will have different effects upon the enzyme, the mechanism indicated by I, III, IV and V must be further enlarged. This leads to an expression for V which cannot be arranged in the form of 7. Thus a plot of V *vs.* pH may be asymmetrical if the pK of a buffer such as phosphate is in the same region as the activity curve. However, if the buffer concentration is high and one form has a sufficiently great affinity to displace the other, the V–pH curve may be symmetrical and the pK values would correspond to the enzyme saturated with the more strongly bound form of the buffer. Buffers of the uncharged-acid or uncharged-base types have the advantage over phosphate that the concentration of the ionized form of the buffer may be held constant over a wide range of pH.

Since enzymes are proteins it is to be expected, in general, that their properties will depend on the concentration and nature of salts in the solution and upon the pH. Although these effects may be too complicated to express by such simple mechanisms as those used here, the fact that the present equations are in good agreement with the results for fumarase is encouraging.

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NOTES

A Synthesis of 1-C^{14}-Labeled Diethyl Ether

BY JEROME G. BURTLE AND WILLIAM N. TUREK

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In the course of other work in this Laboratory, need arose for a sample of C^{14}-labeled diethyl ether. A search of the literature revealed that, although many preparations of ethyl ether are described,[1] no synthesis of the C^{14}-labeled compound could be found. Furthermore, no high yield procedure for small amounts (10–12 g. of product) which could be used directly for this purpose, came to light. It became imperative, therefore, for us to develop a satisfactory process for our own use.

Since it was necessary to label only one ethyl radical, it was decided to use the Williamson synthesis[2] as the basic reaction because it offered maximum economy of radioactive starting material. The procedure ultimately adopted as satisfactory for small batches was based on the experiments of Hunt[3] and of Beilstein[4] on ethyl iodide preparation, and those of Bishop[5] on the reaction of ethyl iodide with sodium ethoxide.[6]

From 11–12 g. of 95% ethanol-1-C^{14} (100 microcuries) 32.4 g. (87.6%) of ethyl-1-C^{14}-iodide boiling at 70–73° was obtained. Treatment of 26.4 g. of this material with sodium ethoxide gave 11.5 g. (92%) of 1-C^{14}-ethyl ether boiling at 33.5–34°.

(1) T. Saussune, *Ann. chim.*, [1] **89**, 273 (1814); J. L. Gay-Lussac, *ibid.*, [1] **95**, 311 (1815); Dumas and Boullay, *ibid.*, [2] **36**, 294 (1827); A. W. Williamson, *ibid.*, [3] **40**, 98 (1854); *Ann.*, **77**, 37 (1851); *ibid.*, **81**, 73 (1852); E. Erlenmeyer, *ibid.*, **162**, 380 (1872); A. W. Titherley, *J. Chem. Soc.*, **79**, 392 (1901).

(2) A. W. Williamson, *ibid.*, **4**, 229 (1852).

(3) B. E. Hunt, *ibid.*, **117**, 1592 (1920).

(4) R. Rieth and F. Beilstein, *Ann.*, **126**, 250 (1863).

(5) W. B. S. Bishop, *J. Soc. Chem. Ind.*, **43**, 23T (1924).

(6) The complete experimental details of this preparation have been deposited as Document number 4193 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting $1.25 for photoprints, or $1.25 for 35 mm. microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

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N-Cycloalkyl- and N,N-Polymethylenesulfamic Acids

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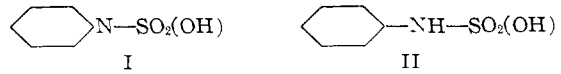
Since considerable quantities of hexa-, hepta- and octamethylenimine were available, it seemed desirable to prepare a few N,N-polymethylenesulfamic acids. These compounds are of interest since they are related to cycloalkylsulfamic acids. The sodium and calcium salt of N-cyclohexylsulfamic acid (Sucaryl or Cyclamate sodium or calcium) are important sweetening agents.[1] It is obvious that N,N-pentamethylenesulfamic acid (I) represents N-cyclohexylsulfamic acid (II) in which the nitrogen atom has been made a part of the ring structure.



I II

The N,N-polymethylenesulfamic acids were obtained by interaction of chlorosulfonic acid with pyrrolidine, hexamethylen-,[2] heptamethylen-[2] or octamethylenimine[2] by the general method used by Audrieth and Sveda[3] for the synthesis of N-cyclohexylsulfamic acid.

No sweet taste could be detected when the solid sodium salts of the N,N-polymethylenesulfamic acids were tested. Furthermore, no sweet taste

(1) *Ind. Eng. News*, **45**, No. 10, 11 (1953).

(2) L. Ruzicka, M. Kobelt, O. Häfliger and V. Prelog, *Helv. Chim. Acta*, **32**, 544 (1949).

(3) L. F. Audrieth and M. Sveda, *J. Org. Chem.*, **9**, 89 (1944).