arated by VPC and/or column chromatographic methods.[31,32]

To convert the α-silylated allylic alcohol products into their desilylated counterparts, advantage was taken not only of the affinity of fluoride ion for silicon, but also for the accelerative effect of the β-hydroxyl group.[33] The most effective conditions uncovered involved heating with tetra-*n*-butylammonium fluoride (10 equiv) in dry acetonitrile. Requisite reaction times varied from 1 to 36 h, with the more flexible, open systems reacting faster. Of particular note here is the preservation of geometry about the π linkage during Si–C bond fission.[34]

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(32) The structures of the cis and trans isomers can be easily delineated on the basis of the chemical shifts of the olefinic proton. When cis stereochemistry exists, the hydroxyl group shields the spatially proximal olefinic proton and shifts it to higher field. In the trans isomers, such effects do not operate. In the isomers produced from 4-trimethylsilyl-3-heptene, the magnitude of $\Delta\delta$ is 0.45. For the 1-trimethylsilyldodecene case, the value is 0.56. See also: Martin, G. J.; Naulet, N.; Lefevere, F.; Martin, M. L. *Org. Magn. Reson.* **1972,** *4,* 121. Sucrow, W.; Richter, W. *Chem. Ber.* **1971,** *104,* 3679.
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(35) (a) The Ohio State University Dissertation Fellow, 1978–1979; (b) Undergraduate research participant, 1976–1978.

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A Novel Pyrimidine to Pyridine Ring Transformation Reaction. A Facile Synthesis of 2,6-Dihydroxypyridines[1,2]

Sir:

The synthesis of a new heterocyclic ring by transformation of another ring system via a nucleophilic reaction has been an important subject of chemistry.[3] It has been known[4] that uracil can be converted into pyrazolone and isoxazolone by reaction with hydrazine and hydroxylamine, respectively. These reactions have been exploited extensively in the chemical modification of nucleic acids.[5] Several examples of the ring conversion of the pyrimidine system into the pyridine system have been reported in the literature;[6-8] however, none of them involves the direct replacement of the N_1–C_2–N_3 portion of the pyrimidine by a C–C–N fragment.

In this report we describe the first transformation of the pyrimidine ring into the pyridine system via direct displacement of the N_1–C_2–N_3 portion by a C–C–N fragment. In this investigation 1,3-dimethyluracil derivatives (**1**) were used as the pyrimidine while various α-substituted acetamides (**2**) served as the ambident C–C–N donors. Thus, treatment of 1,3-dimethyluracil (**1a**) with malonamide (**2a**) in ethanolic sodium ethoxide[9] at reflux for 30 min, followed by neutralization of the reaction mixture with concentrated HCl, afforded the known[10] 2,6-dihydroxynicotinamide (**3a**) and 1,3-dimethylurea. The structure of **3a** was confirmed further by its conversion into 2,6-dihydroxypyridine[11] by hydrolytic decarboxylation.

On the basis of the isolation of 1,3-dimethylurea from the reaction mixture and the fact that the reaction product is a 2,6-dihydroxypyridine derivative (a 2,4-dihydroxypyridine analogue was not detected in this reaction), the plausible mechanism shown in Scheme I is suggested. Nucleophilic attack of the carbanion of **2a** on C_6 of **1a** would occur first to give rise to Michael adduct A.[12,13] Abstraction of the proton from the exocyclic α position of A in basic medium accompanied by scission of the N_1–C_6 bond to give the open-chain intermediate B would then be followed by intramolecular cyclization on C_4 to afford **3a** and 1,3-dimethylurea. The near-quantitative recovery of starting materials from the attempted reaction of **1a** with methylmalonamide (which lacks the abstractable α proton as in A) lends further support to this proposed mechanism.

