

Apparatus and Procedure.—The apparatus and procedure used were the same as those described previously.⁴ The product from the reaction was distilled and the various fractions were analyzed by means of infrared spectroscopy.

Nickel-Kieselguhr.—This catalyst was obtained from Harshaw Chemical Co. in 1/8 inch cylindrical pills. It contained 44% of nickel. Prior to use, it was reduced in a stream of hydrogen at 350°.

3,3-Dimethyl-1-butene was obtained by the pyrolysis of pinacolyl acetate. The latter was passed over glass wool in a nitrogen atmosphere at 400°. It distilled at 41.2–41.7°, n_{20}^D 1.3758.

(4) V. N. Ipatieff, F. J. Pavlik and H. Pines, *THIS JOURNAL*, **75**, 3179 (1953).

(5) J. P. Wibaut and A. J. van Pelt, Jr., *Rec. trav. chim.*, **87**, 1055 (1938); **60**, 55 (1941).

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The Product Derived from the Cyclization of Triglycine Azide

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In describing a new method for the synthesis of macrocyclic peptides we reported¹ the preparation from triglycine azide of a compound to which was assigned tentatively the structure cyclo-(triglycyl). Molecular weight determinations, which were incomplete at the time of the previous publication, have now shown the compound to be the dimer, cyclo-(hexaglycyl). The methods of freezing point depression and boiling point elevation failed to give reproducible molecular weight values, presumably due to the very low solubility of the compound under the conditions employed. An X-ray unit cell measurement² did not distinguish between the cyclo-(triglycyl) and cyclo-(hexaglycyl) possibilities.

However, by the method of isothermal distillation³ using water as the solvent and dextrose as the standard, a molecular weight of 344 was obtained [calcd. for cyclo-(hexaglycyl) 342.31]. Very recently cyclo-(hexaglycyl) was reported⁴ as a reaction product of the polymerization of N-carboxyglycine anhydride. At our request, Dr. C. H. Bamford kindly furnished a sample of his product for comparison. The infrared spectra (potassium bromide pellet) of the samples were superimposable over the range 2–15 μ . A mixed solubility study provided further evidence of identity. Dr. Bamford (private communication) informs us that his group has independently conducted a careful study of the nature of the products obtained by the two methods.

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(1) J. C. Sheehan and W. L. Richardson, *THIS JOURNAL* **76**, 6329 (1954).

(2) The authors are indebted to Prof. D. P. Shoemaker of this Department for the X-ray analysis.

(3) N. D. Cheronis, "Micro and Semimicro Methods of Techniques of Organic Chemistry," Vol. VI, edited by A. Weissberger, Interscience Publishers, Inc., New York, N. Y., 1954, pp. 228–229.

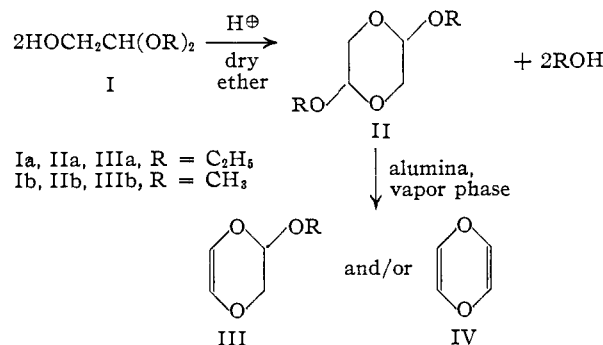
(4) D. G. H. Ballard, C. H. Bamford and F. J. Weymouth, *Proc. Royal Soc. (London)*, **227A**, 155 (1955).

Heterocyclic Vinyl Ethers. X. Dialkoxy 1,4-Dioxanes and Alkoxy 1,4-Dioxenes¹

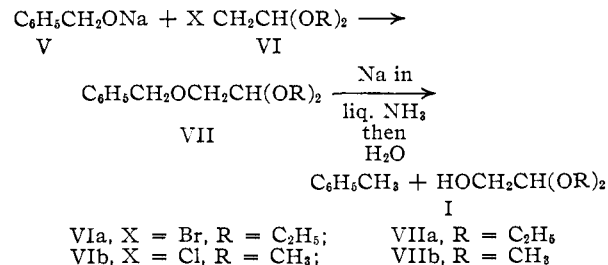
BY WILLIAM E. PARHAM AND HARRY E. REIFF

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In paper III² of this series, a preparation of 1,4-dithiadiene was reported which involved the dealcoxylation of 2,5-diethoxy-1,4-dithiane, which was in turn prepared by the acid-catalyzed condensation of two molecules of mercaptoacetaldehyde diethyl acetal. An investigation of the analogous reactions in the oxygen series appeared to be of interest, and the following reaction sequence has been examined.



Hydroxyacetaldehyde diethyl acetal (Ia) has been prepared previously by reaction of ethanolic potassium hydroxide with bromoacetal at elevated temperatures.³ However, variations in the published values for the refractive index and density of the product of this reaction^{3b} indicated that varying amounts of ethoxyacetaldehyde diethyl acetal were present. Furthermore, we have observed that treatment of chloroacetal with alcoholic potassium hydroxide at elevated temperatures affords a 70% yield of ethoxyacetaldehyde diethyl acetal. Since hydroxyacetaldehyde dialkyl acetals, free of other acetals, were required for the preparation of the dialkoxydioxanes IIa and b, the following reactions leading to these acetals were investigated. Reaction of sodium benzyloxide (V) and bromoacetal (VIa) or dimethylchloroacetal (VIb) afforded the corresponding benzyloxyacetaldehyde dialkyl acetals (VII) in yields of 75–82%. The benzyloxyacetals were cleaved smoothly with sodium in liquid ammonia to give pure hydroxyacetals in good yield.



(1) This work was supported by the Office of Ordnance Research, Contract No. D.A.-11-022-ORD-1716.

(2) W. E. Parham, H. Wynberg and F. L. Ramp, *THIS JOURNAL*, **75**, 2065 (1953).

(3) (a) A. Pinner, *Ber.*, **5**, 147 (1872). (b) W. H. Hartung and H. Adkins, *THIS JOURNAL*, **49**, 2520 (1927); F. Beyerstedt and S. M. McElvain, *ibid.*, **58**, 529 (1936); F. Krausz, *Ann. chim.*, [12], **4**, 811 (1949).