

proximately -70° in a Dry Ice-acetone-bath, resulting in a considerable increase in viscosity and the separation of a white solid. To this well-stirred suspension was added over a period of thirty minutes a total of 60 g. (0.50 mole) of II in 100 ml. of absolute ether, the process being accompanied by separation of a dense white sludge. After all the acid chloride had been added, the mixture was stirred for one hour at -70° . The cooling bath was then removed, and 150 ml. of water added dropwise to the cold solution, with stirring, over a period of an hour. During this decomposition step, the temperature gradually rose to the reflux point of the solvent.

The ether was then distilled off, and the residue steam distilled until about 250 ml. of distillate had been collected. The organic layer was then separated with the aid of a little ether, and the aqueous layer extracted with the ether previously distilled from the reaction mixture. The combined ether phases were dried over anhydrous sodium sulfate, the ether evaporated on the steam-bath, and the residue distilled through a short Vigreux column; yield of ketone I, 32.3 g. (66%); b. p. 134-136 $^{\circ}$, n_D^{20} 1.4283; semicarbazone, colorless plates from diluted ethanol, m. p. 148-149 $^{\circ}$ (lit. value,¹⁸ 148-149 $^{\circ}$).

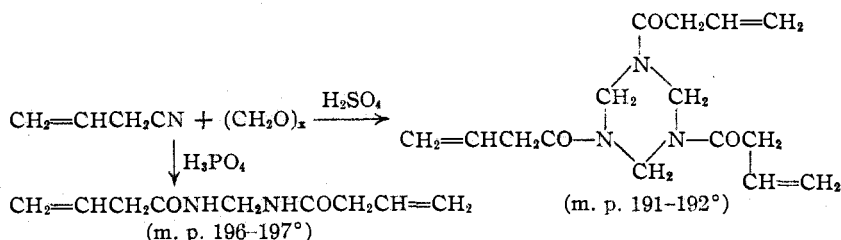
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF ROCHESTER
ROCHESTER 3, NEW YORK

RECEIVED JUNE 14, 1950

The Acid-Catalyzed Reaction of Formaldehyde with Allyl Cyanide

BY CHARLES C. PRICE AND I. V. KRISHNAMURTI¹

A study of the reaction of formaldehyde with allyl cyanide, intended to parallel that with allyl chloride,² revealed that the acid-catalyzed reaction led almost exclusively to the condensation of formaldehyde with the cyanide group rather than the carbon-carbon double bond, as is reported for methallyl cyanide using 50% sulfuric acid.³ The reaction is therefore a new example of the condensation of the nitrile group with formaldehyde recently described by Gradsten and Pollock⁴ as leading to triacylhexahydrotriazines.



Both the *tris*-vinylacetyltriazine and the methyl-ene-*bis*-vinylacetamide were hydrogenated to the corresponding butyryl derivatives and hydrolyzed to produce butyric acid.

Experimental⁵

Preparation of Allyl Cyanide.—A mixture of 680 cc. (10 moles) of allyl alcohol, 845 g. (10.5 moles) of cuprous cyanide and 1000 cc. of concentrated hydrochloric acid was charged into a 5-l., three-necked flask fitted with a mercury-sealed stirrer and a 90-cm. bulb condenser. The

mixture was vigorously stirred. Within half an hour reaction set in and allyl chloride started refluxing vigorously. When necessary the flask was cooled in a bath of ice-water and stirring discontinued temporarily. In 15 minutes the reaction was over. A dark colored liquid was produced, presumably a complex between allyl cyanide and cuprous chloride. The condenser was set downward for distillation. The flask was heated by a Glas-col heating mantle. Most of the distillate came over between 90 and 92 $^{\circ}$. When the temperature reached 95 $^{\circ}$ distillation could be stopped without affecting the yield. The distillate was transferred to a 2-l. separatory funnel and the upper organic layer was separated. It was dried over anhydrous potassium carbonate and redistilled to yield 500-510 g. (75%) of the allyl cyanide boiling between 116-121 $^{\circ}$, n_D^{20} 1.4060, d_4^{20} 0.8318.

