

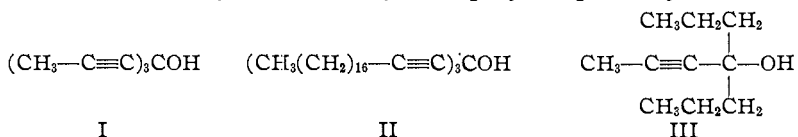
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Trialkylethinylcarbinols

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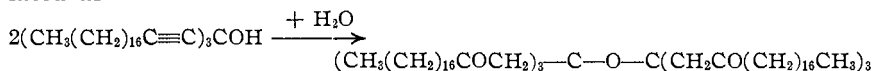
In some recent work¹ it has been shown that carbinols containing the group $-\text{CH}_2-\text{C}\equiv\text{C}-\overset{\text{R}}{\underset{\text{R}}{\text{C}}}-\text{OH}$ behave abnormally when treated with reagents which should yield the corresponding halide. Only two out of the five carbinols previously studied gave the expected halides and even in those cases the halogen compounds were too unstable to be isolated and had to be characterized by conversion to stable derivatives. The further work on compounds of this type has emphasized the peculiar reactions of acetylenic carbinols which have a primary alkyl group adjacent to the carbon atom carrying the triple bond.

Three new acetylenic carbinols, namely, tripropinylcarbinol (I), trinonadecinylcarbinol (II) and di-*n*-propylpropinylcarbinol (III), have been selected for this study because they exemplify, respectively, the lowest



molecular weight compound of this series, a very high molecular weight compound of this series and a compound in which the R group is a primary alkyl group. None of these carbinols which have primary alkyl groups attached to the acetylenic group behaved normally when treated with phosphorus trichloride. Neither trinonadecinylcarbinol nor di-*n*-propylpropinylcarbinol would yield a methyl ether on treatment with methyl alcohol and sulfuric acid.²

A most unusual reaction was observed when trinonadecinylcarbinol was warmed with sulfuric acid in acetic acid. The simple Meyer and Schuster³ rearrangement to yield the unsaturated ketone did not occur. Analysis and molecular weight determinations on the product obtained showed that in this reaction two molecules of the carbinol had combined and apparently the acetylenic bonds had been hydrated. The reaction has been formulated as



However, the carbinol groups may be in the α -position with respect to the ether linkage. This unusual reaction did not occur when either tri-

(1) Ozanne and Marvel, *THIS JOURNAL*, **52**, 5267 (1930).(2) Moureu, Dufraisse and Blatt, *Bull. soc. chim.*, [4] **35**, 1412 (1924).(3) Meyer and Schuster, *Ber.*, **55**, 819 (1922).

propinylcarbinol or di-*n*-propylpropinylcarbinol was treated in a similar manner.

The reactions of the tertiary acetylenic carbinols of the type $\text{—CH}_2\text{—C}\equiv\text{C—}\overset{\text{R}}{\underset{\text{R}}{\text{C}}}\text{—OH}$, which are reported in this communication, are quite different from the normal reactions of acetylenic carbinols of the type $\text{R}_3\text{—C—C}\equiv\text{C—}\overset{\text{R}}{\underset{\text{R}}{\text{C}}}\text{—OH}$, which have been described previously.⁴ Moreover, they are different from the reactions which Liang⁵ has reported for secondary acetylenic carbinols of a related type.

Experimental

Bromo-2-nonadecene-1.—A solution of cetylmagnesium bromide in ether was prepared from 60 g. of cetyl bromide (b. p. 156–160° (1 mm.); m. p. 11.5°; n_D^{20} 1.4625) and 4.7 g. of magnesium in 300 cc. of dry ether according to the standard procedure. The reaction was started by adding a little cetylmagnesium bromide prepared from activated copper–magnesium alloy. The warm solution of cetylmagnesium bromide was filtered under nitrogen and then added to a well-cooled solution of 60 g. of dibromo-2,3-propene-1 in 100 cc. of anhydrous ether. The reaction mixture was then heated under a reflux condenser for about eighteen hours. During all of these operations a nitrogen atmosphere was maintained to avoid excessive oxidation of the Grignard reagent. After working up the reaction mixture in the usual way,⁶ the bromo-2-nonadecene-1 was purified by fractional distillation under reduced pressure. The yield was about 10 g. (14.8% of the theoretical amount).

