Anal. Calcd. for $C_{16}H_{13}ClN_2O_2$: C, 63.90; H, 4.36; N, 9.32. Found: C, 64.24; H, 4.22; N, 9.22.

7-Chloro-1-formyl-2,3-dihydro-5-phenyl-1*H*-1,4-benzodiazepine 4-Oxide (IIIa).—A sample (1 g.) of IIa was melted in an oil bath kept at 165°. After 3 min. the dark melt was cooled and, on addition of methylene chloride and ether, crystallized to yield 0.5 g. of crystals melting at 132–138°. Recrystallization from a mixture of methylene chloride and hexane yielded white prisms melting at 136–139°. From a mixture of methylene chloride and ether a dimorphic form melting at 150–153° was obtained; λ_{max} 233 mμ (ϵ 21,000), λ_{max} 259 mμ (ϵ 14,000); λ_{max} 307 mμ (ϵ 10,000).

Anal. Calcd. for $C_{16}H_{13}ClN_2O_2$: C, 63.90; H, 4.36; N, 9.32. Found: C, 63.72; H, 4.62; N, 9.67.

This product gave a mixture melting point depression with IIa and could be reconverted to IIa by exposure to daylight (2 days) in a 1% isopropyl alcohol solution.

1-Acetyl-7-chloro-4,5-epoxy-2,3,4,5-tetrahydro-5-phenyl-1*H*-1,4-benzodiazepine (IIb).—This compound was prepared in 83% yield from Ib in the same manner as described for the preparation of IIa from Ia. Crystallization from ether gave colorless prisms melting at 161–163°.

Anal. Calcd. for $C_{17}H_{15}ClN_2O_2$: C, 64.87; H, 4.80; N, 8.90. Found: C, 65.07; H, 5.03; N, 9.01.

1-Acetyl-7-chloro-2,3-dihydro-5-phenyl-1*H*-1,4-benzodiazepine 4-Oxide (IIIb).—Compound IIb was rearranged under conditions used for the preparation of IIIa. The product IIIb was obtained in 76% yield and formed, after crystallization from a mixture of methylene chloride and petroleum ether, colorless prisms melting at 218–220°; λ_{max} 234 mu (ϵ 21,000), λ_{infl} 260 mμ (ϵ 12,000), λ_{max} 310 (ϵ 12,000).

Anal. Calcd. for $C_{17}H_{15}ClN_2O_2$: C, 64.87; H, 4.80; N, 8.90. Found: C, 65.17; H, 4.79; N, 8.83.

This product IIIb was photoisomerized in the same manner as IIIa, and the oxaziridine IIb was identified in the customary way.

7-Chloro-2,3,4,5-tetrahydro-5-phenyl-1*H*-1,4-benzodiazepin-4-ol (IV).—A solution of 12.6 g. (0.04 mole) of IIIb in 250 ml. of tetrahydrofuran was added to a solution of 1.52 g. (0.04 mole) of lithium aluminum hydride in 100 ml. of tetrahydrofuran. The temperature of the solution rose to 28°. After stirring for 1 hr. at room temperature, ether and 7 ml. of water were added. Filtration and evaporation of the solution gave white prisms which, after recrystallization from a mixture of ether and hexane, melted at 167–169°. The yield was 6.9 g. (63%).

Anal. Calcd. for $C_{15}H_{15}ClN_2O$: C, 65.57; H, 5.50; N, 10.20. Found: C, 65.54; H. 5.48; N, 10.28.

This compound (0.3 g.) was oxidized with 0.7 g. of mercuric oxide (30 min., 25°) in a mixture of 6 ml. of acetone and 1 ml. of water. This product (0.2 g.) was identical with V.

7-Chloro-2,3-dihydro-5-phenyl-1*H*-1,4-benzodiazepine 4-Oxide (V).—A solution containing 30 g. (0.095 mole) of IIIb in 300 ml. of methanol and 150 ml. of 1 *N* aqueous sodium hydroxide was refluxed for 6 hr. Concentration of the solution gave yellow needles which, after recrystallization from methanol, melted at 242–245°. The yield was 22.8 g. (87%); λ_{max} 240 mμ (ϵ 20,000), λ_{max} 262 mμ (ϵ 15,000), λ_{max} 303 mμ (ϵ 7000).

