[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Reactions of Some Substituted Divinylacetylenes

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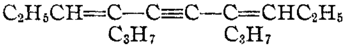
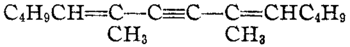
Although the behavior of the more complex conjugated unsaturated systems has been the subject of an increasing number of investigations during recent years, little attention has yet been given to the dienine system, $—C=C—C\equiv C—C=C—$. Vinylacetylene and divinylacetylene have recently been obtained by the polymerization of acetylene[1] and a few of their reactions have been described, but little is known concerning the higher members of this series of hydrocarbons. This communication describes a preliminary study of some of the addition reactions of two higher homologs of divinylacetylene.

Several years ago Dupont[2] described a general method of producing hydrocarbons of this type by the dehydration of acetylenic glycols. By this method, the two hydrocarbons, 4,7-di-*n*-propyldecadiene-3,7-ine-5 (I) and 6,9-dimethyltetradecadiene-5,9-ine-7 (II), were prepared through the glycols obtained from di-*n*-propyl ketone and methyl *n*-amyl ketone, respectively.



$$C_2H_5CH=\underset{C_3H_7}{C}—C\equiv C—\underset{C_3H_7}{C}=CHC_2H_5$$

I



$$C_4H_9CH=\underset{CH_3}{C}—C\equiv C—\underset{CH_3}{C}=CHC_4H_9$$

II

The first of these hydrocarbons was characterized by Dupont.[2] The second compound had not been previously prepared and it was necessary to establish its structure since there were two possible products of dehydration of the corresponding acetylenic glycol. Ozonization yielded *n*-valeric acid and pyruvic acid which proved that dehydration had occurred in the longer chain in accordance with the rule of Thoms and Ambrus[3] for the dehydration of unsymmetrical tertiary alcohols.

These substituted divinylacetylenes (I and II) were completely reduced by hydrogen in the presence of a platinum catalyst[4] to yield the corresponding branched chain paraffins, 4,7-di-*n*-propyldecane and 6,9-dimethyltetradecane. Some experiments in partial hydrogenation using two and four atoms of hydrogen per molecule of hydrocarbon produced complex mixtures of reduction products thus showing that under these conditions there is no preferential point of addition of hydrogen in this conjugated system. Bromination experiments also produced very complex mixtures of unstable compounds. Even at 0° the partially brominated hydrocarbons lost hydrogen bromide and changed into polymeric tars.

These substituted divinylacetylenes were more stable in air than the parent hydrocarbon, which has been found to polymerize and produce a

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(1) (a) Nieuwland, Calcott, Downing and Carter, THIS JOURNAL, **53**, 4197 (1931); (b) Carothers, Williams, Collins and Kirby, *ibid.*, **53**, 4203 (1931).

(2) Dupont, *Ann. chim.*, [8] **30**, 485 (1913).

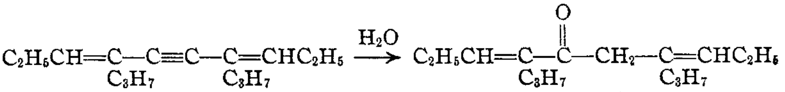
(3) Thoms and Ambrus, *Arch. Pharm.*, **263**, 264 (1925).

(4) Adams and Shriner, "Organic Syntheses," Vol. VIII, 1928, p. 92.

hard film.[1a] The higher homologs did polymerize slowly when exposed in thin layers to the air but tack-free films were not obtained. Oxidation accompanied this polymerization as was shown by the fact that a measurable amount of oxygen was absorbed by a thin layer of 5,9-dimethyltetradecadiene-5,9-ine-7 (II). During this oxidation–polymerization the odor of the volatile fatty acids became apparent.

Maleic anhydride[5] added to this dienine system but the products obtained were amorphous compounds. No definite structure has as yet been determined for these addition products but analyses and titration values indicate that the ratio of unsaturated hydrocarbon to maleic anhydride is one molecule to two molecules.

