

(III).—6-Benzyladenine (I, 1.0 g) was reacted with the ylide prepared from NaH (0.7 g) and trimethyloxosulfonium chloride (4.2 g) in THF. The two main products were obtained pure by chromatography on silica gel (acetone). The minor product (150 mg) eluted faster and was recrystallized from benzene–ligroin to give 9-ethyl-6-benzyladenine III (110 mg) as colorless prisms, mp 141–144°. The nmr spectrum (CDCl<sub>3</sub>) showed peaks at 8.53 (t, *J* = 7.5, CH<sub>3</sub>), 5.81 (q, *J* = 7.5, CH<sub>2</sub>), 5.07 (d, *J* = 7.0, benzylic methylene), 2.68 (aromatic), 2.52 (s, H<sub>2</sub>), and 1.57 (s, H<sub>3</sub>); mass spectrum *m/e* 253 (M<sup>+</sup>); uv λ<sub>max</sub><sup>MeOH</sup> 270 nm.

*Anal.* Calcd for C<sub>14</sub>H<sub>15</sub>N<sub>5</sub>: C, 66.40; H, 5.93; N, 27.67. Found: C, 66.12; H, 5.98; N, 27.86.

Recrystallization of the major product (670 mg) from benzene–ligroin gave 6-benzyl-9-methyladenine (II) as colorless needles; mp 127–128°; nmr (CDCl<sub>3</sub>) 6.27 (s, CH<sub>3</sub>), 5.09 (d, *J* = 6.0, ArCH<sub>2</sub>), 2.70 (aromatic), 2.60 (s, H<sub>2</sub>), 1.60 (s, H<sub>3</sub>); nmr (DMSO-*d*<sub>6</sub>) 1.90 (s, H<sub>2</sub>), 1.76 (s, H<sub>3</sub>); mass spectrum *m/e* 239 (M<sup>+</sup>); uv λ<sub>max</sub><sup>MeOH</sup> 270 nm.

*Anal.* Calcd for C<sub>13</sub>H<sub>15</sub>N<sub>5</sub>: C, 65.27; H, 5.44; N, 29.29. Found: C, 65.28; H, 5.23; N, 28.96.

This product was identical with an authentic sample (mp 128°, nmr, ir, and uv spectra), which was prepared by boiling 6-chloro-9-methylpurine and benzylamine in methyl Cellosolve.

**1-Methylbenzimidazole.**—Benzimidazole (0.8 g) was reacted with the ylide prepared from NaH (0.8 g) and sulfonium chloride (4.8 g) in THF. 1-Methylbenzimidazole was obtained as an oil (0.74 g), which showed singlet peaks at 6.61 (NCH<sub>3</sub>) and 2.33 (H<sub>2</sub>) in addition to aromatic protons in the nmr spectrum (CDCl<sub>3</sub>). The picrate formed in ether was recrystallized from EtOH as yellow needles, mp 250–251°.

*Anal.* Calcd for C<sub>8</sub>H<sub>8</sub>N<sub>2</sub>·C<sub>6</sub>H<sub>5</sub>N<sub>3</sub>O<sub>7</sub>: C, 46.54; H, 3.07; N, 19.38. Found: C, 46.80; H, 3.13; N, 19.21.

**1-Methylindole.**—Indole (1.17 g) was allowed to react with the ylide prepared from NaH (0.7 g) and sulfonium chloride (4.5 g). The product obtained as a reddish yellow oil was purified by chromatography on silica gel (hexane–benzene). The product obtained as a pale yellow liquid was identical with authentic 1-methylindole with regard to ir and nmr spectra. The nmr spectrum showed peaks at 6.47 (s, NCH<sub>3</sub>), 3.60 (d, *J* = 3.0, 3 H), and 3.16 (d, *J* = 3.0, 2 H).

