On the basis of the formula proposed for the alcohol compounds of boron fluoride, the ether compounds may be assumed to be the esters of the complex acids; and the ester compounds may similarly be assumed to be the acetoxy derivatives of the same acids. Both of these latter series of compounds should not, according to the above theory, promote catalytic acetal formation since they are incapable of yielding hydrogen ions; such has been found to be the case, and is further substantiated by the low conductivity found for the ethyl ether compound of boron fluoride.

Summary

1. A number of organic compounds of boron fluoride have been prepared, which, in general, contained monomolecular proportions of the constituents, and were dissociated in the vapor phase.

2. These compounds were fuming liquids or solids, difficult to crystallize, decomposed by water and oxygenated solvents, and insoluble in non-oxygenated solvents.

3. The higher aliphatic alcohols were found to form hydrocarbons by the action of boron fluoride.

4. A possible mechanism is formulated for the catalytic formation of acetals from acetylene; and electronic formulas are proposed for some of the organic compounds of boron fluoride.

NOTRE DAME, INDIANA

THE STABILITY OF HEXA-TERTIARY-ALKYLETHINYLETHANES. THE EFFECT OF INCREASING THE WEIGHT OF THE ALKYL GROUPS
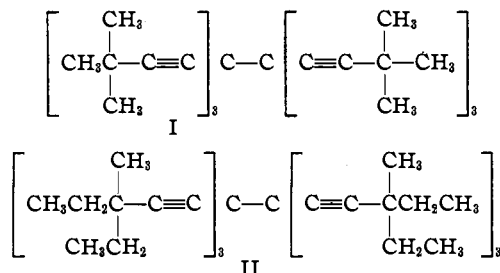
BY D. W. DAVIS AND C. S. MARVEL

Since the discovery[1] that hexa-*tert.*-butylethinylethane (I) had some of the reactions that had previously been thought to be more or less characteristic of the hexa-arylethanes, a considerable amount of work has been done in attempting to determine how this aliphatic molecule could be changed to obtain a substance which would more closely resemble the aryl derivatives. In discussing the causes for the dissociation of ethanes, Lewis[2] has pointed out that weight and unsaturation are the two important properties of the aryl groups which are responsible for causing the dissociation of hexa-arylethanes into free radicals. This suggested that it would be desirable to study a compound in which the size of the tertiary alkyl group attached to the acetylene residue was greater than *tert.*-butyl,

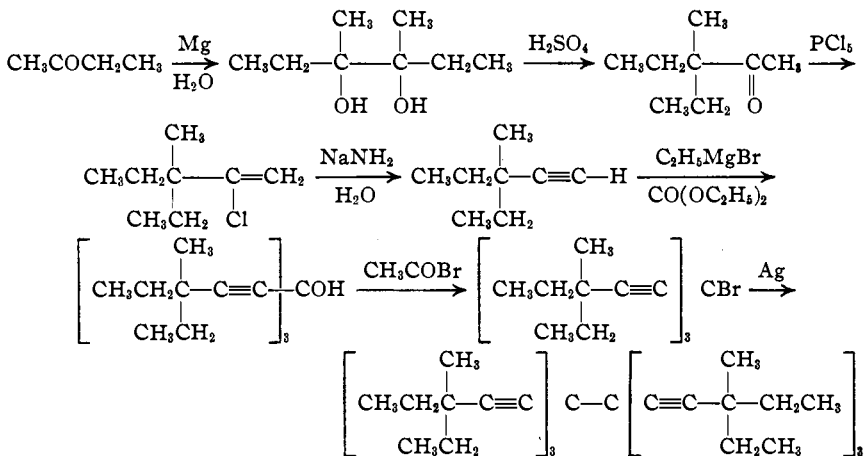[1] Salzberg with Marvel, THIS JOURNAL, **50**, 1737 (1928).

[2] Lewis, *Proc. Nat. Acad. Sci.*, **2**, 586 (1916).

so that a direct comparison could be made between two like compounds which differed only in molecular weight.

The present communication describes the preparation and the properties of hexa-(3-ethyl-3-methylpentinyl-1)-ethane (II) which is strictly homologous with hexa-*tert.*-butylethinylethane.

$$\left[\begin{array}{c} CH_3 \\ | \\ CH_3C-C\equiv C \\ | \\ CH_3 \end{array} \right]_3 C-C \left[\begin{array}{c} CH_3 \\ | \\ C\equiv C-C-CH_3 \\ | \\ CH_3 \end{array} \right]_3$$

I

$$\left[\begin{array}{c} CH_3 \\ | \\ CH_3CH_2C-C\equiv C \\ | \\ CH_3CH_2 \end{array} \right]_3 C-C \left[\begin{array}{c} CH_3 \\ | \\ C\equiv C-CCH_2CH_3 \\ | \\ CH_2CH_3 \end{array} \right]_3$$