Anal. Calcd. for $C_{15}H_{13}ClN_2O$: C, 66.06; H, 4.80. Found: C, 66.15; H, 4.75.

The formyl derivative IIIa was hydrolyzed in the same manner.

The following reactions were carried out with V.

A. **Conversion to VII.**—A solution of 0.15 g. of V in 7 ml. of chloroform containing 0.25 ml. of phosphorus trichloride was refluxed for 30 min. The mixture was cooled, poured onto ice, made basic with aqueous sodium hydroxide, and extracted with methylene chloride. Evaporation gave yellow flakes which, after recrystallization from ether, melted at 171–173° and were found to be identical with VII.[1]

B. **Formylation to IIIa.**—To a cooled mixture of 13.6 ml. of 98% formic acid and 32.8 ml. acetic anhydride which had been kept at 50° for 2 hr. was added 12.6 g. (0.046 mole) of V. A red solution formed which, after standing for 20 min. at 25°, turned yellow and was made alkaline by addition of ice and aqueous ammonia. Extraction with methylene chloride and recrystallization yielded 10.5 g. (76%) of IIIa.

C. **Acetylation to IIIb.**—A solution of 0.5 g. of V in 5 ml. of acetic anhydride and 7 ml. of pyridine was kept at 25° for 20 hr. Concentration *in vacuo* gave a viscous residue which crystallized on addition of ether. Recrystallization from a mixture of methylene chloride and petroleum ether gave 0.32 g. of crystals melting at 213–216°, which were identical with IIIb.

1-Acetyl-7-chloro-2,3,4,5-tetrahydro-5-phenyl-1*H*-1,4-benzodiazepin-4-ol (VI).—A solution of 12.6 g. (0.04 mole) of IIIb in 250 ml. of tetrahydrofuran was added at 15° to a solution of 0.76 g. (0.02 mole) of lithium aluminum hydride in 100 ml. of tetrahydrofuran. The solution was kept at 15–20° for 1 hr., diluted with ether, decomposed with 4 ml. of water, and filtered. The filtrate was concentrated and the residue (12 g.) was dissolved in benzene and adsorbed on a column containing 350 g. of neutral alumina (Woelm, grade I). Elution with a mixture of methylene chloride and ethyl acetate (1:2) gave 0.6 g. of starting material IIIb in the first fractions. Later fractions gave oils which crystallized on standing. These were recrystallized from a mixture of methylene chloride and ether to give 2.3 g. (18%) of white prisms VI melting at 161–163°.

Anal. Calcd. for $C_{17}H_{17}ClN_2O_2$: C, 64.45; H, 5.41; N, 8.84. Found: C, 64.52; H, 5.67; N, 9.02.

This product was reoxidized to IIIb in the manner described for the conversion of IV to V.

Acknowledgment.—We are indebted to Dr. V. Toome and Mr. S. Traiman for the spectrophotometric determinations and to Dr. Al Steyermark and his staff for the microanalyses.

A Novel Deoxygenation Method for Pyridine N-Oxide

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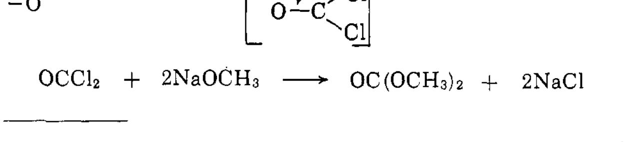
In recent years considerable interest has been manifested in the possible methods that may be employed to deoxygenate pyridine N-oxide.[1] We wish to report a novel deoxygenation reaction for pyridine N-oxide using dichlorocarbene.

Dichlorocarbene was prepared employing the following carbene precursors: potassium *t*-butoxide and chloroform,[2] sodium methoxide and chloroform,[3] sodium methoxide and methyl trichloroacetate,[4] and phenyl(trichloromethyl)mercury.[5]

Dimethyl carbonate was found to be present following the reaction of the dichlorocarbene prepared from sodium methoxide and chloroform with pyridine N-oxide, and its presence suggests the following mechanism.[6]



$$OCCl_2 + 2NaO\dot{C}H_3 \longrightarrow OC(OCH_3)_2 + 2NaCl$$

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[1] (a) T. R. Emerson and C. W. Rees, *J. Chem. Soc.*, 1917 (1962); (b) D. I. Relyea, P. O. Tawney, and A. R. Williams, *J. Org. Chem.*, **27**, 477 (1962), and references cited therein.

