[CONTRIBUTION No. 213 FROM THE RESEARCH CENTER, UNITED STATES RUBBER COMPANY]

# Deoxygenation of Pyridine 1-Oxides[1]

DOUGLAS I. RELYEA, PLINY O. TAWNEY, AND ALLAN R. WILLIAMS

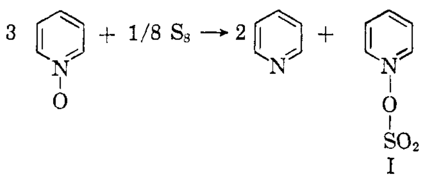
*Received August 7, 1961*

A survey of the reactions of some pyridine 1-oxides with potential reducing agents has been made. Sulfur and some of its compounds react with particular ease at 115–150° forming the free pyridine and other products in which the oxygen atom is either bonded to sulfur or released as water. Only thiophene, among the sulfur compounds examined, did not react with pyridine 1-oxide. Pyridine 1-oxide reacts readily with hydrazobenzene at 140° to form azobenzene, water, and pyridine in good yields. Pyridine 1-oxide reacts only slowly with hydroquinone and not at all with benzylaniline, bibenzyl, diphenylamine, catechol, pyrrole, heptaldehyde, isopropanol, *n*-octene-1, naphthalene, or 1,4-diazabicyclo[2.2.2]octane.

It has been reported by Takeda and Tokuyama[2] that various pyridine 1-oxides react with sulfur to form the free amines. Although the solvent used was liquid ammonia, it was demonstrated that no deoxygenation is caused by the solvent, at least in the system ammonia-4-nitropyridine 1-oxide.[3] Related deoxygenations of pyridine 1-oxides have been effected with phosphorus trihalides,[4] triphenyl phosphite,[5] triphenylphosphine,[6] benzenesulfenyl chloride[7] and sulfur monochloride.[7]

The present report is a survey of the reactions of pyridine 1-oxides with a variety of potential reducing agents. Sulfur and its compounds react with particular ease, forming the free pyridine and other products in which the oxygen atom from the 1-oxide is generally either bonded to sulfur or released as water.

Table I summarizes the successful deoxygenations of pyridine 1-oxides. Three moles of pyridine 1-oxide underwent an exothermic reaction with one g.-atom of sulfur at 135° without solvent to give 97% of two moles of pyridine and 96% of one mole of the pyridine 1-oxide-sulfur dioxide complex (I). Although compound I has not been reported previously, the analogous trimethylamine oxide-sulfur dioxide complex (II) is known to be readily formed and stable at temperatures of about 100°.[8] Like II, compound I can be hydrolyzed in boiling water to give the *N*-oxide and sulfur dioxide, but no sulfate. Hence, sulfur is oxidized by pyridine 1-oxide only to the sulfur dioxide stage and not beyond. Termination of reaction at this stage is consistent with previous demonstrations that sulfur dioxide cannot reduce aromatic *N*-oxides.[9]



(1)

I

Both 2- and 4-picoline 1-oxides were readily deoxygenated by sulfur at 130–140°. However, these reactions were complicated by the simultaneous reaction of sulfur with the alkyl group and accompanying evolution of hydrogen sulfide which prevented detection of sulfur dioxide. Thus, 4-picoline 1-oxide and sulfur gave not only 4-picoline, but also tetra-4-pyridylthiophene, a known product of the reaction of 4-picoline and sulfur.[10]

2-Picoline 1-oxide reacted with di-*n*-butyl sulfide to give only moderate yields of 2-picoline, which was the only material isolable other than unchanged starting materials. Repeated experiments failed to yield either di-*n*-butyl sulfoxide or di-*n*-butyl sulfone and gave instead only recovered di-*n*-butyl sulfide. This suggests that the sulfide is oxidized to the sulfoxide, which is known to be unstable at the temperatures used.[11]

*n*-Butyl mercaptan reacted slowly at 115° with 2-picoline 1-oxide to give good yields of water, 2-picoline and di-*n*-butyl disulfide in a reaction consistent with the stoichiometry of Equation 2,

$$2\ n\text{-}C_4H_9SH + o\text{-}CH_3C_5H_4NO \longrightarrow (n\text{-}C_4H_9)_2S_2 + H_2O + o\text{-}CH_3C_5H_4N \quad (2)$$

Thiophenol took part in an analogous reaction with pyridine 1-oxide with even greater ease.

