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Acetylene Polymers and their Derivatives. VII. Sodium Vinylacetylide and Vinylethinylcarbinols

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Vinylacetylene, like other true acetylenic compounds, reacts with Grignard reagents to form the corresponding organo magnesium halide, and this may be used to introduce the vinylethinyl group into compounds of various types.[1] The present paper is concerned with the formation of sodium vinylacetylide and with its use in a similar manner, especially in the synthesis of vinylethinylcarbinols.

Sodium vinylacetylide is readily obtained by the action of vinylacetylene on metallic sodium. The metal may be applied directly to the liquid hydrocarbon, or the latter may be diluted with an inert solvent such as ether, toluene or liquid ammonia. The reaction occurs with great rapidity if the sodium is dissolved in liquid ammonia. These methods, however, have the disadvantage that the acetylide produced is frequently contaminated with appreciable amounts of polymeric material. More uniformly satisfactory results are obtained by the action of powdered sodamide on the hydrocarbon. The latter is preferably dissolved in ether or liquid ammonia.

The sodium vinylacetylide obtained in this manner is a dusty, white powder, and vinylacetylene is regenerated in high yield when it is cautiously treated with water in the presence of a diluent. Its stability is sufficient to permit its storage for two or three days in a stoppered bottle, and with some care it can be handled in the presence of air. However, if the air is moist the acetylide sometimes ignites spontaneously. It attacks many organic reagents with explosive violence, but cooling and dilution permit sufficient control to obtain smooth reaction in most cases. Isolation of the sodium compound is not necessary for its application as a reagent; the intended reactant is preferably added directly to the mixture resulting from the action of sodamide on vinylacetylene.

In dealing with aldehydes and ketones a still simpler and more satisfactory procedure consists in adding powdered sodamide in portions to a mixture of the carbonyl compound with vinylacetylene. In most cases it is advantageous to have present a diluent such as ether. With simple aliphatic and alicyclic ketones this method is very satisfactory. The yields are good and large scale operations are much simpler than with the vinylethinylmagnesium halides. However, sodium vinylacetylide has a more limited range of applicability in the synthesis of carbinols than has vinylethinylmagnesium bromide. Aliphatic aldehydes are partly resinified by the sodium compound, and unsaturated aldehydes and ketones are

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(1) Carothers and Berchet, THIS JOURNAL, **55**, 1094 (1933).

usually resinified completely. The magnesium compound, however, even with very sensitive aldehydes and ketones, generally yields the expected monomeric carbinols.[2]

Vinylethinyldimethylcarbinol has already been described[1] and the other carbinols listed in Table II resemble it in their properties. They react readily with bromine and decolorize permanganate; in the presence of platinum they are smoothly hydrogenated to the corresponding *n*-butylcarbinols. They can be distilled *in vacuo* without decomposition, but if the temperature of distillation is too high the tertiary carbinols tend to lose water with the production of the corresponding substituted divinylacetylenes. Vinylethinyldi-*n*-propylcarbinol, for example, thus leads to the compound $C_2H_5{-}CH{=}C(C_3H_7){-}C{\equiv}C{-}CH{=}CH_2$. Divinylacetylene itself was obtained by heating vinylethinylmethylcarbinol with *p*-toluenesulfonic acid.

The tertiary carbinols all polymerize spontaneously on standing.[3] The transformation sets in rather quickly and progresses to the stage of a thick sirup during the course of a few days. The mixture then sets to a tough rather elastic mass, but the final product, a hard, transparent glass-like mass, is obtained only after several weeks or months. The transformation is greatly accelerated by certain catalysts, *e. g.*, benzoyl peroxide, especially in the presence of light. The final glass-like products adhere very tenaciously to glass. They are insoluble in the common organic solvents. The polymerization of the carbinols also proceeds more rapidly at elevated temperature, *e. g.*, 100°, but the final product obtained under these conditions is fusible and completely soluble in the common organic solvents. The spontaneous polymerization of the carbinols is strongly inhibited by the presence of a small amount of hydroquinone. The secondary carbinols polymerize very much more slowly than the tertiary carbinols.

