

[CONTRIBUTION NO. 112 FROM THE EXPERIMENTAL STATION OF E. I. DU PONT DE NEMOURS & COMPANY]

## Acetylene Polymers and their Derivatives. VIII. $\alpha$ -Alkyl- $\beta$ -Vinylacetylenes

BY RALPH A. JACOBSON AND WALLACE H. CAROTHERS

Vinylacetylene is a prolific source of new and interesting compounds. The present paper is concerned with homologs of vinylacetylene, which are readily accessible through the mediacy of sodium vinylacetylde.<sup>1</sup> Vinyl-ethynylmagnesium bromide reacts with very active alkyl halides such as triphenylchloromethane,<sup>2</sup> but not with simple alkyl halides. Sodium vinylacetylde on the other hand reacts almost explosively with simple alkyl halides. The reaction can be moderated, however, by employing low temperatures, and when the halide is cautiously added to the acetylde in liquid ammonia it proceeds smoothly and furnishes good yields of the  $\alpha$ -alkyl- $\beta$ -vinylacetylenes. Alkyl sulfates or sulfonates can be used with similar results. The properties of alkyl vinylacetylenes obtained by these methods are indicated in Table I. The compounds are colorless liquids with characteristic odors. On standing they slowly polymerize, yielding viscous, yellow sirups.

TABLE I  
PHYSICAL PROPERTIES OF  $\text{CH}_2=\text{CH}-\text{C}\equiv\text{C}-\text{R}$

Nature of R	B. p., °C.	$d_4^{20}$	$n_D^{20}$	$M_R$ calcd.	$M_R$ found	Exaltation
$\text{CH}_3$	59.2 at 760 mm.	0.7401	1.4496	22.82	23.94	1.12
$\text{C}_2\text{H}_5$	84.5–85.3 at 758 mm.	.7492	1.4522	27.44	28.82	1.38
$n\text{-C}_4\text{H}_9$	62–63 at 61 mm.	.7830	1.4592	36.68	37.71	1.03
$n\text{-C}_7\text{H}_{15}$	74.5 at 9 mm.	.7962	1.4606	50.53	51.65	1.12

### Experimental Part

**1-Methyl-2-vinylacetylene.**—A one-liter, 3-necked flask was fitted with a mercury-sealed stirrer, a dropping funnel, and an exit tube. The exit tube was connected to a vertical condenser which in turn led to a gas-washing train consisting of an empty bottle, a second bottle containing water, and a third containing 10% sulfuric acid. The exit tube from the latter was connected to a calcium chloride drying tower and this in turn led to a receiver immersed in a Dewar flask maintained at  $-78^\circ$ .

To a solution of 104 g. of vinylacetylene in 600 cc. of liquid ammonia was slowly added 58.5 g. (1.5 moles) of powdered sodamide. The mixture was stirred for three hours and then concentrated to approximately 300 cc. by evaporating the ammonia in a current of nitrogen; 189 g. (1.5 moles) of dimethyl sulfate was added slowly through the separatory funnel. The reaction was very vigorous and about four hours were required for the addition. The ammonia was allowed to evaporate and the reaction flask was finally heated on a water-bath. Part of the 1-methyl-2-vinylacetylene collected in the first bottle and part in the second. The portions were combined, dried over calcium chloride, and distilled. Some low-boiling material came over first and then 37.6 g. (38%) of 1-methyl-2-vinylacetylene was collected. It was a colorless, volatile liquid possessing a powerful hydrocarbon odor somewhat similar to that of vinylacetylene.

(1) Carothers and Jacobson, *THIS JOURNAL*, **55**, 1097 (1933).

(2) Carothers and Berchet, *ibid.*, **55**, 1094 (1933).

*Anal.* Calcd. for  $C_6H_8$ : C, 90.91; H, 9.09. Found: C, 90.97; H, 8.63. Mol. wt. calcd.: 66. Found: 66.1, 66.3 (cryoscopic, benzene).

**1-Ethyl-2-vinylacetylene.**—A solution of 104 g. (1.5 moles) of vinylacetylene in 500 cc. of liquid ammonia was treated with 58.5 g. (1.5 moles) of powdered sodamide as in the preceding experiment. After three hours, 231 g. of diethyl sulfate was added slowly through the dropping funnel. The mixture was allowed to stand overnight while the ammonia evaporated. Water was added to the reaction flask and the upper layer, weighing 51 g., was separated. After drying with calcium chloride, the liquid was distilled. A small amount of low-boiling liquid came over first, after which 37 g. of 1-ethyl-2-vinylacetylene distilled. The product was a colorless liquid with an odor similar to that of 1-methyl-2-vinylacetylene.

*Anal.* Calcd. for  $C_6H_8$ : C, 90; H, 10. Found: C, 89.47, 89.73; H, 10.20, 9.44. Mol. wt. calcd.: 80. Found: 78.4, 79.5 (cryoscopic, benzene).

