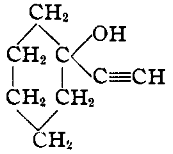
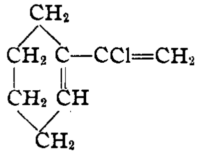
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Rearrangement of Ethynylcarbinols

BY CHARLES D. HURD AND ROBERT E. CHRIST

Recently, it was established[1] that 1-ethynyl-1-cyclohexanol (I) was converted by thionyl chloride and pyridine into 1-α-chlorovinyl-1-cyclohexene (II). Some years earlier, Rupe[2] had announced the transformation of (I) by formic acid into cyclohexylideneacetaldehyde, $(CH_2)_5$-C=CHCHO, not 1-acetyl-1-cyclohexene (III). In its enolized form (III) would be analogous to (II). The improbability that two acidic reagents should influence the ethynylcarbinol by essentially different mechanisms caused us to inspect Rupe's evidence. Curiously, it all supported the ketone (III), yet the aldehyde structure was assigned on the basis of delicate color reactions (Schiff's reagent and Angeli's reagent).


(I)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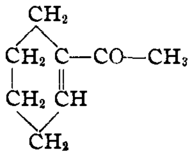
(III)

Evidence against the aldehyde formula was the non-formation of cyclohexylideneacetic acid with silver oxide. Ozonization supported (III) inasmuch as adipic acid was the reaction product instead of cyclohexanone. Excellent evidence for (III) was its behavior on catalytic hydrogenation. The material obtained boiled at 69° (12 mm.) and gave a semicarbazone of m. p. 171–172°. These are the constants for cyclohexyl methyl ketone[3] and its semicarbazone, rather than for cyclohexylacetaldehyde[4] (b. p. 79–80° (10 mm.); semicarbazone, m. p. 132–134°). Fischer and Löwenberg[5] had occasion to doubt the conclusion of Rupe and, in repeating the work, found that the hydrogenated product was actually cyclohexyl methyl ketone.

Rupe has also studied the rearrangement of about a dozen other ethynylcarbinols. In a few cases, namely, 1-ethynyl-3-(and 4-)-methyl-1-cyclohexanol and 1-ethynyl-2-methyl-5-isopropyl-1-cyclohexanol, rearrangement was reported[6] to yield unsaturated ketones of type III. The majority of the reactions, however, have been stated to yield the unsaturated aldehydes. No suggestion was included to explain why ketones were formed in a few cases and aldehydes in others. The aldehyde-forming carbinols included[7] ethynylmethylalkylcarbinol (alkyl = isohexyl, *t*-butyl, phenyl, isobutyl, β-phenylethyl), 1-ethynyl-2-(or 5)-isopropyl-5-(or 2)-methyl-1-cyclohexanol, and ethynylfenchyl alcohol. In these cases, as with 1-ethynyl-1-cyclohexanol, the interpretation of the evidence seemed questionable. Hence this matter was investigated and ethynylmethylphenylcarbinol, 1-ethynyl-1-cyclohexanol, and ethynylbornyl alcohol, a new compound, were selected for study. In none of these cases was any evidence found for the aldehyde structures postulated by Rupe. The evidence for ketones as rearrangement products was very convincing.

That (III) was the rearrangement product of (I) was confirmed by synthesizing 1-acetyl-1-cyclohexene from cyclohexene,[8] acetyl chloride, and aluminum chloride, preparing its semicarbazone (m. p. 220–221°), and proving its identity to the semicarbazone of (III), from (I), by a mixed melting point determination.

Ethynylmethylphenylcarbinol, $C_6H_5\underset{CH_3}{C}(OH)—C{\equiv}CH$, was prepared according to Rupe's directions, but the oil (b. p. 122–130° (12 mm.); semicarbazone, m. p. 201°) which was obtained in small yield during reaction with formic acid was not β-phenylcrotonaldehyde (IV) as stated by Rupe and Giesler[9] but was simply acetophenone.

$$C_6H_5C(CH_3){=}CHCHO \quad (IV)$$
$$CH_2{=}C(C_6H_5)COCH_3 \quad (V)$$

The bulk of the reaction product was a tar which

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[1] Hurd and Jones, THIS JOURNAL, **56**, 1924 (1934).

[2] Rupe, Messner and Kambli, *Helv. Chim. Acta*, **11**, 449 (1928).