II

The new hydrocarbon has been synthesized by the following series of reactions

$$CH_3COCH_2CH_3 \xrightarrow[H_2O]{Mg} \begin{array}{c} CH_3 \quad CH_3 \\ | \quad\quad | \\ CH_3CH_2-C---C-CH_2CH_3 \\ | \quad\quad | \\ OH \quad OH \end{array} \xrightarrow{H_2SO_4} \begin{array}{c} CH_3 \\ | \\ CH_3CH_2C---CCH_3 \\ | \quad\quad \| \\ CH_3CH_2 \quad O \end{array} \xrightarrow{PCl_5}$$

$$\begin{array}{c} CH_3 \\ | \\ CH_3CH_2C---C=CH_2 \\ | \quad\quad | \\ CH_3CH_2 \quad Cl \end{array} \xrightarrow[H_2O]{NaNH_2} \begin{array}{c} CH_3 \\ | \\ CH_3CH_2C-C\equiv C-H \\ | \\ CH_3CH_2 \end{array} \xrightarrow[CO(OC_2H_5)_2]{C_2H_5MgBr}$$

$$\left[\begin{array}{c} CH_3 \\ | \\ CH_3CH_2C-C\equiv C \\ | \\ CH_3CH_2 \end{array} \right]_3 -COH \xrightarrow{CH_3COBr} \left[\begin{array}{c} CH_3 \\ | \\ CH_3CH_2C-C\equiv C \\ | \\ CH_3CH_2 \end{array} \right]_3 CBr \xrightarrow{Ag}$$

$$\left[\begin{array}{c} CH_3 \\ | \\ CH_3CH_2C-C\equiv C \\ | \\ CH_3CH_2 \end{array} \right]_3 C-C \left[\begin{array}{c} CH_3 \\ | \\ C\equiv C-C-CH_2CH_3 \\ | \\ CH_2CH_3 \end{array} \right]_3$$

The reduction of methyl ethyl ketone was accomplished according to the method which Adams and Adams have described[3] for the reduction of acetone to pinacol hydrate. Only the liquid modification of the gycol was isolated. The rearrangement of the glycol to the ketone was accomplished according to the procedure of Nybergh.[4] He has shown that the methyl ketone is obtained to the extent of 80%. No attempt was made to separate the isomeric ethyl ketone as it was easier to separate the isomeric product when the acetylene was obtained. The isomeric ketone gave the acetylene $CH_3CH_2C(CH_3)_2---C\equiv CCH_3$ which did not form

³ Adams and Adams, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1925, Vol. II, p. 87.

⁴ Nybergh, *Ber.*, **55**, 1960 (1922).

a salt with sodamide and hence distilled out of the reaction mixture before hydrolysis. If any of this isomeric acetylene had remained in the reaction mixture it would have been lost in the next operation as it would not have formed a Grignard reagent.

The methyl ketone was converted to 3-ethyl-3-methyl-2-chloropentene-1 by the usual method of heating with phosphorus pentachloride. The acetylene was obtained from this chloro compound by the action of sodamide, following the general directions of Lespieau and Bourguel[5] for the preparation of 3-cyclohexylpropine-1 from 3-cyclohexyl-2-bromopropene-1. The tri-acetylenic carbinol was prepared by the general method which has been used for related compounds in this series.[1] The bromide did not crystallize and decomposed to tarry materials when an attempt was made to distil it. Accordingly the ethane was prepared from the crude reaction product of the carbinol with acetyl bromide.

The preparation of the ethane was first attempted in the presence of air. However, preliminary experiments indicated that a pure hydrocarbon was not produced. When the reaction was carried out in an inert atmosphere the pure hydrocarbon was obtained. The reactions of the new compound were strictly analogous to those of hexa-*tert.*-butylethinylethane but the ethane linkage was noticeably weaker, as indicated by the three characteristic reactions: cleavage with alkali metals, oxidation by free oxygen and rearrangement under the influence of heat. The new ethane was cleaved very rapidly with liquid sodium–potassium alloy and 40% sodium amalgam as indicated by the development of color. It was cleaved also by 1% sodium amalgam at a more rapid rate than was hexa-*tert.*-butylethinylethane.

When the pure hydrocarbon was dissolved in alcohol and the solution was shaken in an atmosphere of oxygen, the gas was absorbed rapidly at first. When absorption slowed down it was found that the reaction flask contained carbon dioxide. When this was removed further absorption of oxygen was noted. It was not possible to isolate a definite peroxide. Oxygen-containing material was obtained but it seemed to be a mixture of the hydrocarbon with an unstable peroxide and careful purification of this product always resulted in the isolation of hydrocarbon material. If the absorption of oxygen was carried out over an extended period, it was possible to isolate from the reaction mixture diethylmethylacetic acid, thus showing that oxidation had broken the compound into smaller units. That the oxygen absorption is really due to a weak ethane linkage in the molecule and not to an unstable triple bond was demonstrated by subjecting the corresponding carbinol to the same treatment. No oxygen was absorbed by the carbinol. None of the other acetylenic ethanes which have been described previously have shown this tendency to oxidize rapidly.

[5] Lespieau and Bourguel, "Organic Syntheses," 1926, Vol. VI, p. 26.