1-Ethyl-2-vinylacetylene was also prepared by treating sodium vinylacetylide with ethyl *p*-toluenesulfonate according to the method recently employed by Truchet:<sup>3</sup> 58.5 g. (1.5 moles) of sodamide was slowly added to a solution of 104 g. of vinylacetylene in 200 cc. of butyl ether at  $-10^\circ$  and the mixture was stirred for three hours. A solution of 300 g. (1.5 moles) of ethyl *p*-toluenesulfonate in 200 cc. of butyl ether was then added drop by drop during several hours. The thick mixture was heated in a water-bath at  $80^\circ$  for three hours and allowed to stand overnight. Water was added but such a troublesome emulsion formed that the mixture was set aside for twenty-four hours in a separatory funnel. The ether layer was separated, dried with calcium chloride, and distilled. A considerable quantity of low-boiling material first distilled, and then a fraction weighing 45 g. and boiling at  $78-88^\circ$  was collected. Upon redistillation 28.5 g. (23.7%) of 1-ethyl-2-vinylacetylene boiling at  $84-85^\circ$  was obtained. Of the two methods of preparing this compound, the first was the better.

**1-Butyl-2-vinylacetylene.**—A solution of 100 g. of vinylacetylene in 400 cc. of liquid ammonia was treated with 39 g. (1 mole) of powdered sodamide. After three hours, 137 g. (1 mole) of butyl bromide was slowly dropped into the solution during about four hours. The mixture was allowed to stand overnight, water was added, and the upper layer separated. The liquid was dried with calcium chloride and distilled. The product was a colorless liquid with a characteristic hydrocarbon-like odor. The liquid polymerized during the course of three months to a yellow viscous sirup.

*Anal.* Calcd. for  $C_8H_{12}$ : C, 88.88; H, 11.12. Found: C, 88.65; H, 10.76. Mol. wt. Calcd.: 108. Found: 103, 104 (cryoscopic, benzene).

**1-Heptyl-2-vinylacetylene.**—A solution of 75 g. of vinylacetylene in 400 cc. of liquid ammonia was treated with 39 g. (1 mole) of powdered sodamide. After three hours, 150 g. (0.84 mole) of heptyl bromide was slowly added during four hours. The mixture was allowed to stand overnight, water was added, and the upper layer (128 g.) separated. After drying with calcium chloride, the liquid was distilled; 101 g. of 1-heptyl-2-vinylacetylene was collected. Based on the heptyl bromide used, the yield was 80% of the theoretical. On standing for two months the liquid polymerized to a yellow viscous sirup.

*Anal.* Calcd. for  $C_{11}H_{18}$ : C, 88.00; H, 12.00. Found: C, 87.65, 87.51; H, 11.55, 11.81. Mol. wt. Calcd.: 150. Found: 143, 145 (cryoscopic, benzene).

### Summary

Sodium vinylacetylide reacts with alkyl halides, sulfates, or sulfonates, yielding  $\alpha$ -alkyl- $\beta$ -vinylacetylenes. Compounds of the formula  $CH_2=$

(3) Truchet, *Compt. rend.*, **191**, 854 (1930).

$\text{CH}-\text{C}\equiv\text{C}-\text{R}$  are described in which R is methyl, ethyl, *n*-butyl and *n*-heptyl.

WILMINGTON, DELAWARE

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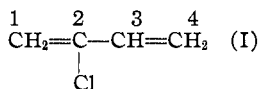
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## Acetylene Polymers and their Derivatives. IX. 1-Alkyl-2-chloro-1,3-butadienes and their Polymers (Fourth Paper on New Synthetic Rubbers)

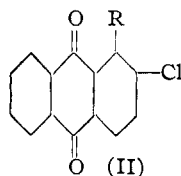
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Chloroprene (I) polymerizes very rapidly to form a rubber-like product of excellent quality.<sup>1</sup>



Replacement of the hydrogen at the 3-position by methyl does not appreciably affect the rate of spontaneous polymerization, but the rubber-like product is somewhat deficient in extensibility.<sup>2</sup> On the other hand, the introduction of methyl at both the 3- and the 4-positions greatly diminishes the tendency to polymerize, and the product, although highly extensible, is lacking in resilience.<sup>2</sup>

The present paper is concerned with chloroprenes in which a hydrogen in the 1-position has been replaced by alkyl. These compounds are readily obtained by the action of hydrogen chloride on the corresponding  $\alpha$ -substituted vinylacetylenes. The latter have already been described.<sup>3</sup> Doubtless because of their lesser solubility in water they react more slowly with aqueous hydrochloric acid than does the parent hydrocarbon, which reacts practically completely when shaken for five hours at room temperature with two moles of concentrated hydrochloric acid containing cuprous chloride.<sup>4</sup> Under the same conditions  $\alpha$ -methylvinylacetylene is less than 40% utilized. Reaction of the higher homologs is still slower, so that elevated temperature was needed for the butyl compound, and the heptyl compound required the addition of alcohol to function as a solvent.



The physical properties of the new homologs of chloroprene are indicated in Table I. They are colorless liquids with characteristic odors. Like chloroprene, they react with  $\alpha$ -naphthoquinone to form addition products, which are readily oxidized to  $\alpha$ -alkyl- $\beta$ -chloroanthraquinones (II), and their identity is established by this reaction.

(1) Carothers, Williams, Collins and Kirby, *THIS JOURNAL*, **53**, 4203 (1931).

(2) Carothers and Coffman, *ibid.*, **54**, 4071 (1932).

(3) Jacobson and Carothers, *ibid.*, **55**, 1622 (1933).

(4) Carothers, Berchet and Collins, *ibid.*, **54**, 4066 (1932).