The reaction of 2-mercaptobenzothiazole (MBT) with pyridine 1-oxide provides a sharp contrast. MBT is commonly considered to be the mercaptan, although there is good infrared spectrophotometric

---

(1) Presented at the 135th Meeting of the American Chemical Society, Boston, April 1959.

(2) K. Takeda and K. Tokuyama, *J. Pharm. Soc. Japan*, **75**, 620 (1955); *Chem. Abstr.*, **50**, 3443d (1956).

(3) K. Takeda and M. Tokuyama, *J. Pharm. Soc. Japan*, **75**, 286 (1955); *Chem. Abstr.*, **50**, 1797f (1956).

(4) M. Hamana, *J. Pharm. Soc. Japan*, **75**, 123, 127, 130, 135, 263 (1955); *Chem. Abstr.*, **50**, 1817, 1818, 4542c (1956).

(5) M. Hamana, *J. Pharm. Soc. Japan*, **75**, 121 (1955); *Chem. Abstr.*, **50**, 1818f (1956).

(6) E. Howard, Jr., and W. F. Olszewski, *J. Am. Chem. Soc.*, **81**, 1483 (1959).

(7) S. Furukawa, *Pharm. Bull. (Japan)*, **3**, 230 (1955); *Chem. Abstr.*, **50**, 8638i (1956).

(8) A. B. Burg, *J. Am. Chem. Soc.*, **65**, 1629 (1943).

(9) (a) A. W. Johnson, T. J. King, and J. R. Turner, *J. Chem. Soc.*, 3230 (1958). (b) E. Ochiai, *J. Org. Chem.*, **18**, 534 (1953). (c) E. C. Taylor and N. E. Boyer, *J. Org. Chem.*, **24**, 275 (1959).

(10) J. L. Keller (to Koppers Co.), U. S. Pat. **2,515,233** (July 18, 1950).

(11) N. Grabowsky, *Ann.*, **175**, 348 (1875).

TABLE I

DEOXYGENATION OF PYRIDINE 1-OXIDES

| 1-Oxide (Moles) | Reductant (Moles) | Solvent | Temp. | Time, Hr. | Products (Moles) |
|---|---|---|---|---|---|
| Pyridine (1.00) | Sulfur (0.042)[a] | — | 135 | 18 | Pyridine (0.64)<br>Pyridine 1-oxide-$SO_2$ (0.32) |
| 2-Picoline (1.00) | Sulfur (0.25[a]) | o-$C_6H_4Cl_2$ | 150 | 64 | 2-Picoline (0.37) |
| 4-Picoline (1.00) | Sulfur (0.25[a]) | o-$C_6H_4Cl_2$ | 150 | 64 | 4-Picoline (0.27) |
| 4-Picoline (0.20) | Sulfur (0.25[a]) | — | 145 | 18 | Tetra-4-pyridylthiophene (0.018) |
| 2-Picoline (1.00) | n-$C_4H_9SH$ (1.00) | — | 115 | 96 | 2-Picoline (0.52)<br>(n-$C_4H_9)_2S_2$ (0.45)<br>n-$C_4H_9SH$ (0.14)<br>2-Picoline 1-oxide (0.45)<br>Water (0.34) |
| 2-Picoline (0.50) | (n-$C_4H_9)_2S$ (0.50) | — | 150 | 24 | 2-Picoline (0.065)<br>(n-$C_4H_9)_2S$ (0.43)<br>2-Picoline 1-oxide (0.32) |
| 2-Picoline (0.50) | (n-$C_4H_9)_2S$ (0.50) | — | 150 | 67 | 2-Picoline (0.14)<br>(n-$C_4H_9)_2S$ (0.46)<br>2-Picoline 1-oxide (0.18) |
| Pyridine (0.50) | MBT[b] (0.25) | — | 150 | 6 | Pyridine (0.30)<br>2-Benzothiazolone (0.036) |
| Pyridine (1.00) | Thiophenol (1.00) | — | 140 | 64 | Pyridine (0.23)<br>Water (0.19)<br>Diphenyl disulfide (0.39)<br>Pyridine 1-oxide (0.52) |
| Pyridine (3.00) | Thiourea (1.00) | — | 140 | 16 | Pyridine (2.80)<br>Iminoaminomethanesulfonic acid (0.98) |
| Pyridine (1.50) | Hydrazobenzene (0.50) | — | 145 | 42 | Pyridine (0.37)<br>Water (0.47)<br>Azobenzene (0.37)<br>Pyridine 1-oxide (0.40) |
| Pyridine (1.00) | Hydroquinone (1.00) | — | 150 | 120 | Pyridine (0.13)<br>Water (0.21)<br>Quinone[c] |