The ethane was quite easily affected by heat. When an alcoholic solution was boiled for one hour in an inert atmosphere, a rearrangement occurred and a new isomeric hydrocarbon was obtained. This rearrangement proceeded more rapidly than it did with the lower homolog. The nature of the rearrangement of the hexa-acetylenic ethanes is not entirely clear but appears to be a rearrangement of the Meyer and Schuster[6] type with the formation of a double allene structure. This will be the subject of a subsequent communication.

From a consideration of the behavior of the new ethane toward the three agents just described, there can be no doubt that it has a central ethane carbon–carbon linkage that is less stable than the one which is present in the lower homolog. The difference between the two hydrocarbons is the twelve extra CH_2 groups in the higher homolog, and since the two molecules are of almost exactly analogous structure, the difference in stability must be due to the added weight in the alkyl groups.

It is of interest to consider in this connection the properties of hexa-ω-*tert.*-butylpropinylethane[7] (III) which is intermediate in the weight of its alkyl group between hexa-*tert.*-butylethinylethane (I) and hexa-(3-ethyl-3-methylpentinyl-1)-ethane (II). The propinyl derivative

$$((CH_3)_3CCH_2-C\equiv C)_3C-C(C\equiv C-CH_2C(CH_3)_3)_3$$
III
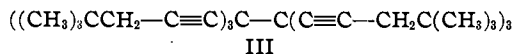
was of slightly greater stability toward alkali metals than either of the other derivatives and it did not absorb oxygen from the air. However, it more readily changed to tarry products on standing than did the other two ethanes which contained tertiary alkyl groups. These differences were undoubtedly due to the fact that a primary alkyl group was attached to the acetylenic residue in the propinyl derivative.

It is of some interest to note that the solutions of the alkali metal alkyls obtained by the cleavage of this ethane varied in color from greenish- to reddish-brown. The differences in color were probably due to different side reactions. The reddish colors are apparently due to the products of the side reactions as more tarry materials and less acid were isolated from the more deeply colored solutions. The best yields of acid were obtained by the action of carbon dioxide on the lighter colored solutions.

Experimental

3,4-Dimethylhexanediol-3,4.—In a 5-liter, three-necked, round-bottomed flask fitted with a 1-liter separatory funnel and an efficient reflux condenser of large bore, were placed 79 g. of magnesium turnings and 800 cc. of dry benzene. The mixture was heated on a steam cone until the benzene was boiling vigorously and then from the separatory funnel was added about 25–50 cc. of a solution of 90 g. of mercuric chloride in 615 cc. of dry methyl ethyl ketone. When the reaction had started, as indicated

[6] Meyer and Schuster, *Ber.*, **55**, 819 (1922).

[7] Ozanne and Marvel, THIS JOURNAL, **52**, 5267 (1930).

by the gray murky appearance of the solution, the flask was removed from the steam cone and placed under the water tap. Then the ketone was added as rapidly as possible without loss of material through the reflux condenser. When this solution of the mercuric chloride in the ketone had been added and the violent reaction had subsided, a second solution of 308 cc. of methyl ethyl ketone in 200 cc. of dry benzene was added at such a rate as to keep the reaction mixture refluxing gently from the heat of the reaction. When all of the ketone had been added, the reaction flask was again placed on the steam cone and the mixture was heated for five or six hours.

To the thick and rather sirupy reaction mixture, 200 cc. of water was added and the mixture was heated for about two hours longer. During this period the mixture was shaken vigorously from time to time in order to break up the lumps of magnesium hydroxide. When the benzene layer had become clear, the mixture was cooled and the benzene layer was decanted. The water layer was refluxed with 200–300 cc. of benzene and after about an hour this benzene layer was decanted and added to the first portion. Sometimes it was necessary to filter a part of the decanted solution in order to get a clear solution. The benzene solution was evaporated and the residue was fractionally distilled under reduced pressure through a good column. The yield of glycol boiling at 100–110° at 20–22 mm. was 100–190 g. (21–40% of the theoretical amount).

The variation in yield seemed to be due to variations in the moisture present in reagents used. When the benzene was dried by distillation and the ketone was dried over anhydrous magnesium sulfate the best yields were obtained. When moisture was present the reaction was slow in starting and on distillation of the final product finely divided mercury usually appeared in the glycol distillate, thus showing that an organic mercury compound had formed and decomposed in the process of distillation.

3-Ethyl-3-methylpentanone-2.—The rearrangement of the glycol was carried out by the procedure of Nybergh.[4] The product was separated from the diluted acid by distillation with steam. Using 100 g. of the glycol and 800 cc. of concentrated sulfuric acid, the yield of mixed ketones boiling at 150–158° was 30–60 g. (34–68% of the theoretical amount). Nybergh has shown that this contains 80% of the methyl ketone. No attempt was made to separate the isomeric ethyl ketone.

