

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 $C_8H_{14}O_2N_2$: 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° (15 mm.), n_D^{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 Methylene-bis-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 methylene-bis-amide.

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

Ten grams of methylene-bis-butylamide 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_D^{20} 1.3982.

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 $C_8H_{14}O_2N_2Br_4$: N, 5.58; Br, 63.69. Found: N, 5.39; Br, 58.54.

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The Reaction of Formaldehyde with Allyl Chloride

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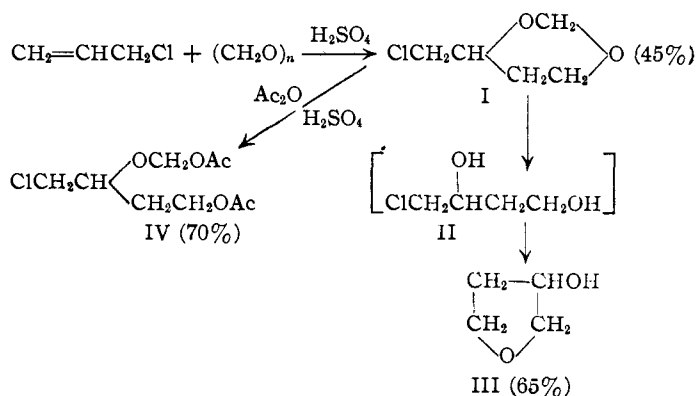
The condensation of methylallyl chloride with formaldehyde in 50% sulfuric acid at 50° was reported by Arundale and Mikeska² to produce

(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].

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-l., 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 l. 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.

collected: n_D^{20} 1.4632; d_4^{20} 1.2115; MR (obsd.), 31.05; MR (calcd.), 31.24.

Anal. Calcd. for $C_8H_9O_2Cl$: C, 43.92; H, 6.63; Cl, 25.93. Found: C, 43.76; H, 6.75; Cl, 25.88.

Hydrolysis of 4-Chloromethyl-1,3-dioxane.—A solution of 20 g. of 2,4-dinitrophenylhydrazine in 800 cc. of approximately 2 *N* hydrochloric acid was prepared and 14 g. of 4-chloromethyl-1,3-dioxane warmed with this solution on a steam-bath for one hour. A voluminous precipitate of formaldehyde-2,4-dinitrophenylhydrazone was formed. After recrystallization from alcohol this melted at 166° either alone or mixed with an authentic sample. The liquid was set aside at room temperature for three days for the precipitation to be complete. The precipitate was collected and the filtrate was made just alkaline with aqueous sodium hydroxide. The solution was evaporated to dryness on a steam-bath. The solids were extracted with 300 cc. of dry acetone, dried over anhydrous potassium carbonate and distilled to evaporate the solvent. The residue, which was colored red, was distilled under reduced pressure to yield 5 g. of a liquid, b. p. 50° (1 mm.); n_D^{20} 1.4486; d_4^{20} 1.090. It had an ether-like smell, was miscible with water, alcohol and ether and did not contain any chlorine. The physical properties agreed with those reported for 3-hydroxytetrahydrofuran. Parisiella⁴ reported the following physical constants: n_D^{18} 1.4478; d_4^{18} 1.07.

Anal. Calcd. for $C_4H_8O_2$: C, 54.53; H, 9.04. Found: C, 54.44; H, 9.14.

The phenylurethan was recrystallized twice from carbon tetrachloride and twice from 50% ethanol; m. p. 120.6° (lit.² m. p. 120°).

Preparation of 3-Hydroxytetrahydrofuran.—4-Chloromethyl-1,3-dioxane (137 g.), 100 cc. of absolute methanol and 18 g. of concentrated sulfuric acid were placed in a flask fitted with a 60-cm. air-condenser which was connected to another water-cooled condenser set downward for distillation. The flask was heated gently to allow the liquid to reflux very slowly. Methylal (b. p. 42°) started to collect in the receiver attached to the second condenser. After adding 35 g. of sodium acetate, the liquid was heated to boiling and filtered. The filtrate was distilled first at 20 mm. to remove the methyl alcohol and acetic acid. Further fractionation at 0.5 mm. yielded 40 g. of 3-hydroxytetrahydrofuran, b. p. 46–48° (0.5 mm.), and 25 g. of another liquid which was evidently the unstable 4-chloro-1,3-butylene glycol, b. p. 90–95° (0.5 mm.).