When acetamide derivatives bearing electron-withdrawing R′ substituents (**2b–d**) were employed instead of malonamide (**2a**) in the above reaction, the corresponding 5-substituted 2,6-dihydroxypyridines (**3b–d**) were obtained.[14] Acetamide

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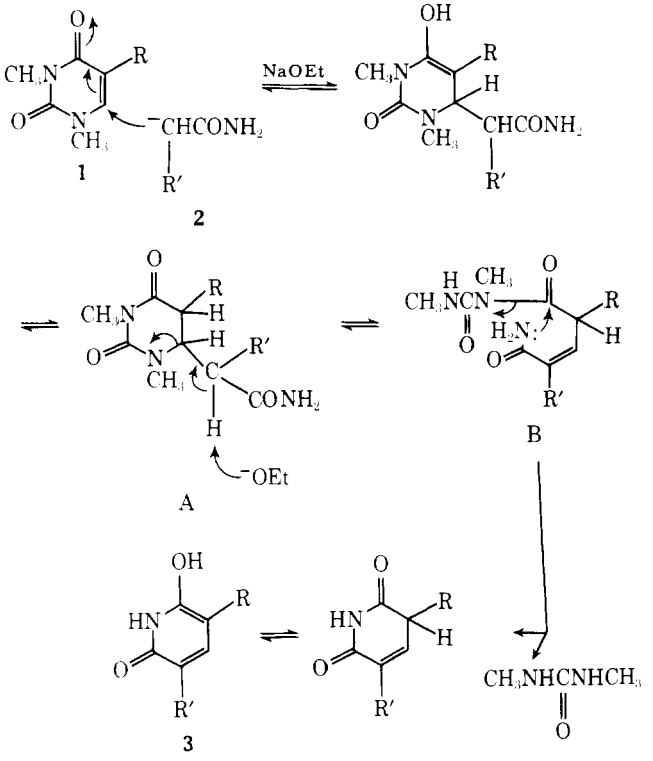
Scheme I



1a, R = H
b, R = CH_3
c, R = CN
d, R = F

2a, R′ = $CONH_2$
b, R′ = CN
c, R′ = $COCH_3$
d, R′ = C_6H_5

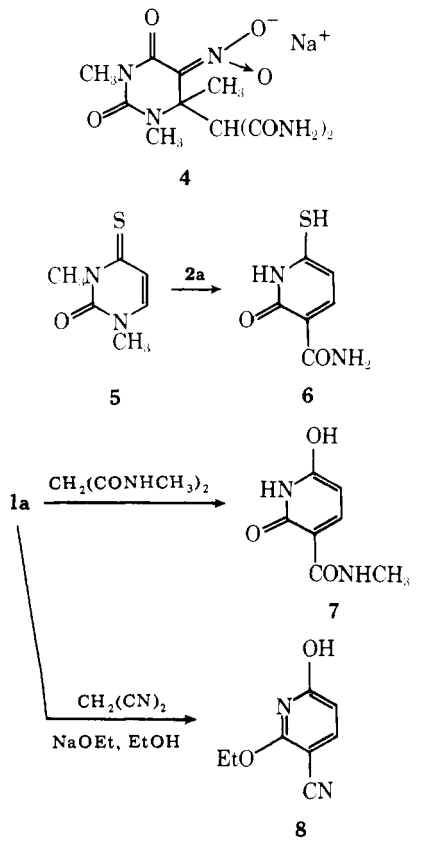
3^{14}

	R	R′	yield, %	mp, °C
3a[10]	H	$CONH_2$	88	268–271 dec
3b[15]	H	CN	97	278–279 dec
3c	H	$COCH_3$	51	243–246
3d[16]	H	C_6H_5	30	225–227
3e	CH_3	$CONH_2$	65	>300
3f[17]	CN	$CONH_2$	58	>300
3g	F	$CONH_2$	38	>300

itself failed to react with **1a** probably as a result of its inability to form a carbanion to any significant extent under these reaction conditions. The reaction of 1,3-dimethyluracils with these ambident nucleophiles is also affected by the nature and location of substituents on C_5 or C_6 of the pyrimidine. Thus, 1,3-dimethylthymine (**1b**) and 5-cyano-1,3-dimethyluracil (**1c**) afforded the corresponding 5-substituted 2,6-dihydroxylnicotinamides (**3e** and **3f**) in good yields. However, 1,3-dimethyl-5-fluorouracil (**1d**) gave the corresponding nicotinamide derivative **3g** in only moderate yield. This is probably due to participation of the halogen substituent in side reactions under basic conditions. The reaction of 5-nitro-1,3,6-trimethyluracil with **2a** yielded the sodium salt of the corresponding Michael addition product (**4**); conversion of **4** into the corresponding nicotinamide was not effected under various conditions. Substitution at C_6 of **1** suppressed the reaction; thus, 1,3,6-trimethyluracil was recovered unchanged in high yield from the attempted reaction with **2a.**