3-Ethyl-3-methyl-2-chloropentene-1.—In a 2-liter three-necked flask fitted with a mechanical stirrer, a reflux condenser and a separatory funnel, was placed 470 g. of phosphorus pentachloride. The flask was surrounded by cracked ice and 286 g. of the mixed ketones from the above reaction was added over a period of one to two hours. The mixture was stirred during this addition. The mixture gradually liquefied and became deep purple in color. After the ketone was added, the ice-bath was removed and the mixture was allowed to come to room temperature. Considerable heat was given off and hydrogen chloride was evolved copiously. This was led off through the condenser to a water trap. The mixture was stirred for about an hour at room temperature and then for one hour on the steam-bath. Another 50 g. of phosphorus pentachloride was then added and the mixture was heated and stirred for two hours longer.

After cooling, the contents of the flask were poured into about 400 cc. of water. The mixture was cooled slightly and stirred while the phosphorus oxychloride and excess phosphorus pentachloride were thus hydrolyzed. An additional liter of water was added and the chloride was distilled with steam. The upper layer of the distillate was separated, washed with dilute sodium carbonate solution, dried over anhydrous magnesium sulfate and distilled. The fraction boiling at 52–70° at 19 mm. was collected. The yield was 214 g. (65% of the theoretical amount). This material was sufficiently pure for the preparation of the acetylene.

For analysis a sample was redistilled. It was then a colorless mobile liquid with a rather pleasant odor: b. p. 53° (20 mm.); 147° (743 mm.); d_4^{20} 0.9147; n_D^{25} 1.4450.

Anal. (Parr bomb). Subs., 0.3421, 0.3332: 23.36, 22.88, cc. of 0.0997 N AgNO$_3$. Calcd. for C$_6$H$_{15}$Cl: Cl, 24.19. Found: Cl, 24.13, 24.27.

This product undoubtedly contained some of the isomeric 4,4-dimethyl-3-chloro-hexene-2 which formed from the 4,4-dimethylhexanone-3 present in the starting material.

3-Ethyl-3-methylpentine-1.—In a 2-liter three-necked flask fitted with a mechanical stirrer, a reflux condenser and a separatory funnel was placed 120 g. of finely ground sodamide suspended in 450 cc. of high-boiling mineral oil. The sodamide was ground under a part of the oil to give a thick paste. It was very important to have the sodamide in fine particles. The reaction mixture was heated in an oil-bath at 160–165° and 146.5 g. of the above chloro compound was added from the separatory funnel with efficient stirring over a period of about two hours. The stirring was continued for three to four hours while the temperature of the oil-bath was maintained at 160–175° and then the mixture was heated overnight at a slightly lower temperature and finally again at 160–175° for another three hours. Stirring was continued through the heating period. Ammonia was slowly evolved during the reaction and was absorbed in a water trap. Careful cooling of the escaping gases gave small amounts (2–3 g. per run) of what was apparently the isomeric acetylene, 4,4-dimethylhexine-2.

Next the reaction mixture was cooled and slowly poured onto about one kilo of cracked ice with good stirring. After the excess sodamide was entirely decomposed, the aqueous layer was removed by means of a siphon. The remaining oily layer was washed with dilute sulfuric acid. It was usually found advisable to allow the oil to stand in a separatory funnel for about two days in order that all of the water could be drawn off the mixture. Considerable insoluble tar was formed in some runs and this was usually removed by decantation before the final settling to remove the water. The oil solution was distilled first at atmospheric pressure until most of the acetylene was collected. Then the pressure was lowered gradually and heating continued until toward the end the pressure was reduced to 8 mm. and the temperature raised to 175°. This was found necessary in order to remove all of the acetylene from the oil solution. If water was present during the distillation, bumping and foaming were very troublesome. The main part of the distillate was always removed from the receiver before the pressure was reduced below 100 mm. and the receiver was then cooled in an ice–hydrochloric acid mixture. The latter part of the distillate was recovered chloro compound.

The distillate was refractionated and the portion boiling at 98–115° amounted to about 50 g. (45% of the theoretical amount). This product was pure enough for use in the next step in the synthesis.

A small sample was purified and then had the following properties: b. p. 98–100° (745 mm.); d_4^{20} 0.7360; n_D^{20} 1.4102.

For analysis the silver derivative was prepared. To a solution of 2.3 g. of silver nitrate in 25 cc. of water was added dilute potassium hydroxide until no further precipitate formed. Aqueous ammonia was added until the precipitate just redissolved. This solution was added to a solution of 2 cc. of the acetylene in about 40 cc. of ethyl alcohol. The white gummy precipitate which formed after the addition of 50 cc. of water was collected on a Hirsch funnel and washed with water. It was dried and recrystallized from 25–30 cc. of boiling petroleum ether (b. p. 65–110°). The silver salt darkened at 167° and melted at 191.5°.

Anal. Subs., 0.2012, 0.2040, 0.2111: Ag, 0.1002, 0.0997, 0.1064. Calcd. for C$_8$H$_{13}$Ag: Ag, 49.74. Found: Ag, 49.80, 48.87, 50.40.

The mercury derivative prepared by the method of Johnson and McEwen[8] did not crystallize.

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[8] Johnson and McEwen, THIS JOURNAL, **48**, 469 (1926).

