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^{26} p 1.4283; semicarbazone, colorless plates from diluted ethanol, m. p. $148-149^\circ$ (lit. value, ^{is} $148-149^\circ$).

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.

$$CH_{2}=CHCH_{2}CN + (CH_{2}O)_{x} \xrightarrow{H_{2}SO_{4}} CH_{2}=CHCH_{2}CO-N \xrightarrow{N-COCH_{2}} CH_{2}=CHCH_{2}CO-N \xrightarrow{N-COCH_{2}} CH_{2}=CHCH_{2}CH_{$$

CH₂=CHCH₂CONHCH₂NHCOCH₂CH=CH₂ (m. p. 196–197°)

Both the *tris*-vinylacetyltriazine and the methylene-*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 5-1., three-necked flask fitted with a mercury-sealed stirrer and a 90-cm. bulb condenser. The

- (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.

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°. When the temperature reached 95° distillation could be stopped without affecting the yield. The distillate was transferred to a 2-1. 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°, π^{20} 1.4060, d^{24} , 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°. 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 Pollock⁸ for the preparation of triacylhexahydrotriazines, in this case, tris-vinylacetylhexahydro-s-triazine. It readily dissolved in boiling water, hot alcohol and chloro-form. It decolorized aqueous permanganate and 5% bromine in carbon tetrachloride. It dissolved readily in strong hydrochloric acid.

Anal. Calcd. for $(C_6H_7ON)_3$: 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 ab-

COCH2CH=CH2

Ń.

sorbed 104 cc. of hydrogen under standard conditions of temperature and pressure. This corresponds to 0.98 mole of hydrogen for every C_8H_7ON or 2.94 moles of hydrogen for (C_6H_7ON)₃.

of hydrogen for (C₆H₇ON)₃. Hydrolysis of Tris-butyrylhexahydro-s-triazine.—The trisbutyrylhexahydro-s-triazine was prepared by reducing the corresponding vinylacetyl compound with hydrogen at an initial pres-

sure 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^{20} D 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°. The paraformaldehyde dissolved slowly and a clear solution was formed in half an hour. After 30 more miautes, 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).

liquid was poured into 300 cc. of ice-water with stirring. The separated white crystalline solid and the liquid was allowed to stand in a refrigerator overnight. The solid (20 g.) was collected and recrystallized from boiling water. After two recrystallizations, it melted at 196-197°. Its properties corresponded to methylene-bis-vinylacetamide.

Anal. Calcd. for C₉H₁₄O₂N₂: C, 59.32; H, 7.74; N, 15.38; mol. wt., 182. Found: C, 59.34; H, 8.00; N, 15.06; mol. wt. (ebullioscopic method in chloroform), 184.

The acid solution was extracted thrice with 300-cc. portions of ether. The dried ether extract on distillation gave 16 g. of allyl cyanide and a small amount of vinylacetic acid, b. p. $73-74^{\circ}$ (15 mm.), n^{20} 1.4224. These values agree with the ones reported in the literature. A few grams of tarry residue was left behind. An additional 8 g. of

the methylene-bis-vinylacetamide was obtained by extracting the phosphoric acid solution with chloroform.

The methylene-bis-vinylacetamide dissolved in boiling water, hot alcohol and chloroform. It readily dissolved in strong hydrochloric acid and was reprecipitated on dilution. Refluxing the hydrochloric acid solution of the compound for one hour and treating the resulting liquid with 2,4-dinitrophenylhydrazine solution gave a yellow precipitate of formaldehyde-2,4-dinitrophenylhydrazone, m. p. 166.0-166.4°.

Quantitative Hydrogenation of Methylenebis-vinylacetamide.—Catalytic hydrogenation of the methylene-bis-vinylacetamide in 95%

ethanol solution was carried out at atmospheric pressure, using palladium-charcoal as catalyst. A 0.3774-g. sample of methylene-bis-vinylacetamide adsorbed 94 cc. of hydrogen under standard conditions. This corresponds to 2.02 moles of hydrogen for every mole of the methylenebis-amide.

Saponification of Methylene-bis-butyramide.—The methylene-bis-butyramide was prepared by the catalytic hydrogenation of methylene-bis-vinylacetamide with palladium-charcoal as catalyst.