The substituted divinylacetylenes were treated with sulfuric acid and acetic acid at about 25°, after the manner used by Grignard and Tchéoufaki[6] for the addition of water to conjugated diacetylenic hydrocarbons. In each case the compound produced had the empirical formula $C_{16}H_{28}O$, which showed that one molecule of water had added to the hydrocarbon. The product of this hydration reaction decolorized a solution of bromine in carbon tetrachloride and also aqueous potassium permanganate, indicating the presence of at least one unsaturated linkage. The presence of a carbonyl group was established by the formation of a 2,4-dinitrophenylhydrazone. The unsaturated ketone was not reduced by zinc and glacial acetic acid, which indicated that the olefinic linkage was not conjugated with the carbonyl group. This observation was surprising since the simple addition of water to the triple bond which was expected, would have led to a ketone with α,β- and β,γ-olefinic linkages (III). Further evidence to show that this simple addition of water was not the only reaction which had occurred was obtained by catalytic reduction of the hydration product to a saturated hydrocarbon, $C_{16}H_{32}$, rather than to the 4,7-di-*n*-propyldecane ($C_{16}H_{34}$) which had been prepared by the reduction of the original unsaturated hydrocarbon (I). A comparison of the physical constants of the hydrocarbon, $C_{16}H_{32}$, with those of 4,7-di-*n*-propyldecane showed about the same differences as are found between cyclohexane or its alkyl substitution products and the corresponding open chain paraffins.



$$C_2H_5CH{=}\underset{C_3H_7}{C}-C{\equiv}C-\underset{C_3H_7}{C}{=}CHC_2H_5 \xrightarrow{H_2O} C_2H_5CH{=}\underset{C_3H_7}{C}-\overset{\overset{O}{\|}}{C}-CH_2-\underset{C_3H_7}{C}{=}CHC_2H_5$$

I III

All of these data support the view that a carbon ring had formed during the hydration of the dienine. In a cyclization reaction the formation of a five or a six membered carbon ring would be predicted. A very reasonable mechanism to account for the formation of a six membered ring

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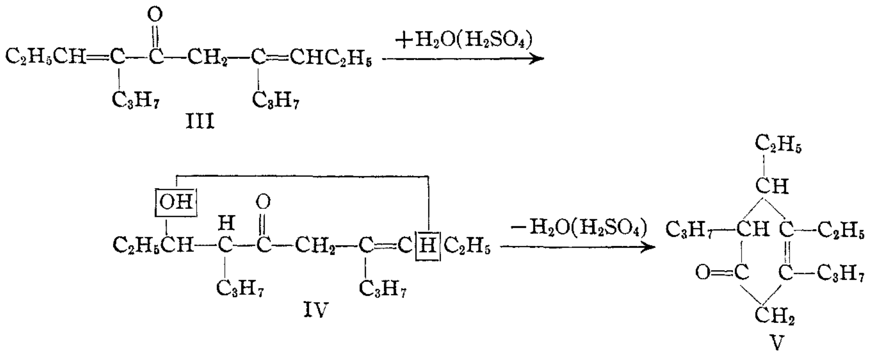
(5) The use of this reagent in the study of unsaturated conjugated systems was introduced by Diels and Alder, *Ann.*, **460**, 98 (1928).

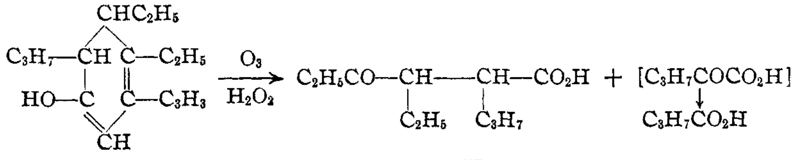
(6) Grignard and Tchéoufaki, *Compt. rend.*, **188**, 527 (1929); *Rec. trav. chim.*, **48**, 899 (1929).

from the ketone (III) formed by the addition of water to the dienine is the following