Tri-(3-ethyl-3-methylpentinyl-1)-carbinol.—In a 200-cc., three-necked flask, fitted with a mechanical stirrer, a separatory funnel and a reflux condenser was placed 96 cc. of 3.14 N ethylmagnesium bromide solution in ether. During a period of twelve hours, 33 g. of the acetylene was added from the separatory funnel. The mixture was stirred during the addition of the acetylene and then for about another twelve hours. The reaction mixture was now warmed for about two hours at the boiling point of ether. When the ethane evolved was collected it was found that the reaction was about 95% complete under these conditions.

Twelve cc. of diethyl carbonate was then placed in the separatory funnel and about one-half was added to the reaction mixture over a period of about three hours. The remainder was diluted with 20 cc. of dry ether and this was slowly added during the next twenty-four hours. Stirring and warming to gentle refluxing was maintained during this period and for about ten hours longer. The reaction mixture was hydrolyzed by pouring it into about 500 cc. of strong ammonium chloride solution. Any undissolved magnesium hydroxide was brought into solution by the addition of dilute hydrochloric acid. The ether solution was separated and the aqueous portion was extracted with more ether. The ether solution was dried over anhydrous magnesium sulfate, filtered and distilled. After the ether was removed the carbinol boiled at 127–136° (0.5 mm.). There was a small low-boiling portion. The yield of pure product was about 30 g. (84% of the theoretical amount).

A carefully purified sample had the following properties: b. p. 130–133° (0.5 mm.); d_4^{20} 0.8607; n_D^{20} 1.4690.

Anal. Subs., 0.1758: CO_2, 0.5428, H_2O, 0.1776. Calcd. for $C_{25}H_{40}O$: C, 84.19; H, 11.31. Found: C, 84.21; H, 11.30.

Tri-(3-ethyl-3-methylpentinyl-1)-bromomethane.—A solution of 10 g. of the carbinol in 50 cc. of dry petroleum ether (b. p. 25–65°) was treated with 2.38 cc. of acetyl bromide. The acetyl bromide was added slowly from a graduated 1-cc. pipette. The flask containing the mixture was stoppered and the flask placed near a light bulb so that the temperature was maintained at 40–45° for about one and one-half hours. The solution was then washed with a solution of 3 g. of sodium bicarbonate in 50 cc. of water in two successive portions. When effervescence had ceased, the aqueous solution was removed to avoid hydrolysis of the bromide. The petroleum ether solution was then washed twice with water and finally dried over anhydrous magnesium sulfate and filtered. The solvent was removed by evaporation under reduced pressure at ordinary temperatures.

Attempts to crystallize the bromide failed. When distilled it decomposed giving tarry products. Hence the product prepared in this manner was used in the subsequent experiments.

Hexa-(3-ethyl-3-methylpentinyl-1)-ethane.—In flask 1 of the apparatus shown in Fig. 1 was placed the bromide prepared from 10 g. of the carbinol. The bromide was dissolved in 40 cc. of dry ether and the air was swept out of the flask with a stream of purified nitrogen. Six grams of molecular silver was added and the ground-glass connection at 2 was put in place and sealed with "picene." All air was removed by applying reduced pressure at 5 and allowing the ether to boil vigorously for a short time. Dry nitrogen was then admitted to make the pressure approximately equal to that of the surrounding atmosphere so that there would be less tendency for leaks to develop. The stopcock 4 was then closed and the mixture was gently shaken for fifty to sixty hours. Preliminary experiments showed that the bromine was removed to the extent of over 90% in this time.

When the ethane had been formed, flask 6 was attached at 5, sealed at the glass joint with "picene" and evacuated to about 1 mm. The stopcock 4 was opened be-

tween flasks 1 and 6 and the ether solution of the ethane filtered through the porous alundum plate 3. To insure complete transfer of the ethane, some ether was distilled from flask 6 back to flask 1 and again filtered into flask 6. The stopcock 4 was closed and flask 1 was removed from the apparatus. Most of the ether was removed from the ethane solution in flask 6 by applying suction at stopcock 10. About 40 cc. of absolute alcohol was then introduced from the separatory funnel 11. The ethane separated from solution as fine white crystals. After thoroughly cooling the mixture

in ice and salt, flask 8 was connected at stopcock 7 and the solution was filtered by applying suction at stopcock 9. To dry the crystals of ethane a current of dry nitrogen was admitted at stopcock 10. The product was purified by introducing an additional 40 cc. of ethyl alcohol through stopcock 7 and repeating the process of filtration. Heat could not be used to insure complete solution of the ethane as it caused rearrangement as shown below. The entire process of washing with alcohol and filtering the solution was repeated a second and third time.

After the purification was complete and the product was dry it could be removed through the opening 13 by removing the rubber stopper. The yield was 4.8 g. (50% of the theoretical amount based on the carbinol).

Fig. 1.

The product was free from halogen. It melted rather sharply at various temperatures from 122 to 127° depending on the rate of heating due to rearrangement at varying rates. On a Maquenne block it melted at 195°.

