-hexyn-2,5-diol (VII), m.p. 95° and mixed m.p. with an authentic sample showed no depression. The oily mother liquor formed a 2,4-dinitrophenylhydrazone, m.p. 146–147°.

Anal. Calcd. for $C_{13}H_{14}N_4O_5$: C, 50.98; H, 4.60; N, 18.27. Found: C, 51.24; H, 4.84; N, 18.23.

The structure of the carbonyl product from which this phenylhydrazone was prepared was established by synthesis and proved to be 5-methyl-2-keto-3-hexyn-5-ol (VIII).

Synthesis of 5-Methyl-2-keto-3-hexyn-5-ol (VIII).—To 14 g. of magnesium in 100 cc. of anhydrous ether was added with stirring 47 g. of ethyl chloride in 100 cc. of ether under an atmosphere of nitrogen. The mixture was refluxed for 2 hours then cooled to 0° and to it was added dropwise 25 g. of 2-methyl-3-butyn-2-ol. The mixture was stirred and heated under reflux for 3 hours then cooled in nitrogen to −78° and to it added slowly with stirring 70 g. of acetic anhydride in 200 cc. of ether. At the end of the addition the mixture was allowed to warm slowly to room temperature then stirred for 3 hours longer. Finally the mixture was hydrolyzed with a saturated solution of ammonium chloride, extracted with ether, dried over magnesium sulfate, filtered and the ether removed. The residue was fractionated under reduced pressure and the fraction boiling at 67–74° (2 mm.) collected; yield 12 g. (30%). The infrared absorption spectrum of this product showed the presence of an hydroxyl group (3.1 μ), a carbonyl conjugated with an unsaturated group (6.07 μ), an acetylene linkage (4.55 μ) and an ester group (5.8 μ). Consequently, this product was believed to be a mixture of 5-methyl-2-keto-3-hexyn-5-ol (VIII) and its acetate. An attempt to hydrolyze the ester portion of the mixture led to condensation which produced mixtures difficult to purify. Therefore the 2,4-dinitrophenylhydrazones of the original mixture were prepared and adsorbed on silica gel. They were eluted with 10% ethyl ether in pentane and the last eluent recrystallized from ethanol; m.p. 145.5–146.5°; mixed m.p. with the same derivative from the thermal decomposition of peroxide I gave a m.p. 145–146°.

Anal. Calcd. for $C_{13}H_{14}N_4O_5$: C, 50.98; H, 4.60: N, 18.27. Found: C, 50.85; H, 4.85; N, 18.31.

Therefore, the synthetic compound and that obtained from the thermal decomposition of I are identical and have the structure 5-methyl-2-keto-3-hexyn-5-ol (VIII).

Ferrous Ion-catalyzed Decomposition of I.—To 5 g. of peroxide I in 20 cc. of water in a three-necked flask equipped with a mercury-sealed stirrer and attached to an airtight system was added 32 g. of ferrous sulfate in 75 cc. of water. The decomposition was rapid and the gaseous products collected amounted to 225 cc. which consisted of oxygen, methane and ethane. Oxygen was absorbed in alkali–pyrogallol solution while methane and ethane were identified by their characteristic infrared spectra. No carbon dioxide, carbon monoxide or unsaturated hydrocarbons were detected in the gaseous products.

The decomposition was repeated with four additional 5-g. samples and the non-gaseous products combined. The iron salts were removed by filtration and the filtrate extracted in a continuous liquid–liquid extractor with ether. The ether extract was dried over magnesium sulfate, filtered and the ether distilled. The residue was fractionated and the fraction boiling at 50–60° was identified as acetone by means of its 2,4-dinitrophenylhydrazone, m.p. 126°. When the residue from this distillation was allowed to cool to room temperature, a solid (9 g.) separated out and was identified as 2,5-dimethyl-3-hexyn-2,5-diol (VII), m.p. 95°, mixed m.p. with an authentic sample 94–95°.

The mother liquor was fractionated under reduced pressure and the fraction boiling at 70° (2 mm.) was identified as 5-methyl-2-keto-3-hexyn-5-ol (VIII). Infrared absorption spectrum showed the presence of an hydroxyl group (3.1 μ), a conjugated carbonyl (6.07 μ) and an acetylenic linkage (4.55 μ).

Anal. Calcd. for $C_7H_{10}O_2$: C, 66.64; H, 7.99. Found: C, 66.78; H, 8.27.

The 2,4-dinitrophenylhydrazone was prepared and found to be identical with the same derivative of a compound obtained from the thermal decomposition of peroxide I, m.p. 146–147°.

