the monohydrochloride by treatment with the calculated amount of methanolic hydrochloric acid. The hydrochloride was crystallized by the addition of ether and separated (m.p. *ca.* 250°). It was then reconverted to the base IX, which on recrystallization from pentane formed pale yellow needles, m.p. 60–62° (52%).

Anal. Calcd. for $C_{16}H_{17}ClN_2$: C, 70.44; H, 6.28. Found: C, 70.33; H, 6.47.

B.—Reduction of VII with lithium aluminum hydride in tetrahydrofuran, by the same procedure as that used for reduction of X and purification of the product by the same methods, gave IX in 20% yield.[5]

The hydrochloride was prepared from the base and methanolic hydrochloric acid, as previously described, and was obtained as colorless needles (from methanol–ether), m.p. 258–259°.

Anal. Calcd. for $C_{16}H_{18}Cl_2N_2$: C, 62.14; H, 5.87; N, 9.06; Cl, 22.93. Found: C, 62.44; H, 6.10; N, 9.09; Cl, 22.56.

The monopicrate was prepared from the base and picric acid in ether and was obtained as yellow prisms, m.p. 202–204° (from ethanol).

Anal. Calcd. for $C_{22}H_{20}ClN_5O_7$: C, 52.64; H, 4.03; N, 13.95. Found: C, 52.89; H, 4.02; N, 14.17.

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Quinazolines and 1,4-Benzodiazepines. XII.[1] Preparation and Reactions of 2,3-Dihydro-1*H*-1,4-benzodiazepine 4-Oxides

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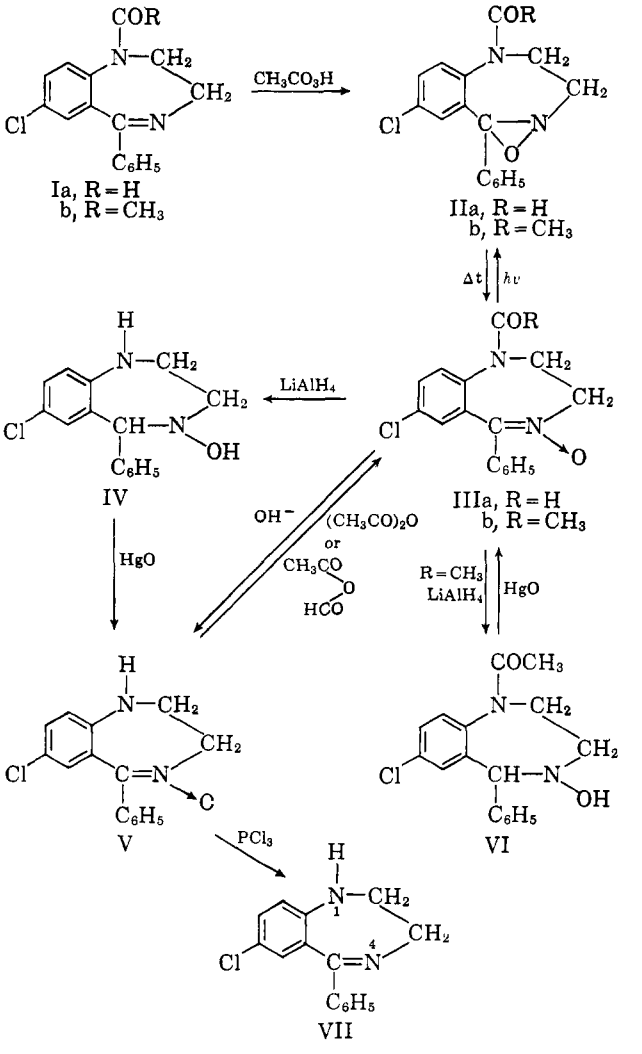
In order to obtain nitrones of type V the oxidation of the acylated 2,3-dihydrobenzodiazepines (Ia and b) with peracetic acid[2] was studied.

The primary oxidation products, the oxaziridines IIa and b, were obtained in good yield. They isomerized on heating to the nitrones IIIa and b which, in turn, rearranged to IIa and b on exposure of dilute solutions to daylight.[3] In contrast to the nitrones, the oxaziridines IIa and b liberated iodine from an acidic potassium iodide solution. According to expectation,[3,4] the ultraviolet spectra of the oxaziridines showed only an inflection at *ca.* 238 mμ, whereas the nitrones IIIa and b had maxima at *ca.* 234, 260, and 310 mμ.

These maxima, also shown by compound V, are characteristic of compounds containing a nitrone function in conjugation with a phenyl group.[4]

The acyl derivatives IIIa and b were hydrolyzed with alkali to the nitrone V, which could be reacylated to the starting materials III. This shows that under the chosen conditions the nitrones did not undergo any structural changes. Further proof was obtained by



treatment of V with phosphorus trichloride which gave the known diazepine VII.[1]

The reduction of III with lithium aluminum hydride did not yield 1-alkyl derivatives. Depending on reaction conditions, either the hydroxylamine IV or VI was obtained from IIIb.[5] Both products could be reoxidized with mercuric oxide to give the corresponding nitrones V and IIIb, respectively.

Experimental

All melting points are corrected. The infrared and ultraviolet absorption spectra of the compounds described were determined to establish structural changes. Identity was proved by mixture melting point and comparison of infrared spectra. The ultraviolet spectra were determined in isopropyl alcohol using a Cary Model 14 spectrophotometer.

7-Chloro-4,5-epoxy-1-formyl-2,3,4,5-tetrahydro-5-phenyl-1*H*-1,4-benzodiazepine (IIa).—Peracetic acid was prepared by dropwise addition of 2.5 ml. of acetic anhydride to a mixture of 3 ml. of methylene chloride, 0.6 ml. of 90% hydrogen peroxide, and 1 drop of concentrated sulfuric acid at 0°. This mixture was kept in an ice bath for 15 min., at 25° for 30 min., and then added to a solution of 5.3 g. (0.019 mole) of Ia[1] in 10 ml. of acetic acid. The solution was left at 25° for 17 hr. and then made alkaline by addition of ice and aqueous ammonia. Crystals separated which, after recrystallization from a mixture of methylene chloride and petroleum ether, formed 3.5 g. (63%) of white prisms melting at 150–152°.

(1) Paper XI, L. H. Sternbach, E. Reeder, and G. A. Archer, *J. Org. Chem.*, **28**, 2456 (1963).

(2) W. D. Emmons, *J. Am. Chem. Soc.*, **79**, 5739 (1957).

(3) See L. H. Sternbach, B. A. Koechlin, and E. Reeder, *J. Org. Chem.*, **27**, 4071 (1962), for comparison and for earlier references.

(4) M. J. Kamlet and L. A. Kaplan, *ibid.*, **22**, 576 (1957).

(5) Compound IIIa, on reduction with lithium aluminum hydride, also gave IV, which was not isolated but oxidized directly to V (over-all yield, *ca.* 25%).

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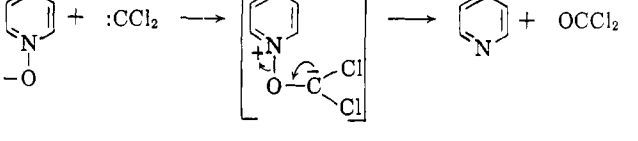
In recent years considerable interest has been manifested in the possible methods that may be employed to deoxygenate pyridine N-oxide.[1] We wish to report a novel deoxygenation reaction for pyridine N-oxide using dichlorocarbene.

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]



$$OCCl_2 + 2NaOCH_3 \longrightarrow OC(OCH_3)_2 + 2NaCl$$

(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.