**9-Methyl-1,2,3,4-tetrahydroharman.**—1,2,3,4-Tetrahydroharman (1.0 g) was treated with the ylide prepared from NaH (0.75 g) and sulfonium chloride (4.5 g). The nmr spectrum of the crude products showed a mixture of starting material and 9-methylharman in a ratio of 2:3. The unchanged compound was removed as a solid by treatment with benzene–ligroin. Evaporation of the mother liquor gave the pure *N*-methylation product (0.6 g) whose nmr spectrum (CDCl<sub>3</sub>) showed peaks at 8.75 (d, *J* = 7.0, CCH<sub>3</sub>) and 6.77 (s, NCH<sub>3</sub>). The picrate was obtained from EtOH–ether as reddish yellow prisms, mp 243–245° dec (lit.<sup>5</sup> 242°).

*Anal.* Calcd for C<sub>18</sub>H<sub>16</sub>N<sub>2</sub>·C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>N<sub>3</sub>: C, 53.15; H, 4.43; N, 16.32. Found: C, 53.39; H, 4.36; N, 16.37.

**1-Methyloxindole.**—Oxindole (2.6 g) was reacted with the ylide prepared from NaH (0.5 g) and sulfonium chloride (3.2 g). The crude products were chromatographed on silica gel (benzene–acetone) to give two main products.

An oily product, which eluted faster, was identified as 1,3-dimethyloxindole by the nmr spectrum (CDCl<sub>3</sub>) which showed signals at 8.57 (d, *J* = 8.0, C-CH<sub>3</sub>), 6.85 (s, NCH<sub>3</sub>), and 6.67 (q, *J* = 8.0, 3 H).

The subsequently eluted product (1.9 g) was obtained as colorless needles from ligroin, mp 89–90° (lit.<sup>6</sup> 88°). The nmr spectrum (CDCl<sub>3</sub>) showed peaks at 6.80 (s, N-CH<sub>3</sub>), 6.51 (s, CH<sub>2</sub>), and around 3.0 (m, aromatic).

**1,3,3-Trimethyloxindole.**—Oxindole (0.9 g) was treated with the ylide prepared from NaH (0.5 g) and sulfonium chloride (3.0 g). A major product obtained by chromatography on silica gel (CHCl<sub>3</sub>) was further purified by distillation at 0.5 mm (120°) to give trimethyloxindole (0.8 g) as a slightly yellow oil. The nmr spectrum (CDCl<sub>3</sub>) showed singlet peaks at 8.64 (6 H) and 6.80 (3 H), mass spectrum *m/e* 175 (M<sup>+</sup>). The uv and ir spectral data were identical with those reported.

**Registry No.**—II, 5440-16-4; III, 25870-60-4; dimethyloxosulfonium methylide, 5367-24-8; 1-methylbenzimidazole picrate, 25870-61-5.

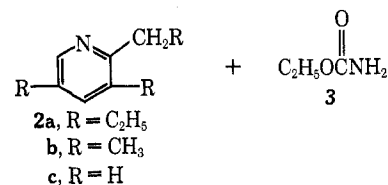
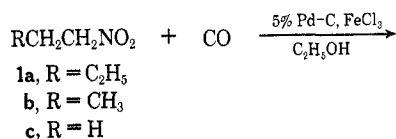
## Reaction of Aliphatic Nitro Compounds with Carbon Monoxide. A New Route to Trialkylpyridines

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Recently, Bennett, Hardy, and coworkers<sup>1</sup> reported that carbon monoxide reacts with aromatic nitro, nitroso, azo, and azoxy compounds in the presence of a noble metal and ferric chloride to yield the corresponding isocyanates. In a patent issued to Mountfield<sup>2</sup> it is stated that urethans may be produced from the reaction of carbon monoxide, aromatic or aliphatic nitro compounds, and alcohols in the presence of a metal carbonyl catalyst system. We have found that certain primary aliphatic nitro compounds yield trisubstituted pyridines when treated with carbon monoxide under pressure using a noble metal–ferric chloride catalyst system. For example, treatment of an ethanol solution of 1-nitrobutane (1a) with carbon monoxide in the presence of palladium on carbon and ferric chloride yields 2-propyl-3,5-diethylpyridine (2a) and ethyl carbamate (3). Likewise, 1-nitropropane (1b) gives rise to 2-ethyl-3,5-dimethylpyridine (2b) and 3. The pyridines were