Anal. Subs., 0.1556, 0.1504: CO_2, 0.4974, 0.4813; H_2O, 0.1591, 0.1548. Calcd. for $C_{50}H_{78}$: C, 88.41; H, 11.59. Found: C, 87.18, 87.28; H, 11.44, 11.52. *Mol. wt.* (cryoscopic in benzene). Subs., 0.4007; benzene, 21.95; Δt, 0.140°; constant for benzene, 5120. Calcd. for $C_{50}H_{78}$: mol. wt., 678.6. Found: 667.

Oxidation of Hexa-(3-ethyl-3-methylpentinyl-1)-ethane with Free Oxygen

Preliminary Experiment.—Preliminary experiments using solutions of the ethane in alcohol and ether showed that oxygen was absorbed fairly rapidly and that the amount taken up was greater than that required for the formation of a peroxide. One typical case may be cited. A solution of the ethane was prepared by converting 3 g. of carbinol to the bromide, dissolving this in 15 cc. of dry ether and shaking with 2 g. of molecular silver. Without separating the silver and silver bromide this solution was connected to a gas buret and shaken mechanically to facilitate oxygen absorption. The absorption of oxygen is shown in Fig. 2.

Several experiments gave results of this general nature. The rates of oxygen absorption in different experiments were not duplicated exactly as no serious attempt was made to standardize the conditions. Carbon dioxide was formed by the oxidation of the ethane and this prevented any easy accurate measure of the oxygen taken up by the solution.
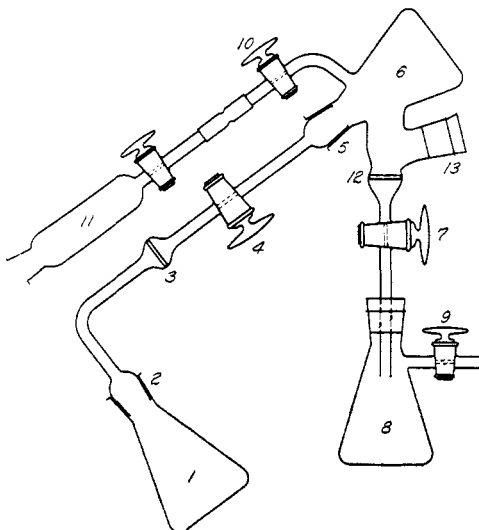
Attempts to Isolate Peroxide.—In an attempt to isolate a peroxide, 1 g. of crystalline ethane was dissolved in 25 cc. of absolute alcohol and 5 cc. of absolute ether. This solution was shaken in an atmosphere of oxygen for about five hours when it had absorbed the theoretical amount (38.9 cc. at 25° and 747 mm.) for the formation of a peroxide. The solution was then evaporated and cooled. About 0.5 g. of material was obtained. This material showed approximately the same behavior as the ethane when an attempt was made to determine its melting point. When a sample was dipped in a bath at 130° and the temperature of the bath raised at the rate of 2–3° per minute
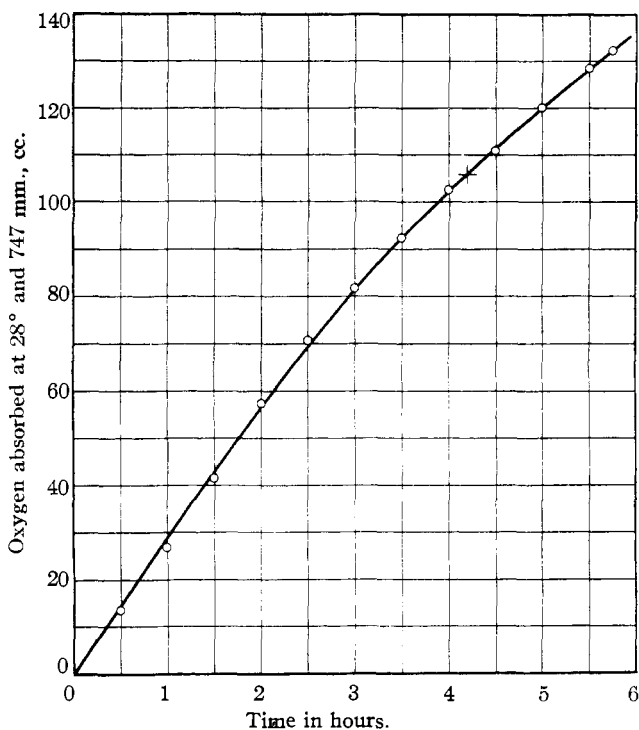

Fig. 2.—Absorption of oxygen by an ether solution of the ethane. The point × on the curve represents the theoretical value for peroxide formation.

it melted sharply at 133.5–134°. If a sample was put in the bath at room temperature and the bath heated at the rate of about 5° per minute it melted at 137–138°. On a Maquenne block, it melted at about 195° as did the ethane. Analysis of this product showed that it was not pure hydrocarbon but neither was it a pure peroxide.