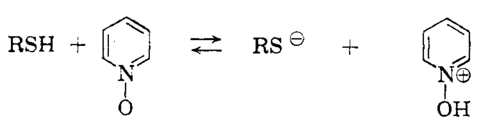
[a] Calculated on the basis of $S_8$. [b] MBT = 2-mercaptobenzothiazole. [c] Small amount of quinone disemicarbazone isolated

evidence that it exists as the tautomeric thioamide.[12] It is therefore interesting that MBT was converted to a 1:1 complex of MBT and 2-benzothiazoline, m.p. 120–122°, formed by oxidative removal of the thione sulfur atom. It was further observed that there was no water formed in this oxidation. This oxidation of MBT is thus similar to that with alkaline hydrogen peroxide, which also yields 2-benzothiazolone. Authentic 1:1 complex of MBT and 2-benzothiazolone was prepared by fusing equimolar amounts of the two and recrystallizing the melt from water.

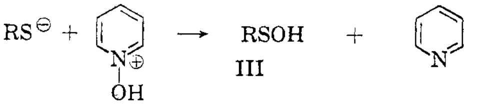
Reaction of thiourea with pyridine 1-oxide also gave pyridine which was completely anhydrous, together with a crystalline compound, m.p. 221–230°, believed to be iminoaminomethanesulfonic acid.

A number of potential deoxygenating agents in which the possible site of reaction was not a sulfur atom were examined. Hydrazobenzene took part in a very facile reaction with pyridine 1-oxide to yield pyridine, water, and azobenzene which were all isolated in approximately the stoichiometric amounts. Attempts to extend the reaction to benzylaniline and 1,2-diphenylethane were completely unsuccessful. Hydroquinone was oxidized to p-benzoquinone only with difficulty and the oxidation of catechol to the higher potential[13] o-benzoquinone did not take place at all.

A possible mechanism for oxidation of mercaptans by pyridine 1-oxide is an initial protonation of the N-oxide (Equation 3) followed by displacement of the pyridine molecule from the OH group (Equation 4). The sulfenic acid (III) is a member of an unstable class of compounds which react with mercaptans to form disulfides,[14] the observed



(3)



(4)

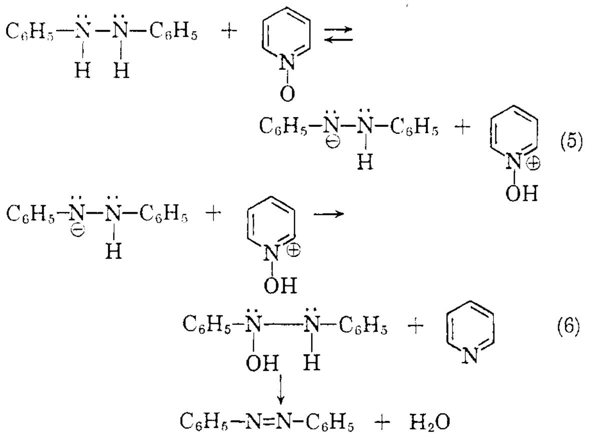
---

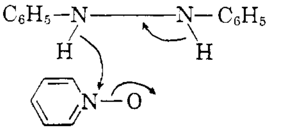
[12] M. St. C. Flett, *J. Chem. Soc.*, 347 (1953).

[13] L. F. Fieser in *Organic Chemistry*, Vol. I, H. Gilman, Ed., Wiley, New York, 1943, p. 159.

[14] E. E. Reid, *Organic Chemistry of Bivalent Sulfur*, Chemical Publishing Co., New York, 1958, Vol. I, p. 264.

product of the reaction. In the oxidation of hydrazobenzene, such a two-step mechanism requires a less favored initial protonation of the *N*-oxide by hydrazobenzene (Equation 5). An alternative is a concerted reaction involving a cyclic transition state IV. This latter mechanism has a close resemblance to that proposed by Zubyk in a thorough study of the oxidation of hydrazobenzene by molecular oxygen.[15]





IV

In a survey of potential deoxygenating agents for pyridine 1-oxides, diphenylamine, pyrrole, thiophene, heptaldehyde, isopropanol, *n*-octene-1, naphthalene, and 1,4-diazabicyclo[2.2.2]octane were heated at 140° with pyridine 1-oxide for forty hours or longer and in no case could any free pyridine be detected.

