$CHCH_3$), 6.25 (s, 2, J = 2 cps, 2 aromatic H), 7.3 (s, 1, phenolic OH), 11.98 (s, 1, H-bonded phenolic OH).

Anal. Calcd for $C_{17}H_{25}ClO_3$: C, 59.21; H, 7.25; Cl, 10.30. Found: C, 59.01; H, 7.21; Cl, 9.79.

1-(5-Benzyloxy-1-penten-1-yl)-3,5-bis(benzyloxy)benzene (11).—A mixture of **8** (0.34 g, 0.67 mmol), 5-chloro-2-pentanol[15] (0.40 g, 3.27 mmol), and *p*-toluenesulfonic acid (0.05 g) in 75 ml of dry benzene was refluxed overnight, water being removed by a Dean-Stark receiver. On cooling, the mixture was washed with 15 ml of 5% $NaHCO_3$ and 15 ml of water, then dried ($MgSO_4$). Benzene was removed to leave a greenish liquid residue which was purified on a preparative tlc plate using chloroform to give 0.25 g (80%) of **11** as a paste. The ir spectrum of **11** showed no carbonyl absorption.

Anal. Calcd for $C_{32}H_{32}O_3$: C, 82.90; H, 6.94. Found: C, 82.40; H, 7.12.

Registry No.—**3**, 6110-30-1; **8**, 37173-19-6; **9**, 37173-20-9; **10**, 37173-21-0; **11**, 37173-22-1.

Acknowledgment.—The assistance of Mr. Carl Wassink and his staff in obtaining elemental analyses and ir spectra is gratefully acknowledged.

A Novel Furan Dimer

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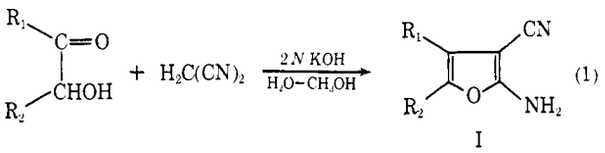
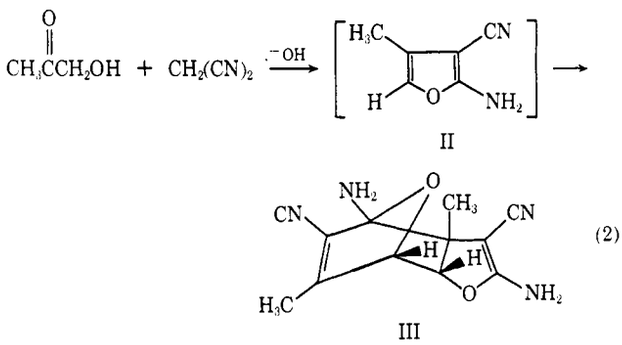
Gewald[1] has reported that the interaction of acyloins with malononitrile in aqueous base yields 2-amino-3-cyanofurans of type I (eq 1).[2] This scheme has subsequently been used to prepare a variety of such substances from readily available acyloins.



(1)

I

We would like to report that our experience with the synthesis of 2-amino-3-cyano-4-methylfuran (II), from hydroxy-2-propanone and malononitrile according to Gewald (eq 2), leads us to conclude that the product is not II but that it is 2,4-diamino-3,5-dicyano-3a,6-dimethyl-3a,4,7,7a-tetrahydro-*endo*-4,7-epoxybenzofuran (III), formed by way of a remarkable Diels–Alder cycloaddition of II with itself.



(2)

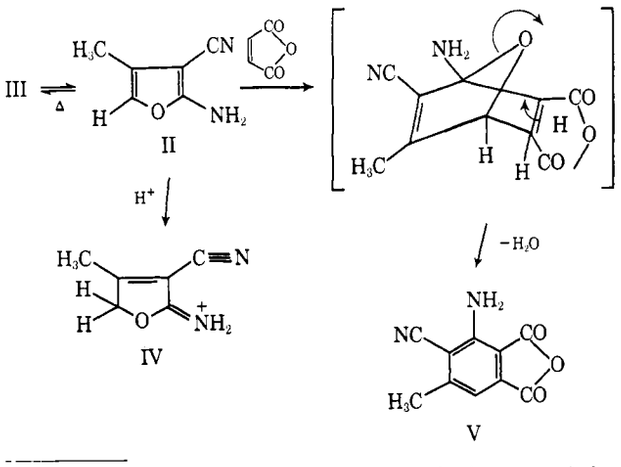
The nmr spectrum of III in pyridine-d_5 consisted of a singlet at 1.62 (3 H, 3a-CH_3), a singlet at 2.20 (3 H, 6-CH_3), an AB quartet centered at 4.37 (2 H, J = 8 Hz, $\Delta\gamma_{AB}$ = 21.6 Hz, 7-CH and 7a-CH), a broad singlet at 8.20 (2 H, 4-NH_2) and an identically broad singlet at 10.00 ppm (2 H, 2-NH_2) downfield from TMS. Upon ^{14}N double-irradiation both singlets underwent a considerable sharpening effect, and upon addition of D_2O the two broad downfield singlets collapsed immediately.