identified by spectral methods (nmr, uv, and mass spectra), from their picrate derivatives and by comparison of their nmr spectra with the spectra of the authentic samples prepared by Falbe.<sup>3,4</sup> It is apparent from the structure of the pyridines that this reaction must involve a trimerization process wherein three molecules combine in a specific fashion to form the heterocyclic ring. The pyridine formation is markedly dependent upon the structure of the nitro compound as indicated by the results summarized in Table I. Although the reaction of aromatic nitro compounds under these conditions gives high yields of the corresponding *N*-arylurethans,<sup>5</sup> *N*-alkylurethans are probably not involved in the cyclization since *N*-1-butylurethan was recovered

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(2) B. A. Mountfield, U. S. Patent 3,338,956 (1967).

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(4) We thank Dr. E. L. Mackor of Koninklijke/Shell-Laboratorium, Amsterdam, for copies of the nmr spectra of 2a and 2b.

(5) R. P. Bennett, American Cyanamid Co., personal communication, 1968.

TABLE I  
EFFECT OF STRUCTURE ON CO REACTION PRODUCTS

Nitro compd	Products <sup>a</sup> (yield, %)	
	3	2a
1a	3 (39)	2a (24)
1b	3 (30)	2b (52)
1c	3 (18)	
2-Nitrobutane	3 (89)	2-Butanone <sup>b</sup> (58)
Nitrocyclohexane	3 (37)	N-Cyclohexylurethan (trace)
2-Methyl-2-nitropropane		Recovered unchanged

<sup>a</sup> Significant quantities of volatile by-products such as ammonia are formed in most of these reactions. <sup>b</sup> Isolated as the 2,4-dinitrophenylhydrazone.

unchanged after being subjected to the reaction conditions.

Ethanol is the preferred solvent for this reaction, but benzene has been employed successfully (reaction is much slower in benzene). Temperatures have been varied from 125 to 200° and pressures from 2000 to 5000 psig with no significant changes in product distributions. Rhodium is equally as effective as palladium for the noble metal portion of the catalyst while carbon or alumina supports appear to be equivalent. All the components of the reaction system (noble metal, ferric chloride, and carbon monoxide) were found to be necessary; if any one is omitted, none of the pyridine product is observed.

Falbe<sup>3</sup> has reported that *n*-butyraldoxime reacts with 1:1 hydrogen-carbon monoxide in the presence of a cobalt carbonyl catalyst to yield 2a (24%) and butyramide (38%). Treatment of this oxime under our conditions also gave 2a (33%) suggesting that oxime intermediates may be involved in the pyridine formation. The 2-butanone isolated from the reaction of 2-nitrobutane could be derived from the corresponding oxime.

These results as well as those previously reported<sup>1-3,5</sup> suggest that nitro compounds can react with carbon monoxide to yield a number of different products depending on catalyst and solvent as well as the structure of the nitro compounds.

#### Experimental Section<sup>6</sup>

**2-Propyl-3,5-diethylpyridine (2a).**—Into a glass-lined autoclave were charged 16.9 g (0.162 mol) of 1-nitrobutane, 2.11 g (0.013 mol) of anhydrous ferric chloride, 4.2 g of 5% palladium on carbon,<sup>7</sup> and 100 ml of anhydrous ethanol. The autoclave was pressurized to 5,000 psig with carbon monoxide<sup>8</sup> and heated for 2 hr at 190°. After cooling and venting, the product mixture was filtered to remove the catalyst. Analysis of the filtrate (vpc, silicone rubber column) indicated 2a and 3 were present in approximately equal amounts. After evaporation of the solvent, the products were distilled, bp 45–70° (0.1 mm), affording 12.3 g of a solid-liquid mixture. Washing of this mixture with petroleum ether left 5.7 g (39%) of 3, which after purification melted at 46–48° and was identical with that of an authentic sample (vpc, ir, mixture melting point). The pyridine 2a, 2.3 g (24%), was recovered from the washings by evaporation and acid extraction. The amine was further purified by preparative vpc: uv max (C<sub>2</sub>H<sub>5</sub>OH), 270 mμ (ε 4400), (HCl, C<sub>2</sub>H<sub>5</sub>OH), 277 (1800); nmr (CDCl<sub>3</sub>) δ 8.28 (d, 1, *J* = 2 Hz, py-H), 7.28 (d, 1, *J* = 2 Hz, py-H), 2.65 (m, 6, py-CH<sub>2</sub>-), 1.75 (m, 3, -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>), and 1.20–0.99 ppm (overlapping t, 9,