## EXPERIMENTAL[16]

*Materials.* Pyridine 1-oxide, m.p. 65–66°, reported[17] 66–68°, was either prepared in 60–70% yield by the hydrogen peroxide–acetic acid oxidation of pyridine described by Ochiai[9b] or purchased from Beacon Chemical Co., Cambridge, Mass. 2-Picoline 1-oxide, m.p. 40–42°, picrate m.p. 122.5–123.5°, and 4-picoline 1-oxide, m.p. 183–184°, reported[18] 186–188°, were obtained from either Matheson, Coleman and Bell or Reilly Tar and Chemical Co.

*Thermal stability of 2-picoline 1-oxide.* A 54.5-g. (0.500-mole) sample of 2-picoline 1-oxide was heated at 150° for 64 hr. in a flask fitted with reflux condenser protected from atmospheric moisture by a calcium chloride tube. Addition of 20 ml. of *o*-dichlorobenzene ($n_D^{20}$ 1.5513) "chaser" and equilibration with a 20-cm. helices-packed fractionating column gave a first 0.5 ml. of distillate with $n_D^{20}$ 1.5496 and a second 0.5 ml. of distillate with $n_D^{20}$ 1.5506. This indicates less than 0.1% thermal deoxygenation to 2-picoline, $n_D^{20}$ 1.5010.

*Reaction of pyridine 1-oxide with sulfur.* In a 2-l. flask fitted with two reflux condensers and a solid addition tube was placed 95.1 g. (1.00 mole) of pyridine 1-oxide. An Erlenmeyer flask connected to the addition tube contained 11.0 g. of sulfur (1/24 mole as $S_8$). The reaction flask was heated with a 150° oil bath and the sulfur added cautiously over a period of 100 min.[19] The reaction mixture was then heated at 135° for an additional 16 hr. The mixture was distilled at atmospheric pressure to give 50.9 g. (0.644 mole) of pyridine, b.p. 112–114°, $n_D^{20}$ 1.5064, reported[20] 1.5092; picrate m.p. 167–168°, reported[21] 167–168°. There remained a 45 g. of crystalline solid, m.p. 160–170° (dec.), which was hydrolyzed by boiling dilute hydrochloric acid to evolve a gas with strong characteristic sulfur dioxide odor. The aqueous residue gave no reaction with barium chloride solution, but addition of base and treatment with picric acid gave pyridine 1-oxide picrate, m.p. 183–184°, mixed m.p. with authentic picrate 183.7–184.7°.

*Reaction of 4-picoline 1-oxide with sulfur without solvent.* In a 2-l. flask fitted with a thermometer and two reflux condensers was placed a dry, well-stirred mixture of 64.1 g. of sulfur (0.25 mole as $S_8$) and 21.8 g. (0.200 mole) of 4-picoline 1-oxide. The flask was heated in an oil bath and the temperature raised slowly from 100°. At 136° a vigorous exotherm occurred and the mixture became fluid. Heating at 145° was continued for eighteen hours. Eighty milliliters of concentrated hydrochloric acid was added and the mixture refluxed for thirty minutes. The mixture was filtered and the residue refluxed with a second 80-ml. portion of hydrochloric acid for three hours. After filtering this mixture the combined filtrate was basified with 100 g. of sodium hydroxide in 400 ml. of water. The dark brown precipitate was separated by filtration, washed twice with 10 ml. of water and dried to give 6.9 g. (31%) of tetra-4-pyridylthiophene, m.p. 248.2–251.2°, reported[10] 251.8–252.6°.

Attempts to prepare a picrate of tetra-4-pyridylthiophene gave only a yellow gum which decomposed when heated to dissolve in 95% ethanol.

*Reaction of 2-picoline 1-oxide with n-butyl mercaptan.* A solution of 109.3 g. (1.00 mole) of 2-picoline 1-oxide in 108 ml. (90.2 g., 1.00 mole) of *n*-butyl mercaptan was heated at reflux (115–118°) for 96 hr. under a stream of nitrogen. The reaction mixture was then distilled through a 20-cm. column packed with protruded nickel to give:

1. Two-phase mixture of 12.8 g. (14% recovery) of *n*-butyl mercaptan $n_D^{20}$ 1.4480, and 6.2 g. (0.34 mole) of water, $n_D^{20}$ 1.3362, reported[22] 1.3332, reaction with phenyl isocyanate gave diphenylurea, m.p. 240.7–242.7°, reported[23] 239.5°.
2. 2-Picoline, 47.9 g. (52%), b.p. 124–127°, $n_D^{20}$ 1.4980, reported[24] 1.5006, picrate m.p. 166.8–167.8°, reported[25] 169°.
3. Di-*n*-butyl disulfide, 79.6 g. (90%), b.p. 128–130° (35 mm.), $n_D^{20}$ 1.5032, reported[26] 1.4946.
4. 2-Picoline 1-oxide, b.p. 140–142° (5 mm.), $n_D^{20}$ 1.5890, reported[18] 1.5874, picrate m.p. 122.9–123.9°, authentic picrate m.p. 122.5–123.5°.