III IV V

The addition of a second molecule of water to the unsaturated ketone would undoubtedly occur as indicated at the α,β-unsaturation and ring closure of this type to give a six membered ring (V) is not unknown.[7] The structure represented in formula V accounts satisfactorily for all of the reactions of the hydration product which have been mentioned above. Confirmation of this structure has been obtained by ozonization of the cyclic unsaturated ketone. This reaction produced *n*-butyric acid and a ketonic acid $C_{11}H_{20}O_3$ which did not have the ketonic group in the alpha or beta position with respect to the carbonyl group. Ozonization of the enol form of the unsaturated cyclic ketone (VI) would be expected to produce first α-ketovaleric acid and γ-keto-α-*n*-propyl-β-ethylcaproic acid (VII). This latter acid has the same empirical composition as the ketonic acid actually isolated from the ozonization. Under the conditions used in the decomposition of the ozonide, the α-ketovaleric acid would be expected to oxidize to *n*-butyric acid, which was actually isolated.



VI VII

Thus, all of the evidence indicates that a cyclohexenone derivative is formed by the action of sulfuric and acetic acids on the dienines.

In connection with this work on the dienines, an attempt was made to duplicate the preparation of a compound which was obtained by Dupont[2] by the dehydration of *sym*-tetra-*n*-propylbutinediol (VIII) and described as a five-membered ring containing a triple bond (IX). With other acetylenic

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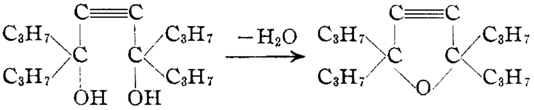
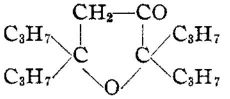
[7] Reactions of this type have been observed in the terpene series, *e. g.*, the conversion of citral to cymene by the action of acetic and sulfuric acids which has been reported by Verley, *Bull. soc. chim.*, [3] **21**, 408 (1899).

glycols Dupont had obtained products which he described as tetrahydrofurans and only the tetrapropyl derivative gave this acetylenic cyclic compound.



VIII IX



X

When this reaction was repeated the product obtained agreed in properties and composition with the expected tetrahydroketofuran (X) and no substance corresponding to the acetylenic ring was isolated. This result shows that the tetrapropylacetylenic glycol is not exceptional in its behavior as Dupont has previously stated.

Some attempts were made to obtain the conjugated trienes corresponding to the substituted divinylacetylenes. It has previously been stated that partial catalytic reduction of the dienines has been found to be an unsatisfactory reaction because of the complex mixtures produced. Catalytic reduction of the acetylenic glycols to the olefinic glycols proceeded very smoothly but dehydration of the olefinic glycols gave only substituted dihydrofurans.

Experimental

Sym-tetra-*n*-propylbutine-diol.—This was prepared in yields of 72–73% as described by Dupont.[2]

Sym-dimethyl-di-*n*-amylbutine-diol.—Following the same general procedure this was prepared in 72–76% yields. The crude product consisted of a mixture of two stereoisomers; one (25 g.) melting at 86–87° after crystallization from petroleum ether (b. p. 65–110°) and the other (55–60 g.), a liquid which boiled at 144–146° (2 mm.). The solid isomer was analyzed.

Anal. Calcd. for $C_{16}H_{30}O_2$: C, 75.52; H, 11.89. Found: C, 75.76; H, 11.91.

Both glycols gave the same hydrocarbon on dehydration. A sample of the liquid isomer weighing 0.2934 g. liberated 48 cc. of ethane when treated with ethylmagnesium bromide; calcd., 50 cc.

4,7-Di-*n*-propyldecadiene-3,7-ine-5.—This was prepared by the method of Dupont.[2] *p*-Toluenesulfonic acid was less satisfactory than sulfuric acid as a dehydrating agent.

6,9-Dimethyltetradecadiene-5,9-ine-7.—This was prepared from 25 g. of the mixture of stereoisomers of *sym*-dimethyl-di-*n*-amylbutinediol by the action of sulfuric acid. The yield was 25 g.; b. p. 95–98° (0.5 mm.); n^{20}_{D} 1.4866; d^{20}_{4} 0.8241.

Anal. Calcd. for $C_{16}H_{26}$: C, 87.99; H, 12.01. Found: C, 87.10; H, 12.08.