[2] W. E. Doering and A. K. Hoffmann, *J. Am. Chem. Soc.*, **76**, 6162 (1954).

[3] H. E. Winberg, *J. Org. Chem.*, **24**, 264 (1959).

[4] W. E. Parham and E. E. Schweizer, *ibid.*, **24**, 1733 (1959).

[5] D. Seyferth, J. M. Burlitch, and J. K. Heeren, *ibid.*, **27**, 1492 (1962).

[6] Similarly, 9-diazofluorene with pyridine N-oxide in refluxing benzene gives over 50% yield of fluorenone and 35% fluorenone azine, suggesting a similar carbene mechanism, in contrast to the reaction of 9-diazofluorene with benzene alone which gives only difluorene. E. E. Schweizer and G. J. O'Neill, unpublished results.

The yields of pyridine, when phenyl(trichloromethyl)-mercury was employed as the carbene precursor, were from 63% (based on the carbene precursor when its mole ratio to pyridine N-oxide was 1:3) to 25% (when the ratio was 1:1). When methyl trichloroacetate[7] was used as the carbene precursor the yields of pyridine were 40%, 28%, and 18% (when the haloacetate to pyridine ratios were 3:1, 2:1, and 1:1, respectively). The reaction of potassium *t*-butoxide and chloroform with pyridine N-oxide gave trace amounts of pyridine.

The usefulness of pyridine N-oxide and dimethyl sulfoxide as oxygen-donating species with a number of nonhalocarbenes[6] is being explored also.

Experimental

Materials.—Powdered sodium methoxide[8] and potassium *t*-butoxide[9] are always transferred in a drybox under an atmosphere of dry nitrogen. The methyl trichloroacetate[10] was prepared according to Dumas, b.p. 151° (atmospheric pressure), and pyridine N-oxide,[11] b.p. 120° (3 mm.), was distilled prior to use.

Phenyl(trichloromethyl)mercury as Carbene Precursor.—Phenyl(trichloromethyl)mercury[12] (17.5 g.), pyridine N-oxide (12.7 g.), and 100 ml. of anhydrous thiophene-free benzene were refluxed with stirring for 44 hr. The benzene was distilled, b.p. to 110°, and treated with a saturated solution of picric acid in benzene. The pyridine picrate (3.12 g., 23%) was recovered (melting point and mixture melting point were identical with an authentic sample).

The residue remaining after the benzene was distilled was concentrated to dryness. This second distillate was extracted with three 5-ml. portions of 10% hydrochloric acid and the combined extracts were made strongly basic with potassium hydroxide pellets while cooling. The basic solution was then extracted with ether, dried (potassium hydroxide), and distilled. Pyridine (1.41 g., 40%) was collected, b.p. 114°. Its infrared spectrum and picrate were identical with an authentic sample. Therefore, a total yield of 63% of pyridine was obtained. The yields of pyridine in all the other experiments mentioned were determined as shown in the following procedure.

Methyltrichloroacetate as Carbene Precursor.—Sodium methoxide (17.6 g.) was added slowly from an enclosed erlenmeyer flask through a flexible tubing to a cold (10–15°) solution of methyl trichloroacetate (18.5 g.) and pyridine N-oxide (49.5 g.) in 250 ml. of anhydrous, thiophene-free benzene. The mixture was stirred at ice–water bath temperature for 1 hr. after completion of the base addition. The mixture was transferred to a rotary evaporator and evaporated to dryness at water aspirator pressure and a temperature not exceeding 65°. The distillate was collected in two Dry Ice–acetone traps. An aliquot (3.0025 g.) of the benzene distillate (166.1 g. recovered) was treated with a saturated solution of picric acid in benzene. The resulting dried pyridine picrate (melting point and mixture melting point checked with an authentic sample) weighed 0.229 g. and represented 1.96% by weight of the aliquot. Therefore, the pyridine obtained was calculated to be 3.25 g. (40% yield). A similar solution of the pyridine N-oxide used was treated in the same manner employed for the work-up described previously and the benzene concentrate was shown to give no picrate of either pyridine or pyridine N-oxide.