Experimental Part

Preparation of Sodium Vinylacetylide.—Powdered sodamide (19.5 g., 0.5 mole) was slowly added to a solution of 75 g. of vinylacetylene in 250 cc. of liquid ammonia. The mixture was stirred for six hours and the ammonia evaporated in a stream of nitrogen, finally at 60°. The residue was a white powder (38 g., calcd. 37 g.) which showed a tendency to ignite spontaneously when exposed to the air. It was covered with toluene, and water was slowly added with constant stirring at 75°. The acetylide finally dissolved without appreciable residue in the aqueous layer. Vinylacetylene was distilled from the mixture and collected in a cold receiver. The yield was 21.3 g. or 82%.

Preparation of the Carbinols.—The general procedure used for the preparation of the tertiary carbinols is illustrated by the following example. The reaction mixture consisted of 555 g. (7.7 moles) of methyl ethyl ketone (Eastman Kodak pract.), 551 g. (10.6 moles) of vinylacetylene, and 500 cc. of dry ether. The solution was contained in

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(2) Unpublished results.

(3) The behavior of the vinylethinylcyclopentanol was exceptional. It had not polymerized after standing for one year at the ordinary conditions.

a 3-necked flask provided with a mercury-sealed stirrer and a coil condenser, which in turn was connected to a trap. The reaction flask and trap were surrounded with carbon dioxide snow and the coil condenser was kept cold in the same manner. To the cold solution was slowly added 300 g. (7.7 moles) of powdered sodamide and stirring was continued for a total of six hours. The reaction mixture was made acid to litmus by means of 10% sulfuric acid, the ether layer separated and dried with sodium sulfate, and then distilled in a vacuum; 677 g. of pure vinylethinylmethylethylcarbinol was obtained; yield 71%. The carbinol was stabilized with 0.1% hydroquinone in order to prevent spontaneous polymerization.

The same procedure was applied to the preparation of the secondary carbinols but the results were less satisfactory. The preparation of vinylethinylmethylcarbinol is used as an illustration. To a solution of 44 g. (1 mole) of freshly distilled acetaldehyde and 75 g. of vinylacetylene in 75 cc. of dry ether at −10° was slowly added 39 g. of powdered sodamide. After a few grams of sodamide had been added, the mixture became so gummy that additional ether was added. Finally, the mixture formed a cake and stirring was discontinued. After four hours the cake was broken up with a stirring rod, more ether added, and the suspension stirred at room temperature for three hours. The reaction mixture was allowed to stand overnight and then decomposed with water and dilute sulfuric acid. The mixture was extracted several times with ether, and the latter dried with sodium sulfate and distilled. A considerable quantity of ether-insoluble resin remained in the reaction mixture. After removal of the ether and a small amount of low boiling liquid, 25 g. (26%) of vinylethinylmethylcarbinol was collected. It was a colorless liquid with an alcoholic odor slightly resembling that of butyl alcohol. It reacted with dinitrobenzoyl chloride to form the **3,5-dinitrobenzoate** of vinylethinylmethylcarbinol, white needles from dilute alcohol; m. p. 106–106.2°.

Anal. Calcd. for $C_{13}H_{10}N_2O_6$: C, 54.27; H, 3.41. Found: C, 54.34; H, 3.47.

Catalytic Reduction of the Vinylethinylcarbinols.—The carbinols derived from acetone and from methyl ethyl ketone absorbed four atoms of hydrogen very rapidly when dissolved in alcohol and shaken with hydrogen in the presence of Adams' platinum oxide catalyst. The resulting *n*-butylcarbinols corresponded in their properties with those already reported in the literature, and the yields were almost quantitative. Hydrogenation of the carbinols derived from methyl octyl ketone and from acetophenone yielded the new saturated carbinols described below.

***n*-Butylmethyloctylcarbinol.**—Colorless liquid, b. p. (3 mm.) 94°; n^{20}_{D} 1.4418; d^{20}_{4} 0.8318; M_R calcd., 68.38; M_R found, 68.03.

Anal. Calcd. for $C_{14}H_{20}O$: C, 78.50; H, 14.02. Found: C, 77.20, 77.30; H, 14.18, 14.25.