---

(15) W. J. Zubyk, Ph.D. thesis, University of Delaware, June 1957.

(16) All melting points are corrected.

(17) J. Meisenheimer, *Ber.*, **59**, 1848 (1926).

(18) O. H. Bullitt, Jr., and J. T. Maynard, *J. Am. Chem. Soc.*, **76**, 1370 (1954).

(19) An attempt to bring the reactants together more rapidly produced a violently exothermic reaction.

(20) B. A. Middleton and J. R. Partington, *Nature*, **141**, 516 (1938).

(21) J. P. Wibaut and L. M. F. van de Lande, *Rec. trav. chim.*, **48**, 1005 (1929).

(22) *Handbook of Chemistry*, N. Lange, Ed., Sixth ed., Handbook Publ., Inc., Sandusky, 1946, p. 272.

(23) C. Graebe and S. Rostovzeff, *Ber.*, **35**, 2747 (1902).

(24) H. C. Brown and M. Nakagawa, *J. Am. Chem. Soc.*, **78**, 2197 (1956).

(25) N. Collie and W. S. Myers, *J. Chem. Soc.*, **61**, 721 (1892).

(26) H. Gilman, L. E. Smith, and H. H. Parker, *J. Am. Chem. Soc.*, **47**, 851 (1925).

*Reaction of 2-picoline 1-oxide with di-n-butyl sulfide.* A solution of 54.6 g. (0.500 mole) of 2-picoline 1-oxide in 73.1 g. (0.500 mole) of di-*n*-butyl sulfide, $n_{\mathrm{D}}^{20}$ 1.4508, was heated at 150° for 24 hr. under a stream of nitrogen. Fractionation of the reaction mixture gave:

1. 2-Picoline, 6.1 g. (13%), b.p. 57–62° (60 mm.), $n_{\mathrm{D}}^{20}$ 1.4980, reported[24] 1.5006, picrate m.p. 166.7–167.3°, reported[25] 169°.
2. Di-*n*-butyl sulfide, 63.2 g. (87% recovery), b.p. 100–106° (60 mm.), $n_{\mathrm{D}}^{20}$ 1.4538.
3. An intermediate fraction, 4.5 g. b.p. 55–97° (3 mm.), $n_{\mathrm{D}}^{20}$ 1.4676.
4. 2-Picoline 1-oxide, 34.7 g. (64% recovery), b.p. 97–99° (3 mm.), $n_{\mathrm{D}}^{20}$ 1.5805, reported[18] 1.5874.
5. A black residue, 10.0 g.

A duplicate experiment in which the mixture was heated for 67 hr. at 150° gave 28% of 2-picoline, 37% of recovered 2-picoline 1-oxide, 91% recovery of di-*n*-butyl sulfide, and 7 g. of residue.

*Reaction of pyridine 1-oxide with thiophenol.* A solution of 95.1 g. (1.00 mole) of pyridine 1-oxide in 107 g. (1.00 mole) of thiophenol was heated at 140° under a slow stream of nitrogen. Entrained material was condensed in a Dry-Ice trap. A brief temperature rise raised the reaction temperature to 151°. Heating at 140° was continued for 64 hr. The reaction mixture was partially distilled to give 21.5 g. of pyridine and water, b.p. 45–52° (200 mm.), $n_{\mathrm{D}}^{20}$ 1.4865. This mixture was calculated to contain 3.3 g. (37%) of water and 18.2 g. (0.23 mole) of pyridine. A mixture prepared from pure materials in this proportion had $n_{\mathrm{D}}^{20}$ 1.4864.

The residue from the distillation was washed three times with 300-ml. portions of water to remove unchanged pyridine 1-oxide. The combined washings were evaporated to give 49.3 g. (52% recovery) of pyridine 1-oxide, m.p. 63–66°. The white solid residue from the washings, weight 110 g., was recrystallized from 600 ml. of 95% ethanol to give 84.3 g. (78%) of diphenyl disulfide, m.p. 60–61°, reported[27] 60–62°.