Furthermore, the reaction of 1,3-dimethyl-4-thiouracil (**5**) with **2a** proceeded smoothly to give 2-hydroxy-6-mercaptonicotinamide (**6**) (Scheme II) in 83% yield, while treatment of **1a** with *N,N′*-dimethylmalonamide afforded the 1-methylpyridone derivative (**7**). On the other hand, reaction of **1a** with malonitrile in ethanolic sodium ethoxide afforded 2-

Scheme II



ethoxy-3-cyano-6-hydroxypyridine (**8**) in 43% yield. Obviously, the solvent participated in this reaction.

The simple transformation of a uracil to a pyridine system described herein represents a new synthetic method with potential importance, especially in the synthesis of 2,6-dihydroxypyridine derivatives, some of which have shown interesting biological activities.[18]

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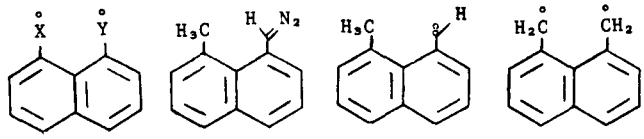
Heteroatomic Biradicals. Electron Spin Resonance Spectroscopy of a Nitrogen Analogue of 1,8-Naphthoquinodimethane

Sir:

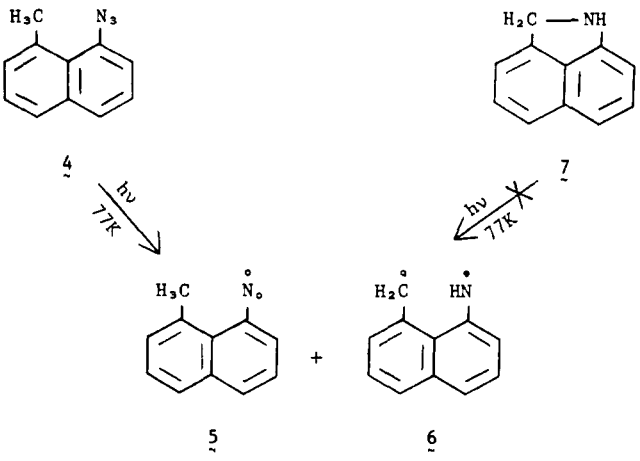
Biradical[1] intermediates play an important role in many thermal[2] and photochemical[3] processes. Over the last 15 years, low temperature ESR spectroscopy has become a powerful, direct probe of these otherwise transient species.[4] It appeared that an ESR study of variously functionalized perinaphthalene diyls (**1**) might provide insight into structure reactivity relationships in biradical chemistry. Previous work in this laboratory has shown that the known 1,8-naphthoquinodimethane[5] biradical (**3**) could be prepared from a diazo precursor.[6] We herein report the use of this technique to prepare a nitrogen-centered biradical by photolysis of an azide.



1 **2** **3**

Treatment of an acetone solution of 8-methyl-1-naphthoyl chloride[6] with aqueous sodium azide, at 25 °C, produces 8-methyl-1-naphthyl isocyanate. Only trace amounts of the intermediate acyl azide could be observed.[7] The isocyanate was hydrolyzed to 1-amino-8-methylnaphthalene with aqueous acid. Diazotization of the amine, followed by treatment with sodium azide, yields 1-azido-8-methylnaphthalene (**4**).[8]

Photolysis of **4** in 2-methyltetrahydrofuran (2MTHF) at 77 K produces ESR absorptions centered at 6100, 3300, and 1588 G (see Figures 1 and 2). The resonance absorptions are characteristic of randomly oriented triplet states[9] and are assigned to 1-methyl-8-nitrenonaphthalene **5** ($|D/hc| = 0.79 \pm 0.02$ cm^{-1}, $|E/hc| < 0.003$ cm^{-1}) and 1-imino-8-naphthoquinomethane ($|D/hc| = 0.0255 \pm 0.0002$ cm^{-1}, $|E/hc| = 0.0008 \pm 0.0002$ cm^{-1}). Control experiments with cyclic amine **7**[10] demonstrate that it is not photochemically converted into **5** or **6**. The spectrum of **6** is consistent with a single conformation;[11] however, the spectra of the syn and anti forms of the biradical may not be appreciably different.