[3] Bouveault, *Bull. soc. chim.*, [3] **29**, 1051 (1903); Wallach, *Ann.*, **360**, 47 (1908); **389**, 192 (1912).

[4] Wallach, *Ann.*, **359**, 313 (1908); Skita, *Ber.*, **48**, 1694 (1915).

[5] Fischer and Löwenberg, *Ann.*, **475**, 203 (1929).

[6] Rupe and co-workers, *Helv. Chim. Acta*, **14**, 701 (1931); **16**, 685 (1933).

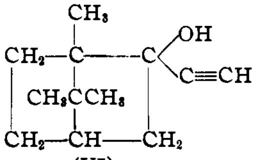
[7] Rupe and co-workers, *ibid.*, **11**, 656, 965 (1928); **12**, 193 (1929); **14**, 687, 708 (1931); **17**, 283 (1934); **18**, 542 (1935).

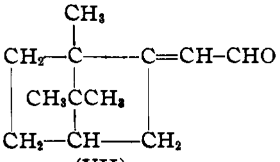
[8] Darzens, *Compt. rend.*, **150**, 707 (1910); Wallach, *Ann.*, **360**, 46 (1908).

[9] Rupe and Giesler, *Helv. Chim. Acta*, **11**, 656 (1928).

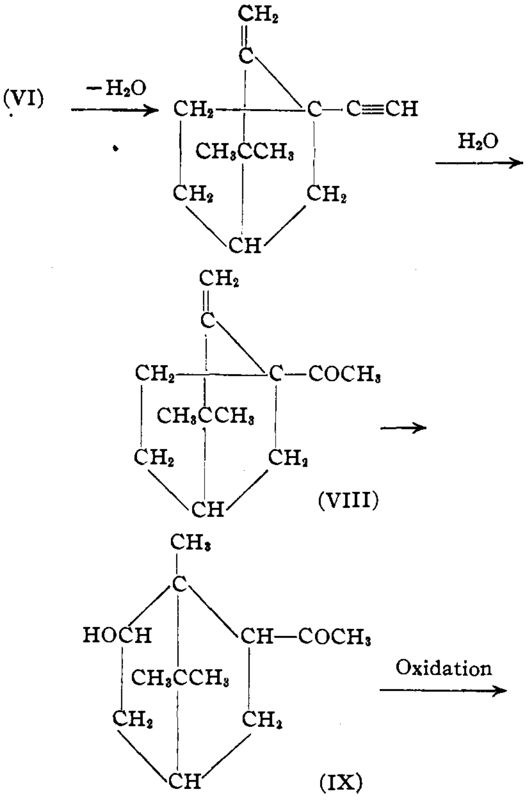
probably came *via* phenylbutenone (V). Both IV and V possess conjugated systems but V, with its unsubstituted methylene carbon, represents a type which is particularly susceptible to polymerization.

Ethynylbornyl alcohol (VI) was synthesized from camphor, acetylene and metallic sodium. A smooth rearrangement occurred with formic acid. The product, however, was not the aldehyde (VII) but was the ketone (IX).

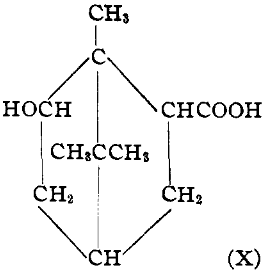

(VI)


(VII)

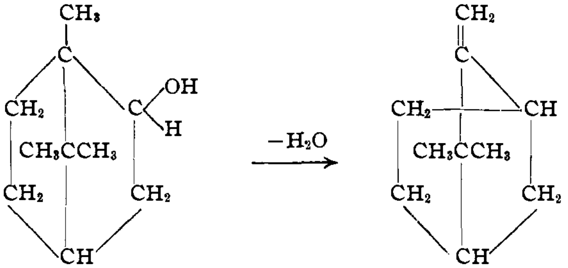
In the first place, no acid was obtainable by the prolonged action of silver oxide. Secondly, analysis corresponded to $C_{12}H_{20}O_2$ rather than $C_{12}H_{18}O$. Finally, oxidation by ozone yielded 6-hydroxy-2-camphanecarboxylic acid (X). From these data, it is apparent that the product of rearrangement is 2-acetyl-6-hydroxycamphane (IX). Since the latter is a γ-hydroxy ketone it may undergo cyclization into a hemi-acetal configuration. The mechanism for the transformation of VI to IX involves two Wagner rearrangements


(VIII)