*Reaction of pyridine 1-oxide with 2-mercaptobenzothiazole.* A mixture of 47.6 g. (0.500 mole) of pyridine 1-oxide and 41.8 g. (0.250 mole) of 2-mercaptobenzothiazole was heated at 150° under a nitrogen atmosphere for a total of six hours. The reaction mixture was distilled to give 22.5 g. (60%) of water-free pyridine, b.p. 50–60° (50–90 mm.), $n_{\mathrm{D}}^{20}$ 1.5090, reported, 1.5092.[20]

The dark residue (65 g.) was boiled briefly in 200 ml. of water. The aqueous extract was filtered and allowed to cool depositing 8 g. of 1:1 complex of benzothiazolone and MBT, white plates, m.p. 126–128°. Two additional extractions of the residue gave a total of 22 g. of this salt. Infrared absorption spectrum showed the following peaks, all given in cm.$^{-1}$: *3170, 3130,* (s., N—H); *3030* (m., aromatic H); *1670* (v.s., —CO—NH—); 1315 (s.,) 1285 (m.), 1255 (m.), 1075 (m.), 1035 (m.), 1035 (s.), and 1010 (m.), all found in spectra of 2-mercaptobenzothiazole or 2-chlorobenzothiazole; and 754 (v.s.) and 703 (w.), *o*-phenylene.

*Anal.* Calcd. for $C_{14}H_{10}N_2OS_3$: C, 52.83; H, 3.17; N, 8.80; O, 5.02; S, 30.17. Found: C, 52.90; H, 3.16; N, 8.88, 8.89; O, 5.34; S, 29.6.

Authentic 2-benzothiazolone was prepared by oxidation of 2-mercaptobenzothiazole with alkaline hydrogen peroxide, giving a 98% yield of material, m.p. 135–136°, reported[28] 135°. A mixture of 1.67 g. (0.100 mole) of 2-mercaptobenzothiazole and 1.51 g. (0.0100 mole) of 2-benzothiazolone was fused and recrystallized from 800 ml. of water to give 2.2 g. of pale yellow plates, infrared absorption spectrum identical with that of the material $C_{14}H_{10}N_2OS_3$ obtained above.

*Reaction of pyridine 1-oxide with thiourea.* A melt of 285.3 g. (3.00 moles) of pyridine 1-oxide at 135° under a nitrogen atmosphere was treated with 76.1 g. (1.00 mole) of thiourea in 1- to 2-g. portions. Each addition caused a temperature rise of 2–3°. The addition was completed in three hours and heating at 135–140° was continued for a total of 16 hr. The reaction mixture was distilled to give 221.7 g. (2.80 moles, 93%) of anhydrous pyridine, b.p. 80–85° (300 mm.), $n_{\mathrm{D}}^{20}$ 1.5097, reported[20] 1.5092, picrate m.p. 169.2–169.7°, reported[21] 167–168°.

The distillation residue was iminoaminomethanesulfonic acid, obtained as 122 g. (98%) of pale yellow, water-soluble material, m.p. 221–230°C. As reported,[29] it is unstable toward water and recrystallization of the entire distillation residue from 150 ml. of water gave 40 g. of orange solid, m.p. 290–295° (dec.).

*Reaction of pyridine 1-oxide with hydrazobenzene.* In a 500-ml. flask fitted with nitrogen inlet tube, thermometer, and reflux condenser connected to a Dry Ice trap protected with a calcium chloride tube were placed 142.4 g. (1.50 moles) of pyridine 1-oxide and 92.1 g. (0.500 mole) of hydrazobenzene. The flask was heated at 140–145° and swept with a slow stream of nitrogen. A steady reflux of pyridine occurred after only a few hours. Heating was continued for a total of 42 hr. The combined reaction mixture and Dry-Ice trap condensate were distilled to give 38.0 g. of pyridine-water mixture, b.p. 42–60° (180 mm.), $n_{\mathrm{D}}^{20}$ 1.4740. The water was identified as diphenylurea, m.p. 240.0–240.7°, reported[23] 239.5°. The pyridine was identified as the picrate, m.p. 167.7–168.7°, reported[21] 167–168°. From the refractive index value it was calculated that the distillate consisted of 0.370 mole of pyridine and 0.472 mole of water. A synthetic mixture prepared from distilled water and reagent pyridine in this proportion had $n_{\mathrm{D}}^{20}$ 1.4742. Thus, the yield of water was 8.5 g. (94%) and the yield of pyridine 29.5 g. (74%).