(6) Melting points were determined on a Mel-Temp block and are uncorrected. Vpc, nmr, uv, and mass spectral measurements were carried out on an F & M Model 500 chromatograph, a Varian A-60, a Beckman DU and a CEC Model 110, respectively.

(7) Obtained from Engelhard Industries in the unreduced form and dried at 350° under nitrogen just prior to use.

(8) Obtained from Air Products and Chemicals, Inc., CP grade.

-CH<sub>3</sub>); mass spectrum (70 eV) *m/e* 177 (M), 162, 148, 134, 129, 91; picrate mp 121–122° (lit.<sup>9</sup> mp 122°).

Anal. Calcd for C<sub>18</sub>H<sub>22</sub>N<sub>4</sub>O<sub>7</sub>: C, 53.20; H, 5.46; N, 13.79. Found: C, 53.18; H, 5.52; N, 13.84.

The nmr spectrum of 2a was identical with the spectrum of the authentic material.<sup>3</sup>

*n*-Butyraldoxime was substituted for 1a in the above experiment and 2a was isolated in 33% yield. No 3 was evident in the product mixture, but the ir spectrum of the ethanol solution showed a strong absorption band at about 2000 cm<sup>-1</sup> suggesting the presence of iron pentacarbonyl.

**2-Ethyl-3,5-dimethylpyridine (2b).**—1-Nitropropane was treated with carbon monoxide under the conditions described above for 1a. The yield of 3 was 30% and 2b, 52%. The structure of 2b was established from the following data: uv max (C<sub>2</sub>H<sub>5</sub>OH) 270 mμ (ε 3400), (HCl, C<sub>2</sub>H<sub>5</sub>OH), 274 (5800); nmr (CDCl<sub>3</sub>) δ 8.19 (broad s, 1, py-H), 7.20 (broad s, 1, py-H), 2.76 (q, 2, *J* = 7 Hz, py-CH<sub>2</sub>CH<sub>3</sub>), 2.23 (s, 6, py-CH<sub>3</sub>), and 1.25 ppm (t, 3, *J* = 8 Hz, CH<sub>2</sub>-CH<sub>3</sub>); mass spectrum (70 eV) *m/e* 135 (M), 134, 120, 107, 91, 79, 77; picrate mp 154–155° (lit.<sup>10</sup> mp 156–157°).

Anal. Calcd for C<sub>15</sub>H<sub>18</sub>N<sub>4</sub>O<sub>7</sub>: C, 49.45; H, 4.43; N, 15.38. Found: C, 49.20; H, 4.18; N, 15.42.

The nmr spectrum of 2b was identical with the spectrum of the authentic material.<sup>3</sup>

**Registry No.**—Carbon monoxide, 630-08-0; 2a, 4808-75-7; 2b, 1123-96-2.

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## Rearrangement of Aromatic *N*-Oxides. IV. The Reaction of Acridine *N*-Oxide with Acetyl Sulfide<sup>1</sup>

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Previous reports from this laboratory have involved mechanistic studies of the rearrangement of aromatic *N*-oxides in acetic anhydride.<sup>3</sup> From a detailed kinetic analysis of such a reaction with acridine *N*-oxide (1), it was concluded that the key step involved an intramolecular rearrangement of the *N*-acetoxyacridinium ion (2).<sup>4</sup> This was somewhat surprising since in the analogous reaction with pyridine *N*-oxide (3) kinetic<sup>5</sup> and oxygen-18<sup>6</sup> studies established that the pathway

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(2) Based on the Honors theses, Williams College, of M.-K. Ahn, 1963, C. G. Carson, III, 1964, and G. A. Lee, 1967.

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