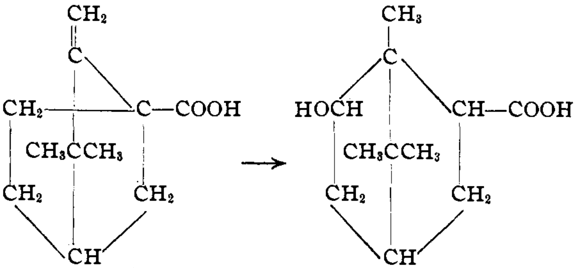
(IX)


(X)

The dehydration of (VI) into (VIII) resembles the transformation of borneol into camphene



whereas that of (VIII) into (IX) is strictly analogous to the transformation[10] of camphenecarboxylic acid (XI) into (X).


(XI) (X)

Our hydroxycamphanecarboxylic acid (X), prepared by oxidation of (IX), was identical with Houben's acid (X), prepared from (XI).

Since these several cases have proven that ketones are the important rearrangement products of ethynylcarbinols, rather than aldehydes, serious doubt is cast on other similar cases wherein aldehydes are stated to be formed but wherein definite proof for the assertion is lacking. Obviously, the various non-discriminatory reactions of the "aldehydes" which appear in the literature (such as with the Grignard reagent, reducing agents, hydroxylamine or semicarbazide) should be reinterpreted on the basis of ketones.

Experimental Part

Preparation of Reagents.—Ethynylcyclohexanol, b. p. 74–76° (12 mm.), was prepared in 30% yield by Rupe's method, as modified by Hurd and Jones.[1] In the prepara-

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[10] Houben, *Ber.*, **59**, 2285 (1926).

tion of ethynylmethylphenylcarbinol, the directions of Rupe and Geisler[9] were modified by using benzene instead of ether. Instead of keeping the solution at ice temperature during the addition of the acetylene, it was kept refluxing gently. Also, the acetylene was led in before the sodium had dissolved. The yield of this carbinol, b. p. 85–90° (4 mm.) and m. p. 49°, was 13.5%. It was accompanied by about thrice the quantity of the pinacol of acetophenone.

Ethynylbornyl Alcohol VI.—One hundred grams of camphor dissolved in 600 cc. of dry benzene was placed in a 3-necked, liter flask to which was attached a long spiral reflux condenser, mercury stirrer and an inlet for acetylene. To this was added 16 g. of finely cut sodium. Then, while the solution was kept gently refluxing, acetylene was passed through for fifteen hours. After standing overnight, the solution was hydrolyzed with water and neutralized with hydrochloric acid. The solution was then steam distilled. The benzene layer was separated and treated with alcoholic silver nitrate, whereupon an abundant white crystalline precipitate formed. Its weight was 37 g. This was filtered, washed with alcohol and dried.

The silver salt was treated with an equal weight of ammonium thiocyanate in water solution. The insoluble layer was extracted with benzene, dried over calcium chloride and the benzene was evaporated. Sublimation attended efforts to distil the residue *in vacuo:* hence, the material was sublimed under reduced pressure. In all, 15.3 g. of ethynylbornyl alcohol was obtained having a m. p.[11] of 97–98°. This is a 13% yield.

Anal. (by Maxwell Pollack). Calcd. for $C_{12}H_{18}O$: C, 80.84; H, 10.18. Found: C, 80.42; H, 10.00.

Ethynylfenchyl Alcohol.—Similar directions were adapted for this synthesis. The chief difference from Rupe and Kuenzy's[12] published directions is the use of hot benzene instead of cold ether as the reaction medium, but it brought about a greatly improved yield. With their directions, reported to yield 8–10%, we obtained about a 7% yield. The modified directions listed below gave about a 29% yield.

Forty grams of finely cut sodium and 600 cc. of benzene were placed in the apparatus and the mixture was saturated with acetylene after which 200 g. of fenchone was added gradually. The solution warmed up to reflux temperature as the stream of acetylene was passed through. The total period of addition was forty-eight hours.

After standing for twelve hours, the solution was hydrolyzed with water and neutralized with hydrochloric acid. The solution was then steam distilled. The benzene layer was separated, dried and evaporated to a small volume under reduced pressure. (No difficulty due to sublimation was observed in this case.) The residue was treated with silver nitrate in alcoholic solution. An abundant white crystalline precipitate formed. This salt was filtered, washed with alcohol, dried, treated with an equal weight of ammonium thiocyanate (in water) and then steam distilled. The insoluble layer was separated, dried over sodium sulfate and distilled. A total of 67.4 g. of ethynylfenchyl alcohol, b. p. 90° (12 mm.), was obtained.