***n*-Butylmethylphenylcarbinol.**—Colorless liquid, b. p. (6 mm.) 107 to 109°; n^{20}_{D} 1.5118; d^{20}_{4} 0.9616; M_R calcd., 55.52; M_R found, 55.52.

Anal. Calcd. for $C_{12}H_{18}O$: C, 80.90; H, 10.11. Found: C, 81.02, 81.16; H, 10.38, 10.24.

***n*-Propyl-5-octadiene-1,5-ine-3.**—When the attempt was made to distil vinylethinyldi-*n*-propylcarbinol *in vacuo* in a flask provided with a long column, dehydration occurred and the non-aqueous distillate was the hydrocarbon *n*-propyl-5-octadiene-1,5-ine-3. On redistillation it was obtained as a pale yellow liquid having a characteristic odor; b. p. (6 mm.) 57 to 58°; d^{20}_{4} 0.8047; n^{20}_{D}, 1.4949; M_R calcd., 50.06; M_R found, 53.62. The sample was perhaps not quite pure.

Anal. Calcd. for $C_{11}H_{16}$: C, 89.19; H, 10.81. Found: C, 87.47, 90.27, 87.73; H, 11.11, 9.94, 10.61.

Preparation of Divinylacetylene by the Dehydration of Vinylethinylmethylcarbinol.—To 25 g. of *p*-toluenesulfonic acid in a 500-cc. flask provided with a stirrer, separa-

TABLE I

ANALYTICAL DATA FOR VINYLETHINYLCARBINOLS

Structural formula of carbinol	Empirical formula	Calcd.			Found		
		C	H	Mol. wt.	C	H	Mol. wt. in freezing benzene
$CH_3CHOH—C\equiv C—CH=CH_2$	C_6H_8O	75.00	8.33	96	74.66	8.34	104
$n\text{-}C_3H_7CHOH—C\equiv C—CH=CH_2$	$C_8H_{12}O$	77.42	9.67	124	76.83	9.83	127
$(CH_3)_2C(OH)—C\equiv C—CH=CH_2$	$C_7H_{10}O$	76.36	9.09	110	76.18	8.88	119
$CH_3(C_2H_5)C(OH)—C\equiv C—CH=CH_2$	$C_8H_{12}O$	77.42	9.67		77.09	9.87	
$(C_2H_5)_2C(OH)—C\equiv C—CH=CH_2$	$C_9H_{14}O$	78.26	10.14	138	78.61	10.09	136, 141
$(n\text{-}C_3H_7)_2C(OH)—C\equiv C—CH=CH_2$	$C_{11}H_{18}O$	79.52	10.84	166	79.89	11.14	167, 171
$CH_3(C_8H_{17})C(OH)—C\equiv C—CH=CH_2$	$C_{14}H_{24}O$	80.77	11.54		80.17	10.87	
$(CH_2)_4C(OH)—C\equiv C—CH=CH_2$	$C_9H_{12}O$	79.41	8.82	136	79.36	8.99	145, 145
$(CH_2)_5C(OH)—C\equiv C—CH=CH_2$	$C_{10}H_{14}O$	80.00	9.33	150	79.70	9.29	137, 144[a]
$CH_3(C_6H_5)C(OH)—C\equiv C—CH=CH_2$	$C_{12}H_{12}O$	83.72	6.97	172	83.23	7.08	173

[a] In boiling benzene.