The residues from the fractional distillation were recrystallized from ether and gave some dotriakontane, m. p. 68–70°. If care was not taken to avoid oxidation of the Grignard reagent cetyl alcohol was present in the final mixture of products and could not be separated entirely from the bromo-2-nonadecene-1.

Bromo-2-nonadecene-1 is a colorless liquid; m. p. 10–10.5°; b. p. 168–172° (0.5 mm.); d_4^{20} 0.9781; n_D^{20} 1.4670; M_{11} , calcd. 97.24; found, 97.86.

*Anal.*⁷ Calcd. for $\text{C}_{19}\text{H}_{37}\text{Br}$: Br, 23.19. Found: Br, 23.29.

Nonadecine-1.—The acetylene derivative was prepared from the bromo compound by the action of sodamide in xylene suspension.⁶ A solution of 79 g. of the bromide in 50 cc. of xylene was added to a suspension of 30 g. of sodamide in 350 cc. of boiling xylene. After twelve hours the suspension was cooled, diluted with 1 liter of ether and worked up in the usual manner. On distillation under reduced pressure 40 g. (73% of the theoretical amount) of nonadecine-1 was obtained; b. p. 144° (1.5 mm.); m. p. 37–38°.

Anal. Calcd. for $\text{C}_{19}\text{H}_{36}$: C, 86.27; H, 13.73. Found: C, 86.51; H, 13.67.

Dinonadecynyl mercury was prepared by the method of Johnson and McEwen.⁸ After recrystallization from *n*-butyl alcohol the product melted at 96–97°.

Anal. Calcd. for $\text{C}_{38}\text{H}_{76}\text{Hg}$: Hg, 27.59. Found: Hg, 27.76.

(4) Salzberg and Marvel, *THIS JOURNAL*, **50**, 1737, 2840 (1928); Rossander and Marvel, *ibid.*, **51**, 932 (1929); Gillespie and Marvel, *ibid.*, **52**, 3368 (1930); Davis and Marvel, *ibid.*, **53**, 3840 (1931); Sweet and Marvel, *ibid.*, **54**, 1184 (1932).

(5) Liang, *Bull. soc. chim.*, [4] **53**, 33, 41 (1933).

(6) Lespieau and Bourguel, "Organic Syntheses," Coll. Vol. I, 1932, pp. 180, 185.

(7) This analysis was made by Mr. G. A. Jones.

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

Trinonadecynylcarbinol.—This carbinol was prepared from nonadecynylmagnesium bromide and diethyl carbonate⁴ in yields of 43% of the theoretical amount. The product was purified by repeated recrystallization from absolute alcohol-ether mixtures; m. p. 71–72°.

Anal. Calcd. for $C_{38}H_{106}O$: C, 85.00; H, 13.05; mol. wt., 819. Found: C, 84.82; H, 12.97; mol. wt., 895.

The carbinol liberated the theoretical amount of ethane from a solution of ethylmagnesium bromide.

Methyl Trinonadecynylmethyl Ether.—To a solution of trinonadecynylcarbinol in benzene was added an ether solution of ethylmagnesium bromide. When the theoretical amount of ethane had been liberated, four times the calculated amount of dimethyl sulfate was added and the mixture was allowed to stand for about two days. The solvent was removed and absolute alcohol was added. On cooling the methyl trinonadecynylmethyl ether separated. After recrystallization from absolute alcohol, the product melted at 44–45°. The yield was better than 90% of the theoretical amount.

Anal. Calcd. for $C_{39}H_{108}O$: C, 85.00; H, 13.07. Found: C, 84.85; H, 12.94.

This ether could not be cleaved to yield a metallic alkyl by sodium-potassium alloy in ether solution. After this treatment the original ether was recovered.

Action of Sulfuric Acid on Trinonadecynylcarbinol.—When 1 g. of trinonadecynylcarbinol dissolved in 30 cc. of either ethyl alcohol or acetic acid was treated with 10 cc. of concentrated sulfuric acid and the solution was boiled for about one-half hour, a blue color developed. On dilution of the reaction mixture with water 0.6 g. of a blue compound was obtained by filtration. After recrystallization from ethyl acetate this product melted at 56–58°. An ether solution of this compound was blue in color but when this solution was treated with aqueous alkali the color changed to light brown. The blue color was regenerated on shaking the ether solution with dilute sulfuric acid. The blue compound did not contain sulfur.