Ozonization of 6,9-Dimethyltetradecadiene-5,9-ine-7.—Ozonized oxygen was passed through a solution of 1.04 g. of the hydrocarbon in 200 cc. of carbon tetrachloride for about twelve hours. The solution of the ozonide was poured into about 40 cc. of 3%

hydrogen peroxide. The mixture was shaken vigorously and then the two layers were separated.

The aqueous layer was treated with phenylhydrazine and after two days the precipitate was filtered and recrystallized from alcohol. The product melted at 185–187° and the melting point was not depressed by mixing the material with an authentic specimen of pyruvic acid phenylhydrazone.

The carbon tetrachloride layer was extracted with 10% sodium hydroxide solution and the aqueous layer was separated. The organic acid was liberated with sulfuric acid, extracted with ether and converted to the *p*-bromophenacyl ester by the method of Judefind and Reid.[8] The ester melted at 61–62° and the melting point was not depressed when the ester was mixed with an authentic specimen of the *p*-bromophenacyl ester of *n*-valeric acid.

Reduction of 4,7-Di-*n*-propyldecadiene-3,7-ine-5.—To a solution of 10.02 g. of the hydrocarbon in 75 cc. of glacial acetic acid was added 0.2 g. of platinum oxide–platinum black.[4] The mixture was shaken under pressure with hydrogen until no more hydrogen was absorbed. The reduction gave 9 g. of 4,7-dipropyldecane, b. p. 92–93° (1.5 mm.); n^{20}_{D} 1.4368; d^{20}_{4} 0.7841. The physical properties differed slightly from those given by Dupont.[2]

Reduction of 6,9-Dimethyltetradecadiene-5,9-ine-7.—Ten grams of this hydrocarbon was reduced as described above. The hydrogen was absorbed very rapidly for two minutes and then insoluble material separated. After the addition of 125 cc. more of glacial acetic acid the reduction went to completion in about five minutes. The yield of 6,9-dimethyltetradecane was 9 g.; b. p. 103–104° (1.5 mm.); n^{20}_{D} 1.4348; d^{20}_{4} 0.7787.

Anal. Calcd. for $C_{16}H_{34}$: C, 84.88; H, 15.12. Found: C, 84.42; H, 15.31.

In other runs the reduction was interrupted after the addition of one and two moles of hydrogen. The reduction product was isolated and carefully fractionated. Various fractions were examined and some were ozonized in an attempt to establish structures. However, all indications were that the products were complex mixtures. Since it is unlikely that the identical mixture of products could be obtained in repeating these experiments no details are recorded here.

Addition of Bromine to the Substituted Divinylacetylenes.—Both of the divinylacetylenes added bromine rapidly when treated in chloroform solution with a solution of bromine in chloroform, but hydrogen bromide was evolved even at 0°. When the solvent was evaporated under reduced pressure at 0° only thick, viscous, greenish tars remained.

Drying Properties of the Substituted Divinylacetylenes.—About a half gram of each of the divinylacetylenes was dissolved in ether and the solution was evaporated on a watch glass to leave a thin film. In about twenty-four hours the film had considerable body but it never completely hardened. The compound with the methyl side chains appeared to dry the more rapidly. The rancid odor of the volatile fatty acids was noticeable after the second day.

A sample (0.0494 g.) of 6,9-dimethyltetradecadiene-5,9-ine-7 was placed on a filter paper and suspended in a flask of dry oxygen which was attached to a eudiometer filled with oxygen. During forty-eight hours this amount of hydrocarbon absorbed 4.54 cc. of oxygen (0°, 760 mm.). This corresponds roughly to one mole of oxygen for one mole of hydrocarbon. The absorption of oxygen was most rapid during the first four hours and was complete in forty-eight hours.

Addition of Maleic Anhydride to Substituted Divinylacetylenes. (a) 6,9-Dimethyltetradecadiene-5,9-ine-7.—A solution of 4.36 g. of the hydrocarbon and 1.96 g. of maleic anhydride in 25 cc. of anhydrous xylene was refluxed for about thirty hours.

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[8] Judefind and Reid, THIS JOURNAL, **42**, 1043 (1920).