The mass spectrum (70 eV) of III using a direct-probe inlet and a relatively cold instrument (T 160°)[3] gave the following significant fragments: *m/e* (rel intensity) 244 (36, dimer molecular ion), 229 (100), 218 (21), 189 (14), 149 (20), 128 (23), 122 (52), and 93 (35). In addition, a well-resolved ir spectrum (KBr) revealed the presence of two closely spaced nitrile bands of equal intensity at 2200 and 2180 cm^{-1}.

The overall spectral evidence quite conclusively points to a dimer structure. More specifically, the two hydrogen AB pattern in the nmr indicates completely selective cycloaddition across the 4,5 double bond in the manner shown. The endo configuration is indicated by the coupling constant of 8 Hz for the AB hydrogens, which implies a dihedral angle near zero in a system such as III.[4]

Dimer III has been mentioned several times in the literature under the guise of the monomeric structure (II). Gewald[1] arrived at a clever synthesis of substituted 2-aminobenzonitriles by subjecting III and several other 2-amino-3-furonitriles to maleic anhydride in refluxing acetone, and Wie, Sunder, and Blanton[5] included III in a study of the enamine behavior of furan, pyrrole, and thiphene aminonitriles. They observed formation of IV upon treatment of III with trifluoroacetic acid. Brief mention is also made of III as structure II in Taylor and McKillop's recent monograph on *o*-aminonitriles.[6] The formation of IV and V indicate that III is quite capable of acting as a precursor for II (Scheme I).

SCHEME I



(1) K. Gewald, *Chem. Ber.*, **99**, 1002 (1966).

(2) Triethylamine in methanol gives comparable results.

(3) The mass spectrum using a Teflon slug showed only monomeric fragments.

(4) (a) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959); (b) F. A. L. Anet, *Can. J. Chem.*, **39**, 789 (1961); (c) K. Ramsey, D. Lini, R. Moriarty, H. Gospal, and H. G. Welsh, *J. Amer. Chem. Soc.*, **89**, 2401 (1967).

(5) C. T. Wie, S. Sunder, and C. D. Blanton, *Tetrahedron Lett.*, 4605 (1968).

(6) E. C. Taylor and A. McKillop, *Advan. Org. Chem.*, **7**, 126, 213 (1970).

To our knowledge, III represents the only reported example of a furan capable of dimerizing in a Diels–Alder fashion and the first member of the 4,7-epoxybenzofuran ring system.[7] We have subsequently examined several other analogs [I, $R_1 = R_2 = CH_3$; $R_1 = R_2 = Ph$; $R_1 = R_2 = (CH_2)_4$] and 2-amino-3-carboxamido-4-methylfuran but encountered no evidence of dimerization in these compounds.

Experimental Section

Compound III was prepared according to the method of Gewald.[1] The nmr spectrum was obtained on a Joel JNM-C60HL instrument. The ^{14}N hetero spin decoupling was performed with a Schomandl MS100M frequency synthesizer. The ir spectrum was recorded on a Perkin-Elmer Model 257 grating spectrophotometer and the low resolution mass spectrum on an Hitachi Perkin-Elmer RMU-6E single-focusing mass spectrometer.

Registry No.—III, 35895-53-5.

(7) The 4,7-epoxyisobenzofuran system is well known: A. M. Patterson, L. T. Capell, and D. F. Walker, "Ring Index," 2nd ed, No. 2245, 1960, p 291.

The Preparation of 5,7-Diamino-3*H*-imidazo[4,5-*b*]pyridine (2,6-Diamino-1-deazapurine)[1]

