

distillation. The pH titrations were carried out as described for pyridine bases.³

(3) A. Gero and J. J. Markham, *J. Org. Chem.*, **16**, 1835 (1951).

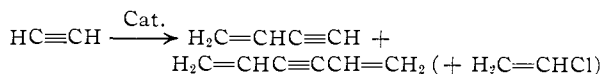
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The Preparation of Vinylacetylene

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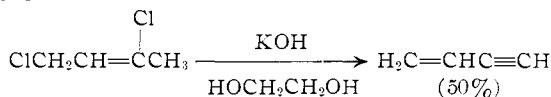
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Several methods for the preparation of vinylacetylene have been reported. Perhaps the best known of these methods is the dimerization of acetylene discovered by Nieuwland.²



Not only is this method inconvenient as a laboratory procedure, but it also suffers from the difficulty that appreciable amounts of divinylacetylene, formed as a by-product, must be eliminated before the vinylacetylene may be safely employed. It is also difficult to remove small amounts of vinyl chloride contaminating the product. Other methods reported^{3a,b} are also not readily adapted to laboratory synthesis.

We have found that the preparation of vinylacetylene by the dehydrohalogenation of 1,3-dichloro-2-butene using potassium hydroxide in ethylene glycol offers a number of advantages for a laboratory scale preparation since it is a one-step process, all the starting materials are readily available, the yields of pure vinylacetylene are better than 50% and there are no hazardous or difficulty-removed by-products.



The apparatus for the dehydrohalogenation is arranged as follows. A 2-l., three-necked flask, heated by means of a Carbowax bath, is equipped with a motor-driven, oil-sealed stirrer, a bulb reflux condenser and a 250-ml. dropping funnel. The dropping funnel is connected to the flask by means of a side-arm test-tube with the end removed. This side-arm is connected through a calcium chloride drying tube and a bubbler to a nitrogen tank.

The top of the condenser is connected to a horizontal tube (ca. 2 × 25 cm.) partially filled with calcium chloride. This in turn is connected to a 100-ml. graduated cylinder immersed in an acetone-Dry Ice mixture. The cylinder is also equipped with an escape tube which is protected by a calcium chloride drying tube.

A typical preparation of vinylacetylene is carried out as follows. Four hundred grams of powdered technical potassium hydroxide flakes is placed in the flask and 500 ml. of ethylene glycol is added. This mixture is stirred vigorously while adding 100 ml. of *n*-butyl cellosolve. The system is swept with a rapid stream of nitrogen for 15–20 minutes while the temperature of the wax-bath is raised to 165–170°. The flow of nitrogen is then reduced to a rate just sufficient to maintain an atmosphere of nitrogen in the system.

(1) General Tire and Rubber Co. Fellow, 1952–1954.

(2) J. A. Nieuwland, W. S. Calcott, F. B. Downing and A. S. Carter, *THIS JOURNAL*, **53**, 4197 (1931).

(3) (a) R. Willstätter and T. Wirth, *Ber.*, **46**, 535 (1913); (b) W. J. Croxall and J. O. Van Hook, U. S. Patent 2,623,077 (Dec. 23, 1952, to Rohm & Haas Co.); *THIS JOURNAL*, **76**, 1700 (1954).

One hundred twenty-five grams (1.0 mole) of 1,3-dichloro-2-butene is then added from the dropping funnel at a rate of about three drops per second. The addition should be complete in less than an hour. During the addition the temperature of the wax-bath is maintained at 165–170° and the reaction mixture is stirred vigorously. Heating is continued for one hour after the addition of dichlorobutene is complete.

The yields of crude product obtained in typical runs were 39–42 ml. (31.2–33.6 g.,⁴ 60–64.7%). The product was purified by distillation through a Davis low temperature column to yield 37–40 ml. (56.9–61.6%) of vinylacetylene, b.p. 0–6°.

The vinylacetylene was identified by formation of the silver salt, using ammoniacal silver nitrate, and by conversion to ethylvinylacetylene, b.p. 83–84°, *n*_D²⁰ 1.4515, *d*₄²⁰, 0.7536, 35% yield, using the method of Jacobson and Carothers,⁵ lit.⁴ *n*_D²⁰ 1.4522, *d*₄²⁰ 0.7492.

(4) Calculated on basis of *d*²⁰ 0.80, extrapolated from data at higher temperatures; K. Kuchinskaya and Anitima, *Khim. Referat. Zhur.*, **2**, 65 (1939) (*C. A.*, **34**, 2783⁷ (1940)).

(5) R. A. Jacobson and W. H. Carothers, *THIS JOURNAL*, **55**, 1622 (1933).

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The Preparation of 1-C¹⁴-Labeled Glucose, Mannose and Fructose¹

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As no convenient method has been described for the direct synthesis of 1-C¹⁴-labeled fructose, the authors have used a procedure, based upon the cyanohydrin method of Isbell, *et al.*,⁴ to prepare this sugar on a millimole scale in addition to 1-labeled glucose and mannose. This was achieved by epimerization of a mixture of the labeled aldoses in phosphate buffer. As no carrier was added at any stage of the reaction or purification the specific activity of the hexoses was equal to that of the starting cyanide.

The procedure of Isbell, *et al.*, was simplified by omitting the separation of the epimeric gluconic acid and γ -mannolactone, thus obtaining, after reduction, a mixture of glucose and mannose instead of the individual sugars. Such a mixture is suitable for epimerization as it theoretically yields the same ratio of glucose, mannose and fructose as does any one of the pure sugars. After epimerization the products were separated and purified chromatographically.

Experimental

C¹⁴-Labeled BaCO₃ was converted to KC¹⁴N,⁵ and then to NaC¹⁴N by distillation of the regenerated HC¹⁴N into NaOH. The reaction between D-arabinose and NaC¹⁴N was carried out in the presence of CaCl₂ by the procedure of Isbell, *et al.* The resultant mixture of epimeric hexonic acids was converted by slow concentration in methyl cellosolve to the corresponding lactone mixture, and this sirup was reduced directly by sodium amalgam in oxalate buffer to yield glucose and mannose. Isbell's procedure was then followed until the deionized sugar solution was collected from the

(1) This work was supported in part by a research contract with the U. S. Atomic Energy Commission.

(2) Rockefeller Foundation Research Fellow.

(3) Chercheur qualifié F.N.R.S.

(4) H. S. Isbell, J. V. Karabinos, H. L. Frush, N. B. Holt, A. Schwebel and T. T. Galkowski, *J. Research Natl. Bur. Standards*, **48**, 163 (1952).

(5) J. A. McCarter, *THIS JOURNAL*, **73**, 483 (1931).