The second fraction was dehydrohalogenated to 3-hydroxytetrahydrofuran by refluxing for half an hour with 50 cc. of pyridine and 100 cc. of diisopropyl ether. The ether and the pyridine were removed by distillation. The residue was fractionated at 1 mm. The fraction boiling between 49–50° (16 g.) was collected.

Acetolysis of 4-Chloromethyl-1,3-dioxane.—Ten drops of concentrated sulfuric acid were added to a mixture of 68 g. of 4-chloromethyl-1,3-dioxane and 52 cc. of acetic anhydride. There was considerable heat evolved. The mixture was heated on a steam-bath for six hours and allowed to stand at room temperature overnight. It was then shaken with 2 g. of sodium acetate, filtered and distilled at 20 mm. Two principal fractions were collected, one up to 140° (20 g.) and the other between 140–142° (86 g.). The latter proved to be the diacetate of 2-oxa-3-chloromethyl-1,5-pentanediol: n_D^{20} 1.4474; n_D^{20} 1.196; MR (calcd.), 53.58; MR (obsd.), 53.38.

Anal. Calcd. for $C_8H_{15}O_5Cl$: C, 45.29; H, 6.34; Cl, 14.87; sapon. equiv., 119.4. Found: C, 45.34; H, 6.14; Cl, 14.80; sapon. equiv., 122.0.

The first fraction appeared to be a mixture of methylene diacetate, the diacetate of 4-chloro-1,3-butylene glycol and the diacetate of 2-oxa-3-chloromethyl-1,5-pentanediol.

Attempted Replacement of Chlorine.—Since the chloromethyl dioxane is a primary alkyl chloride, it was surprising to find it so resistant for replacement reactions. At-

tempts to replace the chlorine by cyanide using boiling alcoholic sodium cyanide, sodium cyanide in ethyl carbitol at 100° and cuprous cyanide in boiling benzene failed, since a major part of the starting material was recovered unchanged in each case. A similar result was obtained in attempting to replace the chlorine by iodine using sodium iodide in boiling acetone.

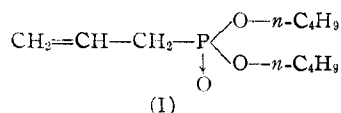
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Anomalous Reaction of Allyl Bromide with Sodium Dibutyl Phosphite

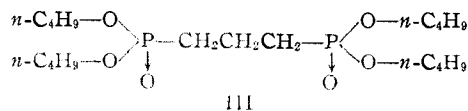
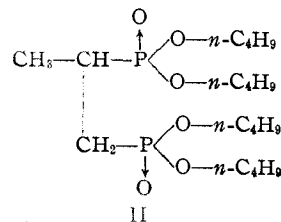
BY WALTER H. C. RUEGGEBERG, JACOB CHERNACK AND
IRA M. ROSE

During the course of preparation of some alkane dibutyl phosphonates from alkyl halides and sodium dibutyl phosphite, it was desired to prepare dibutyl-1-propene-3-phosphonate (I) from allyl bromide.



It has already been shown in the published literature by Kosolapoff¹ that the *n*-alkane phosphonic acid esters can be prepared in good yield by this type of reaction. However, when one mole of allyl bromide was added to one mole of sodium dibutyl phosphite in benzene solution, the reaction mixture yielded a high boiling compound which from analytical results was clearly one containing two phosphorus atoms per allyl unit.

It is believed that the compound formed is either propane bis-(dibutyl phosphonate)-1,2 (II) or propane bis-(dibutyl phosphonate)-1,3 (III).



Experimental

The apparatus used for the synthesis of the unexpected diphosphonic acid ester consisted of an all glass still equipped with a 1-l., 3-neck round-bottom flask as still kettle (bearing a dropping funnel and stirring device), a 24-inch column packed with 1/8-inch glass helices and a total reflux-partial take off fractionation head protected from atmospheric moisture by means of a calcium chloride trap. One mole of sodium methoxide (purity 98.5% obtained from the Mathieson Alkali Works) and 500 ml. of C. P. benzene were placed in the kettle and heated to re-

(1) Kosolapoff, *THIS JOURNAL*, **67**, 1180 (1945); U. S. Patent 2,397,422.

(4) Parisiella, *Ann. chim.*, [8] **24**, 367 (1911).