TABLE II

PHYSICAL PROPERTIES OF VINYLETHINYLCARBINOLS

Ketone or aldehyde reactant	Formula of carbinol produced	Physical properties of carbinol						
		B. p., °C.	Mm.	d_4^{20}	n_D^{20}	MR calcd.	MR found	Exaltation
Acetaldehyde	$CH_3—CHOH—C\equiv C—CH=CH_2$	65	22	0.9112	1.4851	28.97	30.20	1.23
Butyraldehyde	$n\text{-}C_3H_7—CHOH—C\equiv C—CH=CH_2$	74–76	10	.8919	1.4775	38.21	39.32	1.11
Acetone	$(CH_3)_2C(OH)—C\equiv C—CH=CH_2$	68	24	.8872	1.4778	33.32	35.08	1.76
Methyl ethyl ketone	$CH_3(C_2H_5)C(OH)—C\equiv C—CH=CH_2$	75	20	.8878	1.4802	38.21	39.90	1.69
Diethyl ketone	$(C_2H_5)_2C(OH)—C\equiv C—CH=CH_2$	62	4	.8875	1.4800	42.82	44.17	1.35
Dipropyl ketone	$(n\text{-}C_3H_7)_2C(OH)—C\equiv C—CH=CH_2$	98–99	22	.8738	1.4745	52.05	53.44	1.39
Methyl octyl ketone	$CH_3(C_8H_{17})C(OH)—C\equiv C—CH=CH_2$	98–100	5	.8681	1.4734	65.91	67.26	1.35
Cyclopentanone	$(CH_2)_4C(OH)—C\equiv C—CH=CH_2$	104–105	7	1.0181	1.5228	40.62	(40.79)	(0.17)
Cyclohexanone	$(CH_2)_5C(OH)—C\equiv C—CH=CH_2$	84–85	2	0.9742	1.5169	45.24	46.57	1.33
Acetophenone	$CH_3(C_6H_5)C(OH)—C\equiv C—CH=CH_2$	125–126	4	m. p. 40–41°				

tory funnel, and condenser was slowly added 20.8 g. of vinylethinylmethylcarbinol. The flask was warmed on a water-bath to start the reaction, after which it proceeded vigorously. After two hours, the condenser was replaced by a distilling column and the contents of the flask distilled *in vacuo*. Divinylacetylene distilled from the mixture and collected in a trap surrounded by solid carbon dioxide and acetone. The divinylacetylene was not further purified, but was converted into the hexabromide. The melting point of this hexabromide was identical with that of the hexabromide from a known sample of divinylacetylene. The melting points were as follows

Hexabromide from above synthesis	m. p. 105–106°
Hexabromide from known sample of divinylacetylene	104–106°
Mixed m. p.	105–106°

Polymerization of the Carbinols.—The behavior of vinylethinylmethylethylcarbinol is typical of the tertiary carbinols. On standing in a stoppered bottle its viscosity increased very rapidly during the first few days, and at the end of a week the product was a thick, colorless, transparent sirup. After three weeks it had set to a tough, elastic, rather rubber-like mass which still contained a considerable proportion of unchanged carbinol. After six weeks it had changed to a very hard, translucent mass.

Fifty grams of vinylethinylmethylethylcarbinol containing 0.5 g. of benzoyl peroxide was exposed to a Cooper–Hewitt light (mercury arc in glass). The product obtained after seventy-two hours was a hard, transparent, pale yellow, glass-like resin. It was insoluble in the common organic solvents. When heated it softened somewhat at 125 to 150°, but it did not liquefy completely even at much higher temperatures.

Twenty-five grams of the carbinol containing 0.25 g. of benzoyl peroxide was exposed to a 150-watt Mazda light. In four days a product similar to that described in the preceding example was obtained.

Twenty-five grams of the carbinol containing 0.25 g. of uranyl nitrate was exposed to a Cooper–Hewitt light. In seventy-two hours, a hard, transparent, amber-colored resin was obtained. When no catalyst was present under the same conditions, the transformation to a hard resin required about one week.

A sample of vinylethinylmethylethylcarbinol was heated for several hours at 100° while a slow stream of air was bubbled through it. The product was a brown sirup. At room temperature it solidified to a brittle resin which dissolved readily in the common organic solvents.

Summary

Sodium vinylacetylide obtained by the action of sodium or of sodamide on vinylacetylene is a very reactive white powder which shows a tendency to ignite spontaneously in the air. Under properly controlled conditions it is a convenient reagent for introducing the vinylethinyl group into reactive organic compounds. Vinylethinylcarbinols are readily obtained by treating a mixture of vinylacetylene and a ketone with sodamide. The same method can also be applied to aldehydes but with less favorable results. Nine new carbinols prepared by this method are described.

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