On cooling no solid separated, so the solution was refluxed for two hours with 10% sodium hydroxide solution. The aqueous layer was separated, filtered to remove suspended material, cooled to 10° and acidified with dilute hydrochloric acid. A yellow gummy acidic substance separated. This was collected in ether and the solution was washed thoroughly with water to remove maleic acid, dried over magnesium sulfate, filtered and concentrated to about 5–10 cc. On pouring this concentrated ether solution into 150 cc. of petroleum ether (b. p. 65–110°) a yellow amorphous powder separated. The precipitate was quickly collected on a suction filter and transferred to a vacuum desiccator. In this manner about 1 g. of a cream colored amorphous solid acid was obtained. The product was highly electrified. It did not possess a definite melting point when tested in a capillary tube, but slowly decomposed. On the Maquenne block it melted at 163°. It was insoluble in petroleum ether and benzene and soluble in ether, alcohol, acetic acid and acetone.

Analyses of various samples of this product gave carbon, 65.29–65.85% and hydrogen, 8.06–8.26%. Titration gave a neutral equivalent of about 166. However, when the sample was boiled with alkali this value fell to about 115. This was taken to mean that the first product contained some anhydride groups which had not been previously hydrolyzed.

(b) **4,7-Di-*n*-propyldecadiene-3,7-ine-5.**—The hydrocarbon gave results similar to those obtained in the preceding experiment. The product melted at 159° on the Maquenne block. It had a neutral equivalent of 149–153 and the values for carbon and hydrogen content were 64.85–65.09 and 7.47–7.70, respectively. The neutral equivalent dropped to about 115 when the titration was carried out in a boiling solution.

Hydration and Cyclization of 4,7-Di-*n*-propyldecadiene-3,7-ine-5.—To a solution composed of 20 g. of concentrated sulfuric acid and 30 g. of glacial acetic acid was added 6 g. of the hydrocarbon. The temperature was held at room temperature (about 25°) and the mixture was stirred for about fifteen hours. The reaction mixture developed a deep red color during this time. The product was isolated by pouring the acid solution on cracked ice and extracting with ether. The ether solution was washed with 10% sodium carbonate solution and water and then dried over magnesium sulfate. After filtering the ether was evaporated and the residue was distilled under reduced pressure. The yield was 3 g. of a yellowish product, b. p. 107–110° (0.7 mm.); n^{20}_{D} 1.4810; d^{20}_{4} 0.8995.

Anal. Calcd. for $C_{16}H_{28}O$: C, 81.29; H, 11.95. Found: C, 81.49; H, 11.98.

This product decolorized bromine in carbon tetrachloride and aqueous potassium permanganate. When treated with zinc in acetic acid solution some of the color was removed, but the compound was otherwise unchanged. The 2,4-dinitrophenylhydrazone[9] crystallized from alcohol in beautiful scarlet needles; m. p. 97–98°.

Anal.[10] Calcd. for $C_{22}H_{32}N_4O_4$: N, 13.44. Found: N, 13.44.

The ketone could not be reduced with hydrogen and a platinum oxide–platinum black catalyst in alcohol but was reduced when glacial acetic acid was used as a solvent. To a solution of 3.44 g. of the ketone in 50 cc. of glacial acetic acid was added 0.2 g. of catalyst and the mixture treated with hydrogen under pressure. Absorption of hydrogen ceased in about eighteen hours. A second 3.04 g. of ketone was reduced and the two reduction mixtures were combined. The product obtained boiled at 97–100° (1.5 mm.), n^{20}_{D} 1.4579; d^{20}_{4} 0.8370; M_D calcd. for $C_{16}H_{32}$ (cyclic) 73.92. Calcd. for $C_{16}H_{34}$ (open chain) 76.12. Found: 73.09.

Anal. Calcd. for $C_{16}H_{34}$: C, 84.85; H, 15.15. Calcd. for $C_{16}H_{32}$: C, 85.61; H, 14.38. Found: C, 85.96; H, 14.44.

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[9] Allen, This Journal, **52**, 2955 (1930).