Ten grams of methylene-bis-butyramide was refluxed with 40 cc. of 20% aqueous sodium hydroxide for four hours. The amide dissolved very slowly. When the evolution of ammonia ceased, the cooled solution was neutralized to congo red with 50% sulfuric acid and extracted twice with 100-cc. portions of ether. The residue from the dried extract gave on distillation 3.5 g. of butyric acid, b. p. 161-162°, n^{20} p 1.3982. Bromination of Methylene-bis-vinylacetamide.—Five

Bromination of Methylene-bis-vinylacetamide.—Five grams of methylene-bis-vinylacetamide was dissolved in just enough chloroform and 5% bromine in carbon tetrachloride was added with shaking until the color of bromine persisted. The bromine addition compound precipitated. It was recrystallized from absolute alcohol, m. p. 147.0-147.4°.

Anal. Calcd. for $C_9H_{14}O_2N_2Br_4$: N, 5.58; Br, 63.69. Found: N, 5.39; Br, 58.54.

DEPARTMENT OF CHEMISTRY

UNIVERSITY OF NOTRE DAME

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The Reaction of Formaldehyde with Allyl Chloride

By Charles C. Price and I. V. Krishnamurti¹

The condensation of methylallyl chloride with formaldehyde in 50% sulfuric acid at 50° was reported by Arundale and Mikeska² to produce

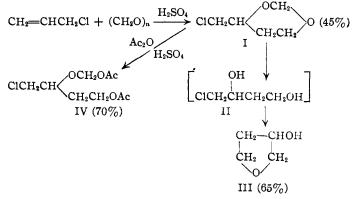
(1) Abstracted from a portion of the Ph.D. dissertation submitted to the Graduate School by I. V. Krishnamurti.

(2) Arundale and Mikeska, U. S. Patent 2,296,375 [Oct. 12, 1939].

Notes

4-methyl-4-chloromethyl-1,3-dioxane in 76% yield. No details were reported for the reaction with allyl chloride but it has now been shown that by operating with concentrated sulfuric acid at 0° it is possible to effect a similar condensation.

Attempts to replace the chlorine atom of the resulting 4-chloromethyl-1,3-dioxane (I) by cyanide or iodide failed; starting material was recovered unchanged.



Hydrolysis to eliminate formaldehyde produced the chloroglycol (II) which, however, spontaneously eliminated hydrogen chloride to form 3-hydroxytetrahydrofuran (III). Acetolysis cleaved the ring to give an oxydiacetate (IV) without elimination of formaldehyde.

Experimental³

4-Chloromethyl-1,3-dioxane.—A mixture of 300 g. of paraformaldehyde and 180 cc. of concentrated sulfuric acid was stirred in a 3-1, three-necked flask provided with a mercury-sealed stirrer and condenser while 480 cc. of allyl chloride was added drop-wise. The flask was cooled initially in a bath of ice-water. After about half the amount of allyl chloride had been added, the addition could be made much more rapidly. The whole operation occupied 1.5 hours. The stirring was continued for half an hour more when a wine-colored liquid was obtained. It was poured with stirring into 1.5 1. of ice-water. The heavy organic layer was separated, washed with 200 cc. of 5% potassium carbonate solution and dried over anhydrous sodium sulfate.

The acid solution was extracted twice with 200-cc. portions of ether. The ether solution was washed with 10 cc. of 5% potassium carbonate solution and dried over anhydrous sodium sulfate. The ether was distilled off and the residual liquid was added to the main portion.

The organic liquid was distilled first at atmospheric pressure to remove the unreacted allyl chloride (75 cc.). Distillation was continued under reduced pressure (1 mm.), a stream of nitrogen being bubbled through the liquid. The main portion which came over above 45° was collected. Considerable decomposition appeared to take place, with copious amounts of hydrogen chloride and sulfur dioxide being evolved. A dark voluminous mass (some 100 g.) which crumbled to powder was left behind. The acid distillate (310-320 g.) was shaken with 200 cc. of 5% potassium carbonate solution, dried over anhydrous sodium sulfate and distilled under reduced pressure in an atmosphere of nitrogen. Some 300 g. (45%) of 4-chloromethyl-1,3-dioxane, b. p. 83-86° (20 mm.), was

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