Chloroform as the Carbene Precursor.—Sodium methoxide (17.6 g.), chloroform (12.3 g.), and pyridine N-oxide (49.5 g.) were allowed to react in benzene (250 ml.) solution as described previously. The work-up procedure was identical with that used in the preceding experiment and the calculated yield of pyridine was 17%. The gas chromatogram of the benzene concentrate showed a peak for dimethyl carbonate; peak enhancement also was observed when an authentic sample of carbonate was introduced with the benzene concentrate. The infrared spectrum of the benzene layer contained all the characteristic carbonate peaks of particular interest are the peaks at 790 cm.$^{-1}$ and 1265 cm.$^{-1}$, which are not found in the spectrum of methyl orthoformate, indicating that the carbonate was obtained.

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[7] The ratio of sodium methoxide to methyl trichloroacetate was always 3:1 in order to absorb the phosgene proposed as an intermediate in the reaction.

[8] The Matheson Co., Inc., East Rutherford, N. J.

[9] MSA Research Corp., Callery, Pa.

[10] J. Dumas, *Ann. Chem.*, **32**, 111 (1839).

[11] Reilly Tar and Chemical Corp., Indianapolis 4, Ind.

[12] Prepared according to E. E. Schwiezer and G. J. O'Neill, *J. Org. Chem.*, **28**, 851 (1963).

The Formation of Substituted Pyridines from the Reaction of the Sodium Salt of Malononitrile with Haloforms in the Alcohol–Alkoxide System

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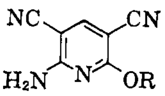
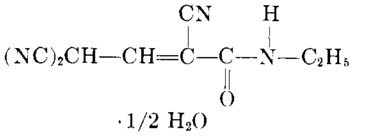
In continuation of a study of the reaction of carbanions with haloforms in the alcohol–alkoxide system,[2] we have investigated the reaction of the sodium salt of malononitrile and wish to report a convenient one-step synthesis of pyridines of type I.

The reaction of the sodium salt of malononitrile with chloroform and sodium ethoxide in ethanol has been reported by Kötz and Zörnig[3] as yielding a product formulated as either II or III. The questionable structural assignment rested solely on an elemental analysis, and a degradation attempt was reported as being unsuccessful. A reexamination has shown that the structure of the product is I (R = C_2H_5) rather than II or III. This was readily established by an infrared comparison and by a mixture melting point determination with the pyridine prepared according to the procedure reported by Little, *et al.*[4]

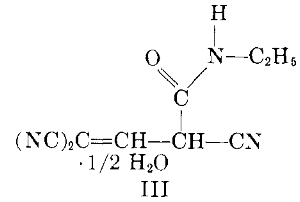


I



$$(NC)_2CH{-}CH{=}\overset{CN}{\overset{|}{C}}{-}\underset{\overset{\|}{O}}{C}{-}\overset{H}{\overset{|}{N}}{-}C_2H_5 \cdot 1/2\ H_2O$$

II



III

To test the general applicability of this method for the synthesis of 2-amino-3,5-dicyano-6-alkoxypyridines, several alcohols and alkoxide ions were utilized. The results of this study are recorded in Table I.

It can be seen from Table I that fairly good yields of the pyridines were obtained in all cases except with potassium *t*-butoxide in *t*-butyl alcohol where no pyridine could be isolated from the reaction mixture.

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[1] National Defense Education Act Fellow.

[2] A. P. Krapcho, P. S. Huyffer, and I. Starer, *J. Org. Chem.*, **27**, 3096 (1962).

[3] A. Kötz and W. Zörnig, *J. prakt. Chem.*, **182**, 425 (1906).

[4] E. L. Little, Jr., W. J. Middleton, D. D. Coffman, V. A. Engelhardt and G. N. Sausen, *J. Am. Chem. Soc.*, **80**, 2832 (1958).