Rearrangements

Ethynylcyclohexanol.—Rupe's procedure, that of heating the compound with formic acid, was followed except for minor variations. The product of rearrangement (57% yield) boiled at 60–64° (4 mm.). As reported by Rupe, this material gave a positive test with Schiff's reagent. Its semicarbazone melted at 220–221° after three crystallizations from alcohol.

1-Acetyl-1-cyclohexene (III).—This compound was made from cyclohexene (86 g.), acetyl chloride (78 g.), carbon disulfide (600 cc.) and aluminum chloride (133 g.) by Darzens' method.[13] The yield of (III), b. p. 195–202°, was 26 g. or 21%. Its semicarbazone melted at 220–221°. A mixed melting point determination of this semicarbazone and that of the previous paragraph was 220–221°.

Behavior of Ethynylmethylphenylcarbinol toward Formic Acid.—Analogous to the yield of 1 g. of product, b. p. 122–130° (12 mm.), from 10 g. of the carbinol which was reported by Rupe and Giesler,[9] we obtained 1.7 g. (b. p. 100–110° at 6 mm.) from 12 g. The residue was a dark red tar. The liquid product reacted positively toward Schiff's reagent. Its semicarbazone melted at 201° (Rupe and Giesler reported 201-202°). A mixed melting point determination with authentic acetophenone semicarbazone, m. p. 201°, was 201°.

Further evidence that this material was acetophenone, not β-phenylcrotonaldehyde (IV) as postulated by Rupe and Giesler, was its behavior on ozonolysis. Acetophenone (unused) and benzoic acid, m. p. 121°, were the products obtained. The latter would not be expected from (IV).

To make sure that acetophenone did not preëxist in the carbinol taken for rearrangement, more of the carbinol was prepared and purified rigorously. A portion of the product, collected at 83–86° (6 mm.), was treated with alcoholic silver nitrate solution. The yellow precipitate was collected on a filter, washed repeatedly with alcohol, then dried. Part of the salt was lost when it exploded violently. Equal weights of the salt and of ammonium thiocyanate were warmed in a flask with water to recover the ethynylcarbinol. The insoluble layer was extracted with benzene, dried, distilled, and twice recrystallized from petroleum ether. The m. p. was 49° and no semicarbazone was obtainable from it.

This pure ethynylmethylphenylcarbinol (4.4 g.) was heated with 50 cc. of 90% formic acid until spontaneous reaction occurred. When this had subsided it was refluxed for thirty minutes. Then the solution was neutralized with alkali and the insoluble layer extracted with benzene. Distillation yielded 0.5 g. at 100–110° (6 mm.) which, as before, was acetophenone; semicarbazone, m. p. and mixed m. p., 201°.

Rearrangement of Ethynylbornyl Alcohol (VI).—Ten grams of (VI) was placed in an all-glass refluxing apparatus with 60 cc. of 90% formic acid. The mixture was heated until a spontaneous reaction took place. The solution turned first to a red then to a deep brown color. Heating was continued for an additional hour. The solution was

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[11] After the completion of the present study notice appeared of the synthesis of this compound by Dulou, *Bull. inst. pin*, **178**, 197 (1934); *C. A.*, **29**, 2945 (1935). Dulou's compound melted at 85° whereas ours was 98°.

[12] Rupe and Kuenzy, *Helv. Chim. Acta*, **14**, 708 (1931).

[13] Darzens, *Compt. rend.*, **150**, 707 (1910); Wallach, *Ann.*, **360**, 46 (1908).

neutralized with sodium hydroxide. The insoluble layer was extracted with benzene, dried over calcium chloride and then distilled under reduced pressure. A total of 7.5 g. (75% yield) of the rearranged product was obtained; b. p. 96–98° (6 mm.); $n^{24}\mathrm{D}$ 1.4733. The substance gave a positive iodoform reaction, indicative of the $-\mathrm{COCH_3}$ group. Schiff's reagent required considerable time for a slight color change. When 0.5 g. of this material in 50 cc. of alcohol was refluxed for five hours with freshly prepared silver oxide, no acid was obtainable on working up the products. Crystallization of this material was a difficult matter but it was found that solidification set in after about two weeks at room temperature. Recrystallization of this product from petroleum ether yielded crystals which melted at 77–78°. Analysis was satisfactory for 2-acetyl-6-hydroxycamphane (IX).