Anal.   Subs., 0.1971: CO_2, 0.6319; H_2O, 0.1998.   Calcd. for $C_{50}H_{78}$:   C, 88.41; H, 11.59.   Calcd. for $C_{50}H_{78}O_2$:   C, 84.43;   H, 11.06.   Found: C, 87.44;   H, 11.34.

Continued Oxidation with Oxygen.—In one case the pure ethane was allowed to absorb as much oxygen as it would take up in order to determine what oxidation products were formed. A solution of 1 g. of the crystalline ethane was prepared as above and shaken in an atmosphere of oxygen for two weeks. After seven days the gases in the flask were removed and found to be very rich in carbon dioxide. This was done again

after the eleventh day.   The rate of absorption of oxygen increased after the removal of the accumulated carbon dioxide.   Figure 3 shows the amount and rate of absorption which was observed.

During this oxidation experiment the color of the solution changed from light yellow to a deep orange.   After two weeks the solvent was evaporated.   The residue was dissolved in ether and extracted with dilute sodium hydroxide solution.   Acidification of the alkaline extract gave a few drops of an oily acid.   This was carefully distilled and at about 170° two drops of viscous yellow oil came over.   Treatment with *p*-toluidine as described in a later experiment gave a crystalline *p*-toluidide which melted at 111–112°.
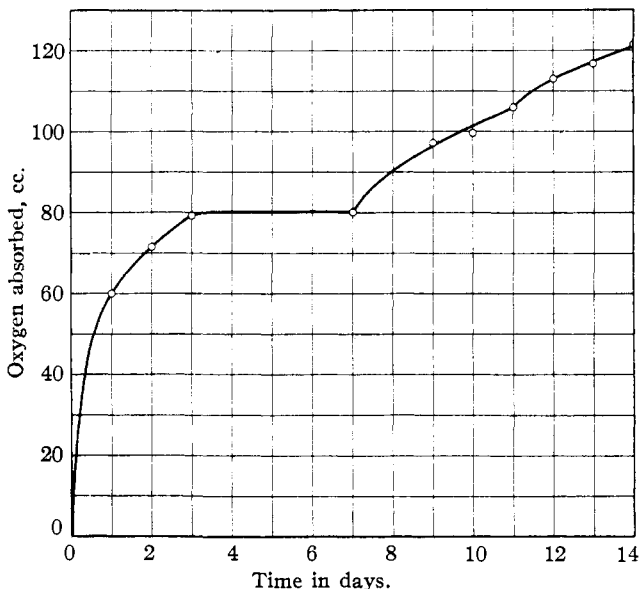
Fig. 3.—Absorption of oxygen by an ether solution
of 1 g. of pure ethane.

When three grams of ethane was similarly oxidized, 200 cc. of oxygen was absorbed in a week.   This yielded 0.5 g. of acidic substance boiling at 198–205°.   A part of this material was converted to the *p*-toluidide as described below.   The derivative melted at 113.5–114°.   A sample of this amide was mixed with the *p*-toluidide of known diethylmethylacetic acid which melted at the same temperature.   The melting point of the mixed sample was 113–114°.

Diethylmethylacet-*p*-toluidide.—Diethylmethylacetic acid was synthesized from diethylmethylcarbinol.   The chloride was prepared according to the method described by Norris and Olmsted[9] for *tert.*-butyl chloride.   The yield was 76% of the theoretical amount.   The desired acid was prepared from the chloride through the Grignard reaction by the method described by Puntambeker and Zoellner[10] for trimethylacetic acid.   The yield was 27% of the theoretical amount.   The *p*-toluidide was prepared by converting 1 g. of the acid to the acid chloride by warming it for about ten minutes

[9] Norris and Olmsted, "Organic Syntheses," 1928, Vol. VIII, p. 50.
[10] Puntambeker and Zoellner, *ibid.*, p. 104.

with 1 cc. of thionyl chloride. The excess thionyl chloride was distilled and the residual acid chloride was treated with 0.82 g. of p-toluidine. The product was thoroughly washed with hot water to remove the p-toluidine hydrochloride and then crystallized from hot 80% alcohol. The yield of product was 0.5 g.; m. p. 113.5–114°. Further crystallization did not change the melting point.

Anal. (Kjeldahl). Subs., 0.3012: 15.95 cc. of 0.0894 N H_2SO_4. Calcd. for $C_{14}H_{21}ON$: N, 6.39. Found: N, 6.63.

Preparation of Tri-(3-ethyl-3-methylpentinyl-1)-acetic Acid.—A solution of the ethane in dry ether was shaken with potassium–sodium alloy or liquid sodium amalgam. The solution developed a green to red-brown color as the metal alkyl was formed by cleavage of the ethane. Dry carbon dioxide was then passed into the solution for a half hour. The color was dispelled almost immediately. The ether solution was decanted from the residual metal, which was then washed with two portions of dry ether and the washings added to the main portion. Alcohol and then water were carefully added to the ether solution. The aqueous layer was acidified with an excess of dilute hydrochloric acid which was then shaken with the ether solution until the whole was acidic. The ether solution was separated and the ether evaporated. Considerable red tarry material was present in the semi-solid acid residue. One recrystallization from petroleum ether (b. p. 65–110°) gave the "crude acid" which was weighed to determine the approximate yield. Attempts to isolate the acid by extraction from the ether solution with aqueous alkali were unsuccessful.