Reaction of Allyl Cyanide and Paraformaldehyde in the Presence of Concentrated Sulfuric Acid as Catalyst.—A mixture of 68 g. (1 mole) of allyl cyanide and 31 g. (1 mole) of paraformaldehyde and 0.5 g. of concentrated sulfuric acid was charged into a 300-cc., two-necked flask fitted with mercury-sealed stirrer and condenser. The mixture was stirred vigorously and refluxed for one hour. Most of the paraformaldehyde sublimed into the condenser. After 1 g. of sodium acetate was added to the clear yellow liquid left in the flask, the liquid was distilled at 20 mm. to remove the unreacted allyl cyanide (50 g.). The residue was dissolved in the minimum of boiling alcohol. Cooling the alcoholic solution yielded about 5 g. of a white crystalline solid. After two recrystallizations from hot water, it melted at 191-192 $^{\circ}$. It proved to be identical with the compound prepared from allyl cyanide and trioxane with sulfuric acid as catalyst following the method of Gradsten and Pollock³ for the preparation of triacylhexahydrotriazines, in this case, *tris*-vinylacetylhexahydro-*s*-triazine. It readily dissolved in boiling water, hot alcohol and chloroform. It decolorized aqueous permanganate and 5% bromine in carbon tetrachloride. It dissolved readily in strong hydrochloric acid.

Anal. Calcd. for $(\text{C}_8\text{H}_7\text{ON})_3$: N, 14.62; mol. wt., 291. Found: N, 14.44; mol. wt. (ebullioscopic method in chloroform), 287.

Quantitative Hydrogenation of *Tris*-vinylacetylhexahydro-*s*-triazine.—The hexahydro-*s*-triazine was subjected to quantitative catalytic hydrogenation in the presence of 10% palladium-on-charcoal. A 0.4580-g. sample of the substance dissolved in about 25 cc. of 95% ethanol absorbed 104 cc. of hydrogen under standard conditions of temperature and pressure. This corresponds to 0.98 mole of hydrogen for every $\text{C}_8\text{H}_7\text{ON}$ or 2.94 moles of hydrogen for $(\text{C}_8\text{H}_7\text{ON})_3$.

Hydrolysis of *Tris*-butyrylhexahydro-*s*-triazine.—The *tris*-butyrylhexahydro-*s*-triazine was prepared by reducing the corresponding vinylacetyl compound with hydrogen at an initial pressure of 60 lb. in the presence of 10% palladium-on-charcoal as catalyst.

Ten grams of the *tris*-butyrylhexahydro-*s*-triazine was refluxed with 30 cc. of 20% sodium hydroxide for four hours by which time ammonia ceased to be evolved. The cooled solution was acidified to congo red with 50% sulfuric acid and extracted with 100 cc. of ether. The dried extract was distilled to remove the solvent. Distillation of the residue gave 6 g. of butyric acid, b. p. 161-162 $^{\circ}$, n_D^{20} 1.3982.

Reaction of Allyl Cyanide and Paraformaldehyde in 85% Phosphoric Acid Medium.—A mixture of 68 g. of allyl cyanide, 31 g. of paraformaldehyde and 10 cc. of 85% phosphoric acid was charged into a three-necked flask, provided with a mercury-sealed stirrer and a condenser. The mixture was stirred on a water-bath at 60 $^{\circ}$. The paraformaldehyde dissolved slowly and a clear solution was formed in half an hour. After 30 more minutes, the

(1) Abstracted from a portion of the Ph.D. dissertation submitted to the Graduate School by I. V. Krishnamurti.

(2) Price and Krishnamurti, *THIS JOURNAL*, **72**, 5335 (1950).

(3) Arundale, U. S. Patent 2,384,268 [C. A., **40**, 613 (1946)].

(4) Gradsten and Pollock, *THIS JOURNAL*, **70**, 3079 (1948).

(5) Analyses by Micro-Tech Laboratories, Skokie, Ill.