Anal. Calcd. for $C_{13}H_{14}N_4O_5$: C, 50.98; H, 4.60; N, 18.27. Found: C, 51.37; H, 4.52; N, 18.32.

The residue from the above distillation was dissolved in ether and precipitated with pentane into a brownish solid. This was dissolved in benzene and chromatographed on a column of acid-washed alumina and the eluate recrystallized several times from ether–pentane mixtures, m.p. 180°.

Anal. Calcd. for $C_{11}H_{12}O_3$: C, 68.70; H, 6.25. Found: C, 68.79; H, 7.08.

To this product was tentatively assigned structure XVII.

Acid-catalyzed Decomposition of I. (a) **In Glacial Acetic Acid.**—To 25 cc. of glacial acetic acid containing 2 g. of 2,5-dimethyl-3-hexyn-2,5-dihydroperoxide was added dropwise in the course of 1 hr. at 100° with stirring (magnetic stirrer), a mixture of 25 cc. of glacial acetic acid and 5 g. of concd. sulfuric acid. No gas was evolved during the decomposition. The mixture became dark to almost black. Heating and stirring were continued for 5 hr. longer, then the mixture cooled to room temperature and diluted with 3 volumes of water. The final mixture was cooled to 0° whereby a polymeric product separated out and was removed by filtration (0.6 g.). The filtrate was treated, at water-bath temperatures, with excess 2,4-dinitrophenylhydrazine reagent. The solid phenylhydrazone which precipitated only after prolonged heating was separated, dried and weighed; 1.7 g. This was extracted several times with hot chloroform and the residue (0.9 g.) recrystallized several times from nitrobenzene and pyridine; m.p. 292–293° dec. Another sample, prepared in this Laboratory by Dr. O. Mageli from a decomposition reaction carried out essentially the same way as above, was recrystallized several times alternately from pyridine and nitrobenzene; m.p. 298–299° dec.; lit., 299–300° dec.,[9] 295° dec.,[10] 288–289° dec.[11] A mixed m.p. with an authentic sample of bis-2,4-dinitrophenylhydrazone prepared from methylglyoxal[12] gave no depression. Mixed m.p. with authentic samples of bis-2,4-dinitrophenylhydrazones of glyoxal and diacetyl gave nearly 20° depression in each case. Several analyses of our derivative also confirmed these results.

Anal. Calcd. for $C_{15}H_{12}N_8O_8$: N, 25.92. Found: N, 25.64, 25.56, 25.78.

The chloroform extracts from the above experiment were combined and the chloroform evaporated. The residue was then separated into methanol-soluble and methanol-insoluble portions. The former was recrystallized several times from hot methanol containing small amounts of water, m.p. 205–206°; lit.[13] m.p. for the 2,4-dinitrophenylhydrazone of 4-methyl-4-hydroxypentanone-2, 202–203°.

Anal. Calcd. for $C_{12}H_{16}N_4O_5$: N, 18.91. Found: N, 18.72.

The 2,4-dinitrophenylhydrazone of acetone was also isolated on several occasions, m.p. 125° (methanol + water); mixed m.p. with an authentic sample gave no depression.

(b) **In Aqueous Sulfuric Acid.**—A mixture of 130 cc. of 10% sulfuric acid and 5 g. (0.0287 mole) of 2,5-dimethyl-3-hexyn-2,5-dihydroperoxide was heated at 80° in an airtight apparatus for 24 hr. and the gas liberated, collected

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[8] E. A. Braude, E. R. H. Jones, F. Sondheimer and J. B. Toogood, *J. Chem. Soc.*, 607 (1949).

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and analyzed. It was found to consist of equal volumes of carbon dioxide (200 cc., 0.0083 mole) and carbon monoxide (200 cc., 0.0083 mole) by means of their absorption in potassium hydroxide and ammoniacal cuprous chloride solutions, respectively.

The solution from the decomposition reaction was filtered to remove a small amount of tarry polymer which could not be identified. Aliquot samples of the filtrate were treated at water-bath temperature with 2,4-dinitrophenylhydrazine reagent whereby an abundant red precipitate was formed only after prolonged heating. This was extracted with hot chloroform as before and the residue recrystallized from nitrobenzene and pyridine; m.p. 292–293°dec.; mixed m.p. with an authentic sample of bis-2,4-dinitrophenylhydrazone of methyl glyoxal gave no depression.