Anal. Calcd. for $C_{116}H_{222}O_7$: C, 80.56; H, 12.95; mol. wt., 1728. Found: C, 80.61, 80.65; H, 12.50, 12.40; mol. wt., 1688, 1705.

Attempts to Prepare Trinonadecynylmethyl Bromide and Chloride.—When 2 g. of the carbinol was treated with 2 g. of acetyl bromide in ether or benzene at about 35° or when a solution of 5 g. of the carbinol in 5 cc. of ether was refluxed for forty-eight hours with 5 cc. of 40% aqueous hydrobromic acid, there was obtained a light yellow bromine-containing compound which melted at 37–38° after recrystallization from a mixture of benzene and alcohol. The bromine in this compound could not be removed with molecular silver but was removed completely by the action of 40% sodium amalgam or liquid sodium-potassium alloy. No metallic alkyl was produced by this latter treatment. The analysis and molecular weight indicate that the substance is not the expected bromide. No satisfactory explanation of the reaction involved here can yet be given.

Anal. Calcd. for $C_{38}H_{105}Br$: C, 78.93; H, 12.00; Br, 9.06; mol. wt., 882. Found: C, 74.33, 74.33, 74.8; H, 11.43, 11.23, 11.51; Br, 13.68, 13.68; mol. wt., 1132, 1167.

The carbinol in ether solution was treated with thionyl chloride and pyridine. There was thus obtained a chloro compound, m. p. 40–42°, which was also anomalous.

Anal. Calcd. for $C_{38}H_{105}Cl$: C, 89.74; H, 12.64. Found: C, 78.57; H, 11.71.

Tripropinylcarbinol.—Propine was prepared by heating 1390 g. of propylene bromide in a solution of 1750 g. of potassium hydroxide in 2 liters of *n*-butyl alcohol. The gaseous hydrocarbon was passed through two large U-tubes containing anhydrous calcium chloride and phosphorus pentoxide in order to remove alcohol and any possible moisture. The purified propine was passed into a solution of three moles of ethyl-

magnesium bromide in ether. This operation required about thirty-six hours. Unless this large excess of propine was used, ethylmagnesium bromide remained in the solution and produced mixtures of products.

To this solution of propinylmagnesium bromide was added 118 g. of diethyl carbonate over a period of about ten hours and the reaction carried out as usual for the preparation of acetylenic carbinols.⁴ On final evaporation of the ether the carbinol remained as a dark colored solid weighing about 100 g. After repeated crystallization from hot benzene-petroleum ether (1-100) mixtures about 60 g. (41% of the theoretical amount) of yellow crystals (m. p. 134-135°) was obtained. Usually it was necessary to use decolorizing charcoal on the hot benzene solution to remove the deep color. The petroleum ether was then added and the crystals were obtained by cooling to 0° for several hours.

Anal. Calcd. for $C_{10}H_{10}O$: C, 82.15; H, 6.90; mol. wt., 146. Found: C, 82.58, 81.98; H, 7.07, 6.86; mol. wt., 141, 144, 145.

The structure of the carbinol was established by catalytic reduction to tri-*n*-propylcarbinol. A solution of 8 g. of the acetylenic carbinol in 150 cc. of 95% alcohol in the presence of 0.1 g. of platinum oxide catalyst⁹ was reduced by hydrogen in about one hour. On working up the solution about 3 cc. of tri-*n*-propylcarbinol was isolated. This product had the following constants: b. p. 89-90.5° (21 mm.); d_4^{20} 0.8304; n_D^{20} 1.4337. A known sample of tri-*n*-propylcarbinol was found to have the following properties; b. p. 90-93° (21 mm.); d_4^{21} 0.8338;¹⁰ n_D^{20} 1.43557.¹⁰ No solid derivatives could be prepared for comparison.

Action of Phosphorus Trichloride on Tripropinylcarbinol.—A solution of 3 g. of the carbinol in 30 cc. of dry benzene was treated with 1 g. of phosphorus trichloride in 10 cc. of the same solvent under the conditions previously used for the conversion of acetylenic carbinols to the corresponding halides.^{2,11} The product obtained after recrystallization from a mixture of alcohol and ether weighed 2 g. It was a yellow crystalline compound melting at 153-154° with violent decomposition. Analysis showed that the chlorine content was that expected but molecular weight determinations showed that the compound was a dimer.

