124°); *p*-nitrobenzoate, m.p. 112–113° (lit. 114–115°); methiodide, m.p. 102–103° (lit. 103–104°). The benzyl bromide derivative was also prepared by reaction of the pyridine compound with an excess of benzyl bromide at room temperature. The crystalline derivative which separated was recrystallized twice from ethanol; m.p. 155–156°.

Anal. Calcd. for $C_{15}H_{18}NOBr$: C, 58.44; H, 5.89; N, 4.54. Found: C, 58.64; H, 5.95; N, 4.60.

2-Methyl-3-(β-ethoxyethyl)-4,6-dichloropyridine (II).—One-hundred and fifteen grams of 2-methyl-3-(β-ethoxyethyl)-4,6-dihydroxypyridine (I) was dissolved in 540 ml. of phosphorus oxychloride. The solution was heated in a glass-lined bomb nearly full for six hours at 140° under a nitrogen pressure of about 400 p.s.i. The excess phosphorus oxychloride was removed under reduced pressure and the residue was poured into an excess of crushed ice. No precipitate formed. The mixture was diluted, and partially neutralized with 30% sodium hydroxide solution to about *p*H 3. The solution was extracted several times with chloroform, which extract was washed, dried, and concentrated, leaving a brown, oily residue. It was distilled under reduced pressure; b.p. 96–97° (1 mm.). The yield of 2-methyl-3-(β-ethoxyethyl)-4,6-dichloropyridine (II) was 106 g. (90%).

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Concerning *trans*-Acylation in Azlactone Synthesis

BY SERGE N. TIMASHEFF AND F. F. NORD

Although it is considered that in the synthesis of azlactones[1] no *trans*-acylation occurs,[2] Bennett and Niemann have reported that in the preparation of some azlactones of fluorinated benzene they were able to detect products of *trans*-acylation by means of ultraviolet absorption analysis[3] and in one instance by isolation. These authors reported that in the product obtained some benzamido groups from the expected phenyloxazolone had become replaced by acetamido groups from the acetic anhydride in which medium the reaction is carried out.

Realizing the significance of such a *trans*-acylation in the recently reported synthesis of thiophene azlactones,[4] a similar study was carried out using the first member of this series, namely, 2-phenyl-4-(2-thenal)-5-oxazolone. The ultraviolet absorption spectra of both the crude phenyloxazolone and the purified material along with that of the methyl compound are presented in Fig. 1. It can be seen that the curves of the absorption spectra of the phenyloxazolone preparations are very similar, both possessing peaks at 270 and 394 mμ. The crude preparation displayed neither a peak nor a plateau in the region of 362–364 mμ, which is characteristic for the methyloxazolone. Thus, it can be concluded that in the case of the phenyloxazolone derived from thiophene-2-aldehyde[5] *via* the Erlenmeyer–Plöchl synthesis using acetic anhydride as the medium, no *trans*-acylation occurs.

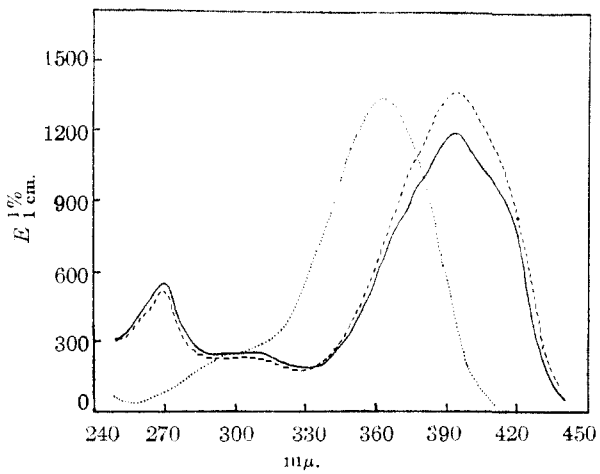

Fig. 1.—Ultraviolet spectra of thiophene azlactones: ....., methyloxazolone; - - - - - -, phenyloxazolone (purified); ——, phenyloxazolone (crude).

(1) J. Plöchl, *Ber.*, **16**, 2815 (1883); E. Erlenmeyer, *Ann.*, **275**, 1 (1893).

(2) J. W. Cornforth, "The Chemistry of Penicillin," Princeton University Press, Princeton, N. J., 1949, p. 733, 784.

(3) E. L. Bennett and C. Niemann, THIS JOURNAL, **72**, 1803 (1950).

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(5) W. J. King and F. F. Nord, *ibid.*, **13**, 635 (1948).

DEPARTMENT OF ORGANIC CHEMISTRY AND ENZYMOLOGY
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The Synthesis of DL-Aspartic Acid-4-C^{14} [1]

BY S. C. WANG, T. WINNICK AND J. P. HUMMEL

Aspartic acid, labeled in the carboxyl adjacent to the substituted methylene group, has been synthesized in one step from ethyl formylaminomalonate and methyl bromoacetate-1-C^{14} (purchased from Tracerlab, Inc.). The procedure required no special equipment. The yield of the purified product was 63%. The specific radioactivity was about 16,000 counts per minute per mg., starting from 0.025 mole of methyl bromoacetate containing 1 mc. of C^{14}.

The position of the labeling, already established by the method of synthesis, was further confirmed by the Van Slyke ninhydrin–carbon dioxide method. Both carboxyls of aspartic acid are ninhydrin-labile.

Attempts were also made to prepare aspartic acid by the reduction of ethyl oxalacetate-4-C^{14} oxime with sodium amalgam. Only a 42% yield was obtained in this reduction. The potassium salt, from which the oxime was made, was prepared in 87% yield from sodium acetate-1-C^{14} by converting the latter to ethyl acetate with diethyl sulfate and condensing the ethyl acetate with ethyl oxalate in the presence of potassium.

(1) For detailed descriptions order Document 3125 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting $1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $1.05 for photocopies (6 × 8 inches) readable without optical aid.

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The Structure of Ethylketene Dimer

BY R. L. WEAR

The structure of alkylketene dimers, prepared by the dehydrohalogenation of acyl halides, continues to be of interest.[1,2]

(1) C. D. Hurd and C. A. Blanchard, THIS JOURNAL, **72**, 1461 (1950).

(2) J. D. Roberts, R. Armstrong, R. F. Trimble, Jr., and M. Burg, *ibid.*, **71**, 843 (1949).