[10] This analysis was made by Mr. K. Eder

The hydrocarbon was different from the 4,7-di-*n*-propyldecane obtained by the reduction of the original 4,7-di-*n*-propyldecadiene-3,7-ine-5 and was obviously a cyclic compound.

Ozonization of the Cyclic Ketone.—Ozonized oxygen was passed through a solution of 12 g. of the ketone in 150 cc. of carbon tetrachloride for about twelve hours. More solvent was added as needed to maintain the original volume. The ozonide was decomposed by shaking the solution with about 100 cc. of 3% hydrogen peroxide. The carbon tetrachloride solution was separated and washed with three successive 100-cc. portions of water. These washings were added to the hydrogen peroxide solution, made alkaline with sodium hydroxide and concentrated to about 100 cc. This solution was acidified with sirupy phosphoric acid and distilled until about 65 cc. of distillate was obtained. This distillate was exactly neutralized with sodium hydroxide and evaporated to dryness. The sodium salt was converted to the *p*-bromophenacyl ester[8] (3 g.) m. p. 62–63°. This melting point checks that of the *p*-bromophenacyl ester of *n*-butyric acid. A mixed melting point of the product with an authentic specimen of the *n*-butyric ester confirmed the identification.

The carbon tetrachloride layer remaining after the removal of the water-soluble material was extracted with 100 cc. of 5% sodium hydroxide solution. This alkaline solution was separated and acidified with hydrochloric acid. A sirupy acid separated and was collected in ether. After drying the ether solution over anhydrous magnesium sulfate and filtering, the ether was evaporated and the acid was distilled under reduced pressure, b. p. 110–112° (0.6–0.7 mm.). About 2 g. of this acid was obtained.

Anal. Calcd. for $C_{11}H_{20}O_3$: C, 66.00; H, 10.07; neutral equivalent, 200. Found: C, 65.74; H, 10.02; neutral equivalent, 193.

A semicarbazone was prepared from 0.1 g. of this acid but the small quantity of available material prevented complete purification, m. p. 194–195°. However, the analysis indicated that the desired derivative had been obtained.

Anal.[10] Calcd. for $C_{12}H_{23}O_3N_3$: N, 16.35. Found: N, 15.56.

A neutral compound (about 3 g.) was obtained by evaporating the carbon tetrachloride solution which remained after the extraction of the keto acid. This material was a yellow oil which boiled at 82–88° (0.1 mm.); n^{20}_{D} 1.4710; d^{20}_{4} 1.043.

Anal.[10] Found: C, 61.05, 60.95; H, 8.39, 8.46. This compound was not further characterized.

Hydration and Cyclization of 6,9-Dimethyltetradecadiene-5,9-ine-7.—Following the same procedure that was outlined above, 14 g. of this hydrocarbon gave 5.5 g. of an unsaturated ketone, b. p. 128–131° (1.5 mm.); n^{20}_{D} 1.4750; d^{20}_{4} 0.8958.

Anal. Calcd. for $C_{16}H_{28}O$: C, 81.29; H, 11.95. Found: C, 81.41; H, 12.01.

The 2,4-dinitrophenylhydrazone crystallized in beautiful carmine plates which melted at 104–105°.

Anal.[10] Calcd. for $C_{22}H_{32}N_4O_4$: N, 13.44. Found: N, 13.38.

Catalytic hydrogenation of the ketone in glacial acetic acid over a platinum catalyst gave a hydrocarbon; b. p. 101–103° (1.5 mm.); n^{20}_{D} 1.4533; d^{20}_{4} 0.8306.

Anal. Calcd. for $C_{16}H_{32}$: C, 85.64; H, 14.37. Found: C, 85.96; H, 14.47.

Hydration and Cyclization of Sym-tetra-*n*-propylbutine-diol.—A mixture of 10 g. of *sym*-tetra-*n*-propylbutine-diol and a solution of mercuric sulfate, which was prepared by dissolving as much mercuric oxide as possible in 100 cc. of water containing 5 cc. of concentrated sulfuric acid, was heated at 100° with stirring, under a reflux condenser for two days. The material was then steam distilled and the oil thus obtained was taken up in ether. After drying, the ether was removed and the residue distilled. About 5 g. of the tetrahydroketofuran was obtained; b. p. 96–100° (0.9 mm.); n^{20}_{D} 1.4609; d^{20}_{4} 0.9003.