Anal. (by M. Pollack). Calcd. for $C_{12}H_{20}O_2$: C, 73.41; H, 10.27. Found: C, 73.43; H, 10.03.

Ozonization of 2-Acetyl-6-hydroxycamphane.—Eighty cc. of carbon tetrachloride was used as solvent for 4.14 g. (0.021 mole) of (IX) and 62.3 liters of an 8–10% ozone mixture was run in during twenty hours. The ozonide was hydrolyzed by warming on the steam-bath with an equal volume of water. There was formed 0.040 mole of acidic material (97.0 cc. of 0.4170 *N* sodium hydroxide solution was required). The neutral aqueous solution was extracted twice with carbon tetrachloride, then concentrated and acidified with hydrochloric acid. A brown, viscous mass separated which, after three crystallizations from alcohol–water, yielded 2.8 g. (0.014 mole) of white, crystalline 6-hydroxy-2-camphanecarboxylic acid(14) (X), m. p. 221°.

Neut. eq. Calcd. for $C_{11}H_{18}O_3$, 198.2. Found: 198.8 (0.2649 g. required 12.20 cc. of 0.1091 *N* NaOH).

Anal. (semi-micro). Calcd.: C, 66.62; H, 9.15. Found: C, 66.62, 66.40; H, 9.07, 9.16. ***Anal.*** (macro, by M. Pollack). Found: C, 66.64; H, 9.02.

Semicarbazone.—This derivative, prepared in the usual manner from IX, melted at 202°. That it was the semicarbazide of 1-acetylcamphene (VIII), rather than of IX, was shown by analysis. Evidently a dehydration process occurs during semicarbazone formation.

Anal. Calcd. for $C_{13}H_{21}ON_3$: N, 17.88. Calcd. for $C_{13}H_{23}O_2N_3$: N, 16.60. Found (Dumas): N, 17.84, 17.81.

Summary

Rearrangement of ethynylcyclohexanol by hot formic acid yields 1-acetyl-1-cyclohexene, not cyclohexylideneacetaldehyde, since it is identical to the substance prepared from cyclohexene, acetyl chloride and aluminum chloride. Other evidence for the structure of the product is cited also.

No evidence could be found to support the statement in the literature that an isomeric aldehyde is produced from ethynylmethylphenylcarbinol by rearrangement with formic acid. Instead of β-phenylcrotonaldehyde, the product formed is acetophenone. The bulk of the product is a tar which probably arises *via* 2-phenylbutenone.

Ethynylbornyl alcohol, prepared from camphor, acetylene and sodium, undergoes rearrangement to 2-acetyl-6-hydroxycamphane. On oxidation, this substance yields 6-hydroxy-2-camphanecarboxylic acid. Improved directions are given for the synthesis of ethynylfenchyl alcohol.

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(14) Houben, *Ber.*, **59**, 2285 (1926), reported a melting point of 216–220°.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF DUKE UNIVERSITY]

The Removal of HX from Organic Compounds by Means of Bases. III. The Rates of Removal of Hydrogen Bromide from Substituted N-Bromobenzamides and their Relative Ease of Rearrangement in the Presence of Alkali. The Hofmann Rearrangement

BY CHARLES R. HAUSER AND W. B. RENFROW, JR.

According to the most generally accepted mechanism for the Hofmann rearrangement of a bromoamide in the presence of alkali,[1] hydrogen bromide is removed to form an unstable univalent nitrogen compound which undergoes the rearrangement to give an isocyanate. Since it is possible to isolate the alkali salts, (RCONBr)Na, of certain bromoamides, the reaction apparently involves first, the removal of the hydrogen as a proton, followed by the release of bromide ion and rearrangement of the molecule; this might be represented as follows

$$\mathrm{RCONHBr} \xrightarrow{+\mathrm{OH}^{\ominus}} \mathrm{RCONBr}^{\ominus} \xrightarrow{-\mathrm{Br}^{\ominus}} (\mathrm{RCON}) \longrightarrow \mathrm{RCNO}$$

We have taken the view that the rate determining step of this process is the release of bromide ion from the negative ion of the salt, and that the rearrangement, if it is a separate step, occurs rela-

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[1] See especially Porter, "Molecular Rearrangements," The Chemical Catalog Co., New York, 1928, pp. 13–30.