The distillation residue was poured while molten into 400 ml. of cold water with vigorous stirring. The brown crystalline azobenzene was separated by filtration and recrystallized from 300 ml. of 95% ethanol. Azobenzene was obtained as orange plates, weight 61.0 g. (67%), m.p. 68.7–69.2°, reported[30] 68°. A second crop of 7.0 g., m.p. 69.0–70.0°, brought the yield to 75%.

The aqueous solution and washings from the precipitation of azobenzene were evaporated to give 38.0 g. (26% recovery) of pyridine 1-oxide, m.p. 60.2–65.8°, picrate m.p. 182.6–183.6°, authentic picrate m.p. 183.7–184.7°.

*Reaction of pyridine 1-oxide with hydroquinone.* A mixture of 110.1 g. (1.00 mole) of photographic grade hydroquinone and 95.1 g. (1.00 mole) of pyridine 1-oxide was heated for 120 hr. at 150° in the apparatus described for the reaction of pyridine 1-oxide and hydrazobenzene. The Dry-Ice trap condensed 2.5 g. of pyridine-water mixture, $n_{\mathrm{D}}^{20}$ 1.4287. Distillation of the reaction gave 11.6 g. of pyridine-water mixture, b.p. 40–60° (150 mm.), $n_{\mathrm{D}}^{20}$ 1.4810. Comparison of these mixtures with known mixtures prepared from pure materials indicated a total yield of 10.2 g. (13%) of pyridine, picrate m.p. 168–169°, reported[21] 167–168°, and 3.9 g. (21%) of water, diphenylurea m.p. 240.2–241.2°, reported[23] 239.5°.

An attempt to separate the quinone and unchanged hydroquinone from unchanged pyridine 1-oxide by precipitation from 200 ml. of water gave very little solid. The presence of quinone was demonstrated by treating one fourth of the aqueous solution with 7 g. of semicarbazide hydrochloride in 20 ml. of water and heating on a steam bath for ninety minutes. Quinone disemicarbazone separated as 0.4 g. of dark red crystals, m.p. 242–244°, reported[31] 243°.

*Attempted reactions of pyridine 1-oxide with other potential reductants.* Reactions of pyridine 1-oxide were attempted with benzylaniline, bibenzyl, diphenylamine, isopropyl

---

(27) H. Lecher, *Ber.*, **48**, 524 (1915).

(28) R. F. Hunter, *J. Chem. Soc.*, 125 (1930).

(29) J. Boeseken, *Proc. Acad. Sci. Amsterdam*, **41**, 70 (1938); *Chem. Abstr.*, **32**, 3758$^7$ (1938).

(30) P. Griess, *Ber.*, **9**, 132 (1876).

(31) J. Thiele and W. Barlow, *Annalen*, **302**, 311 (1898).

alcohol, catechol, pyrrole, heptaldehyde, *n*-octene-1, naphthalene, and 1,4-diazabicyclo[2.2.2]octane using the technique and reaction conditions described above for reaction with hydrazobenzene. In each case no pyridine could be detected and only unchanged starting materials could be isolated.

WAYNE, N. J.

---

[CONTRIBUTION FROM SINCLAIR RESEARCH, INC.]