Anal. Calcd. for $C_{16}H_{30}O_2$: C, 75.53; H, 11.88. Found: C, 76.02; H, 12.05.

Hydration and Cyclization of Sym-dimethyl-di-*n*-amylbutine-diol.—The same procedure was used in this experiment as described for the propyl isomer. From 5 g. of the low melting isomer of the glycol there was obtained 3 g. of the substituted tetrahydroketofuran; b. p. 112–113° (1.0 mm.); n_D^{20} 1.4494; d_4^{20} 0.8977.

Anal. Calcd. for $C_{16}H_{30}O_2$: C, 75.53; H, 11.88. Found: C, 75.15; H, 11.85.

Sym-tetrapropylbutene-diol.—A solution of 12.7 g. of *sym*-tetrapropylbutine-diol in 150 cc. of alcohol was reduced catalytically according to the method of Adams and Shriner[4] until one molecular equivalent of hydrogen had added. Eleven grams of a thick viscous colorless liquid was obtained. The olefinic glycol boiled at 136–138° (1.5 mm.).

Anal. Calcd. for $C_{16}H_{32}O_2$: C, 74.94; H, 12.57. Found: C, 74.72; H, 12.68.

Sym-dimethyl-di-*n*-amylbutene-diol.—Using the same procedure 12.71 g. of the low-melting isomer of *sym*-dimethyldi-*n*-amylbutine-diol gave 11.5 g. of the olefinic glycol; b. p. 128–130° (0.4 mm.); n_D^{20} 1.4657; d_4^{20} 0.9022.

Anal. Calcd. for $C_{16}H_{32}O_2$: C, 74.94; H, 12.56. Found: C, 75.08; H, 12.43.

Similarly 12.7 g. of the pure high-melting isomer of the acetylenic glycol gave 11.8 g. of the olefinic glycol; b. p. 149–151° (2.0 mm.).

Anal.[10] Calcd. for $C_{16}H_{32}O_2$: C, 74.94; H, 12.56. Found: C, 74.31; H, 12.59.

Dehydration of Sym-tetrapropylbutene-diol.—The same procedure was used in this dehydration as was described in the preparation of the substituted divinylacetylenes. From 10 g. of the butene-diol there was obtained 7 g. of 2,2,5,5-tetrapropyl-2,5-dihydrofuran, which was a colorless liquid; b. p. 92–94° (1.5 mm.); n_D^{20} 1.4635; d_4^{20} 0.8510.

Anal. Calcd. for $C_{16}H_{30}O$: C, 80.60; H, 12.64. Found: C, 80.78; H, 12.81.

Dehydration of Sym-dimethyl-di-*n*-amylbutene-diol.—From 10 g. of the olefinic glycol prepared from the low-melting acetylenic glycol there was obtained 7.5 g. of 2,5-dimethyl-2,5-di-*n*-amyl-2,5-dihydrofuran; b. p. 100–101° (3 mm.); n_D^{20} 1.4445.

Anal. Calcd. for $C_{16}H_{30}O$: C, 80.60; H, 12.69. Found: C, 80.77; H, 12.86.

Ten grams of the olefinic glycol obtained from the high-melting isomer of the acetylenic glycol yielded 7.5 g. of the same dihydrofuran derivative.

Summary

1. Two substituted divinylacetylenes, 4,7-di-*n*-propyldecadiene-3,7-ine-5, and 6,9-dimethyltetradecadiene-5,9-ine-7, have been prepared and their reactions with oxygen, bromine, hydrogen in the presence of a platinum catalyst and maleic anhydride have been investigated.

2. Treatment of these unsaturated hydrocarbons with a mixture of sulfuric and acetic acids has yielded cyclic unsaturated ketones which are apparently derivatives of cyclohexanone.

3. Some experiments on the dehydration and reduction of the intermediate acetylenic glycols have been performed and some di- and tetrahydrofuran derivatives have been described.

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