Several such cleavage experiments are described below. The crude acid from these experiments was further purified by recrystallization from petroleum ether (b. p. 65–110°). The acid crystallized in small white clusters of needles and melted at 171–174° (corr.).

Neutral equivalent. Subs., 0.2009: 12.17 cc. of 0.0422 N NaOH. Calcd. for $C_{26}H_{40}O_2$: 384.3. Found: 391.3. *Anal.* Subs., 0.1341, 0.1328: CO_2, 0.3972, 0.3931; H_2O, 0.1242, 0.1240. Calcd. for $C_{26}H_{40}O_2$: C, 81.18; H, 10.49. Found: C, 80.78, 80.73; H, 10.37, 10.45.

Cleavage of the Ethane by Alkali Metals

By Potassium–Sodium Alloy.—A solution of 0.7 g. of ethane in 25 cc. of dry ether was shaken with 3 cc. of potassium–sodium (10/4) alloy for one hour. The solution was distinctly red after shaking for one minute. The color deepened to red-brown in about five minutes and showed little further change at the end of one hour. The solution was then treated with carbon dioxide and the acid isolated as described above. The yield of crude acid was 0.15 g. (19% of the theoretical amount).

When the ethane solution was shaken with the alloy for eleven hours there was so much tarry material in the product that no acid could be isolated.

By 40% Sodium Amalgam.—A solution of 0.7 g. of ethane in 50 cc. of dry ether was shaken with 10 cc. of 40% sodium amalgam for thirty-five hours. The solution was of a light green color after shaking for forty-five minutes. After two hours it was deep green in color and showed little further change in color at the end of thirty-five hours. Carbon dioxide dispelled the color and the yield of crude acid obtained as above was 0.5 g. (63% of the theoretical amount).

By 1% Sodium Amalgam.—A solution of 0.7 g. of ethane in 50 cc. of dry ether was shaken with 10 cc. of 1% sodium amalgam for sixty to seventy hours. The solution was distinctly green in color after shaking for twenty-four hours. At the end of thirty-six hours a trace of yellow or red appeared to be present with the green color. The solution showed little further change in color at the end of the experiment. Carbon dioxide dispelled most of the color and the acid was isolated as above. The concen-

trated ether solution was red in color. The crude acid weighed 0.3 g. (38% of the theoretical amount).

Preparation of the Rearranged Hydrocarbon.—A solution of 0.5 g. of the ethane in 15 cc. of alcohol was heated to boiling in an atmosphere of nitrogen for one hour. Concentration and cooling of the solution yielded 0.25 g. of white crystals melting at 72–76°. When further purified by recrystallization from methyl alcohol this hydrocarbon melted at 82.3–83° (corr.).

Mol. wt. (Rast's Method[11]). Subs., 0.0069; camphor, 0.0218; Δt, 19.07° (average calcd. for mean f. p. and mean m. p. for five observations); constant for camphor: 39.7. Calcd. for $C_{50}H_{78}$: mol. wt., 678.6. Found: 658.9. *Anal.* Subs., 0.0979: CO_2, 0.3155; H_2O, 0.1016. Calcd. for $C_{50}H_{78}$: C, 88.41; H, 11.59. Found: C, 87.89; H, 11.61.

Summary

1. Hexa-(3-ethyl-3-methylpentinyl-1)-ethane has been synthesized.

2. This ethane has been shown to contain a weaker central ethane linkage than hexa-*tert.*-butylethinylethane by comparing their stability toward oxygen, ease of cleavage with alkali metals and tendency toward rearrangement.

3. It is thought that the decrease in stability is due to increasing the molecular weight of the alkyl group.

URBANA, ILLINOIS

COBALT COMPLEXES OF CYSTEINE

BY MAXWELL P. SCHUBERT

The necessity of a more thorough working out of the chemistry of the heavy metal internal complexes of thiol acids arises out of the great interest shown lately in the catalytic oxidation by iron salts of thiol acids to the corresponding disulfide acids. The beginning of such a purely descriptive chemical study was made with cobalt and thioglycolic acid.[1] The study has now been extended and in this paper will be described the preparation and properties of complexes of cobalt and cysteine.

In the case of cobalt and thioglycolic acid only one type of complex could be found, of which several derivatives were prepared in crystalline form. The complex nucleus in these compounds contains two thioglycolic acid radicals for each cobalt atom and is at an oxidation level corresponding to cobalti bisthioglycolate. The situation with cobalt and cysteine was soon found to be more complicated as crystalline complexes were prepared containing cobalt and cysteine in the ratios one to one, one to

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[11] Rast, *Ber.*, **55**, 1051, 3727 (1922); Smith and Young, *J. Biol. Chem.*, **75**, 289 (1927).

[1] L. Michaelis and M. Schubert, THIS JOURNAL, **52**, 4418 (1930).