Anal. Calcd. for $C_{10}H_9Cl$: Cl, 21.06; mol. wt., 164.5. Found: Cl, 21.03; mol. wt., 319, 324.

The chlorine in the dimer was not removed by shaking with molecular silver at ordinary temperature during three days. Sodium amalgam (40%) removed the halogen but did not form a metallic alkyl.

Some evidence was obtained that the monomeric chloride was formed and could be dehalogenated by silver if the reactions were all carried out at temperatures below -10°. However, it was impossible to obtain a hydrocarbon of sufficient stability to characterize.

Di-*n*-propylpropinylcarbinol.—The propine prepared from 606 g. of propylene bromide was passed into a solution containing 0.75 mole of ethylmagnesium bromide. Then 80 g. of di-*n*-propyl ketone was added and the reaction carried out in the usual fashion.⁴ The carbinol boiled at 196-197° at atmospheric pressure. The yield was 64 g. (59% of the theoretical amount); d_{20}^{20} 0.8709; n_D^{20} 1.4518.

Anal. Calcd. for $C_{10}H_{18}O$: C, 77.92; H, 11.77. Found: C, 77.02, 77.49; H, 11.61, 11.58.

Catalytic reduction⁹ of this carbinol gave tri-*n*-propylcarbinol; d_{20}^{20} 0.8340; n_D^{20} 1.4357.

(9) Adams, Voorhees and Shriner, "Organic Syntheses," 1932, Coll. Vol. I, p. 452.

(10) Konowaloff, *Chem. Zentr.*, I, 1271 (1902).

(11) Moureu, Dufraisse and Mackall, *Bull. soc. chim.*, [4] **33**, 934 (1923).

Treatment of the carbinol with phosphorus trichloride or tribromide gave liquid products which decomposed on distillation and were too low melting to crystallize. The same difficulty was met when thionyl chloride was used in place of phosphorus trichloride.

Summary

Three new acetylenic carbinols, tripropinylcarbinol, trionadecynylcarbinol and di-*n*-propylpropinylcarbinol, which contain the group $-\text{CH}_2-\text{C}\equiv\text{C}-\underset{\text{R}}{\overset{\text{R}}{\text{C}}}-\text{OH}$ have been characterized. Their behavior toward various reagents shows that they do not react in the manner which would be predicted from the knowledge gained previously from the study of closely related acetylenic carbinols containing the group $\text{R}_3\text{C}-\text{C}\equiv\text{C}-\underset{\text{R}}{\overset{\text{R}}{\text{C}}}-\text{OH}$.

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The Direct Carboxylation of Carbon Compounds. II

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In a recent study of the equilibrium $\text{C}_6\text{H}_6\text{CO}_2\text{H} \rightleftharpoons \text{C}_6\text{H}_6 + \text{CO}_2$ it was found that benzene was carboxylated directly by carbon dioxide.¹ Temperatures of about 300° and pressures of about 30 atmospheres were used and the catalyst was of the Zn-Cu-Cr oxide type. Since the yield of acid product as well as the rate of the reaction was quite low, we have continued the search for a more active catalyst. In addition we have studied the direct carboxylation of a variety of compounds.

The experiments were all conducted in glass bomb tubes having a volume of 160 to 200 cc. Pressures of 20 to 30 atmospheres were obtained by introducing into each tube before sealing 0.1 mole of solid carbon dioxide. The tubes were heated for eight hours in a Carius furnace at the temperatures recorded in the table for each specific substance.

A catalyst was found to be quite essential for the carboxylation under the conditions given. The catalyst mentioned in the first paper was replaced by a similar mixture of oxides, but supported on asbestos. This change increased the activity of the catalyst based on the weight of metal oxides in the mixture. It was made by mixing thoroughly the well washed moist hydroxides obtained from 99 g. of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 93.5 g. of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ by precipitation with ammonium hydroxide, with 7.7 g. of chromic oxide and 40 g. of asbestos. After drying the mixture was ignited to convert the hydroxides to oxides. This type of catalyst was found to decrease in activity with use. Upon using the same catalyst over

(1) Kinney and Langlois, *THIS JOURNAL*, **53**, 2:89 (1931).