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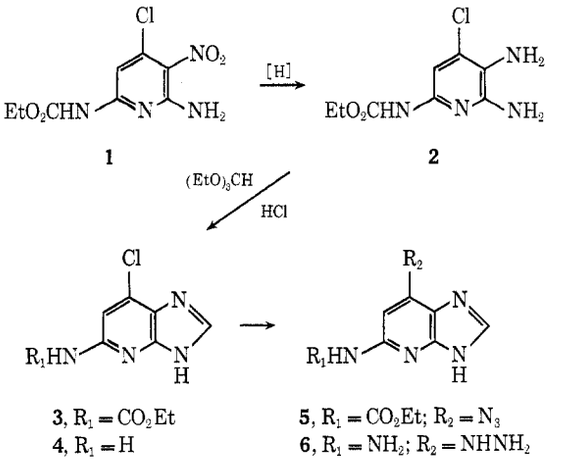
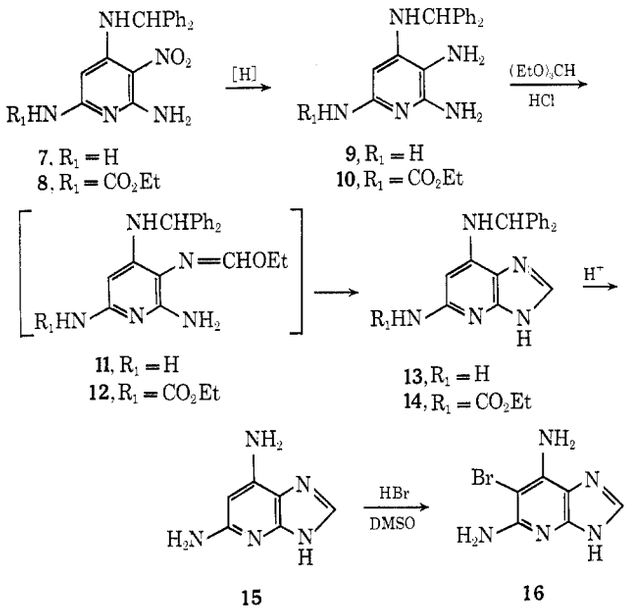
Recently the lack of reactivity of the chloro groups of both 5-amino-7-chloro- and 7-amino-5-chloro-3*H*-imidazo[4,5-*b*]pyridine (2-amino-6-chloro- and 6-amino-2-chloro-1-deazapurine) was reported.[2,3] We considered two approaches for the preparation of 5,7-diamino-3*H*-imidazo[4,5-*b*]pyridine (**15**). The first method involved the preparation of ethyl 7-chloro-3*H*-imidazo[4,5-*b*]pyridine-5-carbamate (**3**) in which the ethoxycarbonyl moiety was expected to decrease the electron-donating ability of the 5-amino group and increase the reactivity of the 7-chloro group. Hydrogenation of **1**[4] with Raney nickel gave **2**, which was cyclized with the ethyl orthoformate–concentrated HCl reagent[5] to give **3**. However, treatment of **3** with sodium azide to give **5** either in hot 1:1 EtOH–H_2O or hot 1:1 $EtOCH_2CH_2OH$–H_2O was unsuccessful. The stability of the chloro group was demonstrated by treatment of **3** with NaOMe in refluxing PrOH to give the known 5-amino-7-chloro compound **4**.[2,3] In contrast, hydrazinolysis of **3** HCl with anhydrous hydrazine at reflux resulted in displacement of both the chloro and (ethoxycarbonyl)amino groups to give the 5,7-dihydrazino compound **6**.[6] Under milder conditions reaction of **4** with hydrazine was reported to give the corresponding 5-amino-7-hydrazino derivative.[3]



Simultaneously with the above work, a route involving the cyclization of the 2,3,6-triamino-4-(diphenylmethyl)aminopyridines **9** and **10** was investigated. Hydrogenation of **7**[4] with Raney nickel at atmospheric pressure and room temperature gave **9**, isolated as a dihydrochloride. The cyclization of **9** with the ethyl orthoformate–concentrated HCl reagent at room temperature gave a mixture which was not purified but was shown to contain **13** as a major component (tlc). Hydrogenation of **8** with Raney nickel gave **10**, which was cyclized with ethyl orthoformate at room temperature to give **14**.[7] Presumably the cyclization of both **9** and **10** involves the ethoxymethyleneamino intermediates **11** and **12**, respectively.[8] Because of the greater nucleophilicity of the (diphenylmethyl)amino group of **11** and **12** compared with that of the 2-amino group, cyclization to the nitrogen of the (diphenylmethyl)amino group should be favored. How-



(1) This investigation was supported by funds from the C. F. Kettering Foundation, and Chemotherapy, National Cancer Institute, National Institutes of Health, Contract No. NIH-71-2021.

(2) D. G. Markees and G. W. Kidder, *J. Amer. Chem. Soc.*, **78**, 4130 (1956).

(3) J. E. Schelling and C. A. Salemink, *Recl. Trav. Chim. Pays-Bas*, **91**, 650 (1972).

(4) R. D. Elliott, C. Temple, Jr., and J. A. Montgomery, *J. Org. Chem.*, **31**, 1890 (1966).

(5) C. Temple, Jr., C. L. Kussner, and J. A. Montgomery, *J. Med. Pharm. Chem.*, **5**, 866 (1962).

(6) C. W. Whitehead and J. J. Traverso, *J. Amer. Chem. Soc.*, **82**, 3971 (1960), report exchange aminations for purines and pyrimidines.

(7) C. Temple, Jr., B. H. Smith, and J. A. Montgomery, *J. Med. Chem.* in press.

(8) J. A. Montgomery and C. Temple, Jr., *J. Org. Chem.*, **25**, 395 (1960).