4 **7** **5** **6**

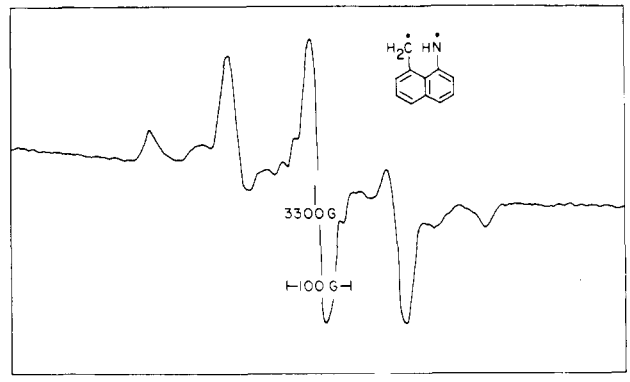


Figure 1. The ESR spectrum of biradical **6** in 2MTHF (77 K).

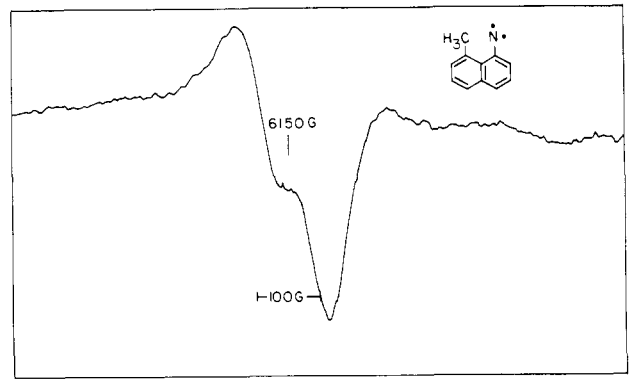


Figure 2. The ESR spectrum of nitrene **5** in 2MTHF (20 K).

The $|D/hc|$ value of **6** is 17% larger than that of **3**,[5,6] indicating an average, closer proximity of the two unpaired electrons in the aza diyl.[12] This is similar to tris(imino)trimethylenemethane[13] which has a larger $|D/hc|$ value than trimethylenemethane itself.[4a] The heteroatomic biradical **6** strictly obeys the Curie-Weiss Law over the temperature range 17 to 83.5 K.[14] Therefore the nitrogen-centered diyl has a triplet ground state, in agreement with 1,8-naphthoquinodimethane.[5d,6,15]

At 77 K the nitrene ESR spectrum does not interconvert into that of the biradical; both species are indefinitely stable at this temperature. The heteroatomic triplet biradical is, in fact, more thermally labile than the triplet nitrene. Warming of the sample to 98 K results in the rapid and complete dissipation of the ESR spectrum of **6**, but very little diminution of the nitrene signal intensity. Clearly **6** is not formed from triplet **5** in a thermally activated process at 77 K.

To test whether the triplet biradical arises via secondary photolysis of the triplet nitrene, the signal intensities of **5** and **6** were studied as a function of irradiation time (Figure 3). The ratio of **5**/**6** was invariant with the duration of photolysis (230 $< \lambda <$ 449 nm). At 77 K the nitrene and the biradical are both formed simultaneously; secondary photolysis of the triplet nitrene is not a major source of the biradical. The hydrogen atom transfer may occur from an excited state (electronic or vibrational) of the azide, an aza cycloheptatetraene,[16] or singlet 1-methyl-8-nitrenonaphthalene.

There are significant differences between the nitrene-heteroatomic biradical system (**5** and **6**) and the hydrocarbon case (**2** and **3**). The lifetime of 1,8-naphthoquinodimethane at 98 K is at least an order of magnitude longer than that of the aza

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