The remaining solution was extracted with ether in a continuous extraction apparatus. The ether extracts were dried over magnesium sulfate, fractionated and the fractions boiling at 40–57° and 58–65° collected and refractionated. From the low boiling fraction acetone was isolated, b.p. 56–57°; 2,4-dinitrophenylhydrazone, m.p. 125°; mixed m.p. with an authentic sample showed no depression.

Anal. Calcd. for $C_9H_{10}N_4O_4$: C, 45.37; H, 4.20; N, 23.53. Found: C, 45.20; H, 4.26; N, 23.50.

The high boiling fraction gave a strong aldehyde test with fuchsine reagent. It was fractionated twice to obtain a fraction of b.p. 63°. A 2,4-dinitrophenylhydrazone was prepared and recrystallized from ethanol-water mixture; m.p. 187°. An authentic sample of this derivative was prepared from isobutyraldehyde and a mixed m.p. taken; there was no depression.

The decomposition was repeated several times using higher temperatures (100°) with essentially the same results. In one experiment the final aqueous sulfuric acid solution was steam distilled and the distillate which was strongly acidic was distilled to determine the Duclaux constants. These corresponded very closely to isobutyric acid.

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[CONTRIBUTION FROM THE ROHM & HAAS CO., REDSTONE ARSENAL RESEARCH DIVISION]

The Preparation and Reactions of β-Chloroethyl- and γ-Chloropropylborane Derivatives

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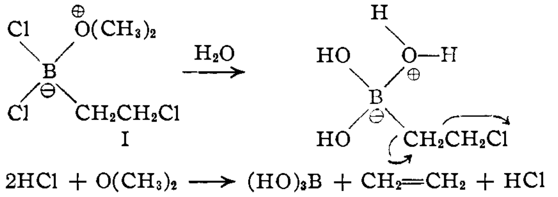
Diborane has been found to add electrophilically to vinyl chloride in ethereal solvents to yield thermally unstable β-chloroethylborane derivatives. Crystalline β-chloroethylboron dichloride dimethyl etherate was obtained in this fashion. Similarly, allyl chloride reacts with diborane in diethyl ether to produce a mixture of tri-(γ-chloropropyl)-borane and di-(γ-chloropropyl)-boron chloride. Treatment of the β-chloroethyl and γ-chloropropyl derivatives with base results in the near quantitative formation of ethylene and cyclopropane, respectively.

Although the preparation and reactions of (chloroalkyl)-silane derivatives have been examined in some detail[1] the corresponding borane derivatives have remained unknown. It was therefore of interest to attempt the preparation of these novel materials by the method of Brown and Subba Rao,[2] a method which provides a direct path to trialkyl boranes by addition of diborane to the corresponding olefins.

Diglyme, tetrahydrofuran and diethyl ether solutions of vinyl chloride were found to react with diborane to produce thermally unstable product mixtures which defied separation. Dimethyl ether solutions of vinyl chloride were later employed in an attempt to simplify the separation of these reaction products. Vinyl chloride in dimethyl ether solution and at −80° smoothly absorbed diborane; however, on warming the product solution to room temperature violent exothermic decomposition often occurred and fires resulted on many occasions. In several instances the products survived this exothermic reaction and high boiling materials were obtained which were too unstable for fractional distillation and were not amenable to clean vacuum line separation at low temperatures. Vacuum line manipulation did allow the separation in very low yield, of a slightly volatile product which solidified and could be recrystallized from diethyl ether at low temperatures. This material melted at 54–56° and gave analyses which were in agreement with the empirical formula $C_4H_{10}BCl_3O$. Treatment of this material with water produced boric acid, hydrogen chloride and ethylene (contaminated with dimethyl ether) in the ratio 1:3:1, respectively. Ethylene was produced quantitatively if the assumption was made that the crystalline material was the dimethyl etherate of β-chloroethylboron dichloride (I). The production of ethylene from



$$+ 2HCl + O(CH_3)_2 \longrightarrow (HO)_3B + CH_2{=}CH_2 + HCl$$

this material is reminiscent of the similar reaction of β-chloroethylalkylchlorosilanes with hydroxide ion observed by Sommer and co-workers.[3] The fact that dimethyl ether was retained in a coördination complex which was recrystallized unchanged from diethyl ether is interesting. Although exchange most likely occurred, the crystalline character of the dimethyl etherate would provide driving force for its separation. The violent exothermic decomposition of the crude reaction product might be interpreted in terms of the reaction sequence

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[1] See P. D. George, M. Prober and J. K. Elliot, *Chem. Revs.*, **56**, 1065 (1956).

[2] H. C. Brown and B. C. Subba Rao, *J. Org. Chem.*, **22**, 1136 (1957).

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