# Hydrogen Fluoride-Catalyzed Reactions of Hydrocarbons with Carbon Monoxide

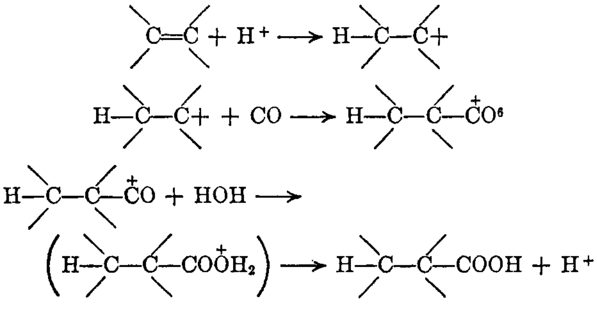
B. S. FRIEDMAN AND S. M. COTTON

*Received July 5, 1961*

Hydrogen fluoride catalyzes the condensation of olefins with carbon monoxide at room temperature to form acyl compounds. If an alkylatable hydrocarbon such as an isoparaffin or a branched naphthene, R'H, is used as a solvent for this condensation, the solvent undergoes a hydride transfer reaction with the olefin-derived carbonium ion, resulting in a new cation, $R'^+$. This cation reacts with carbon monoxide to form an acid, R'COOH (after hydrolysis). Hydride transfer also occurs between an acyl fluoride, RCOF, and a branched hydrocarbon *via* decarbonylation and formation of the carbonium ion, $R^+$. Use of *cis*-decalin as a solvent leads to formation of decalin-9-carboxylic acid, but *trans*-decalin is substantially unaffected. Carboxylic acid solvents containing a tertiary hydrogen do not undergo the hydride transfer reaction, thus ruling out this route to dicarboxylic acids. Hydrogen fluoride does not promote the acylation of benzene or toluene by pivalyl fluoride, but instead produces *t*-butyl derivatives of these aromatics. Treatment of *t*-butylbenzene with carbon monoxide yields pivalyl fluoride. Cumene does not form isobutyryl fluoride. The mechanism of these reactions is discussed.

Some years ago Simons and Werner[1] reported that certain alcohols and alkyl halides condense with carbon monoxide at about 160° in the presence of hydrogen fluoride to form organic acids.

More recently, H. Koch and co-workers have shown that olefins[2,3,5] and alcohols[4,5] condense quite readily at room temperatures and moderate pressures with carbon monoxide in the presence of sulfuric acid to produce (after hydrolysis) good yields of organic acids. They frequently employed formic acid as the source for carbon monoxide. Koch[4] suggested the following mechanism:



Stork and Bersohn[7] and Pincock, Grigat, and Bartlett[8] have found Koch's reaction to be a remarkably smooth synthetic method for complex tertiary acids, in some instances with a high degree of stereospecificity. Koch as well as Bartlett,[8] Meinwald[9] and Lundeen[10] have shown that skeletal and *cis-trans* isomerization may occur, but these reactions often afford excellent yields of the favored isomer. Roe and Swern[11] determined optimum conditions for preparing polycarboxylic acids from oleic, linoleic, and other unsaturated acids.

Although anhydrous hydrogen fluoride[3] and monohydroxyfluoboric acid[12] have been mentioned as catalysts for this reaction of olefin with carbon monoxide, the data for the former are very sparse. We have employed anhydrous hydrogen fluoride as catalyst for the reaction of various hydrocarbons with carbon monoxide,[13] and wish to record some of our findings.

*Alkanes and cycloalkanes.* In recent papers Wolfgang and Koch[14] reported the synthesis of carboxylic acids from saturated hydrocarbons *via* a hydride-transfer reaction. These authors found that concurrent contact of (a) an olefin or alcohol, with (b) an isoparaffin or a naphthene, and (c) carbon monoxide or formic acid, in the presence of

---

[1] J. H. Simons and A. C. Werner, *J. Am. Chem. Soc.*, **64**, 1356 (1942).

[2] H. Koch, *Riv. Combustibili*, **10**, 77 (1956); *Brenn. Chemie*, **36**, 321 (1955).

[3] H. Koch, U. S. Patent **2,831,877** (April 22, 1958); Belgium Patent **518,682** (March 4, 1955).

[4] H. Koch, *Fette und Seifen*, **59**, 493 (1957).

[5] (a) H. Koch and W. Haaf, *Angew. Chem.*, **70**, 311 (1958); (b) *Ann.*, **618**, 251 (1958).

[6] This may be written: $R^+ + \overset{-}{C}\equiv\overset{+}{O} \longrightarrow R-C\equiv O^+ \longleftrightarrow R\overset{+}{C}=O$. See refs. 9 and 11.

[7] G. Stork and M. Bersohn, *J. Am. Chem. Soc.*, **82**, 1261 (1960).

[8] R. E. Pincock, E. Grigat, and P. D. Bartlett, *J. Am. Chem. Soc.*, **81**, 6332 (1959).

[9] J. E. Meinwald, H. C. Hwang, D. Christman, and A. P. Wolf, *J. Am. Chem. Soc.*, **82**, 484 (1960).

[10] A. Lundeen, *J. Am. Chem. Soc.*, **82**, 3228 (1960).

[11] E. T. Roe and D. Swern, *J. Am. Oil Chem. Soc.*, **37**, 661 (1960).

[12] H. Koch and W. Huisken, U. S. Patent **2,876,241** (March 3, 1959).

[13] B. S. Friedman and S. M. Cotton, U. S. Patent **2,975,199** (March 14, 1961); *J. Org. Chem.*, **26**, 3751 (1961).

[14] H. Wolfgang and H. Koch, *Ann.*, **638**, 122 (1960); *Angew. Chemie*, **72**, 628 (1960).