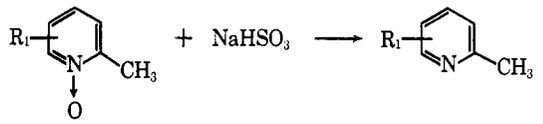
vent a solid formed during the course of the reaction. This is believed to be a pyridine–sulfur trioxide complex.

The use of aqueous sodium bisulfite was also investigated in a few selected cases with moderate success. This work is summarized in Table II. Further studies

TABLE II
DEOXYGENATION OF PYRIDINE N-OXIDES WITH AQUEOUS SODIUM BISULFITE



R_1	% yield
4-OCH_3	44
5-$COOC_2H_5$	19
6-$NHCOCH_3$	27
5-C_2H_5	66

with this reagent may be warranted since significant amounts of starting material were recovered in most cases investigated. Thus, the reaction of ethyl 6-methylnicotinate N-oxide with a mole excess of aqueous sodium bisulfite at reflux for 6 hr led to the formation of a 19% yield of the deoxygenated product and the recovery of 25% of the starting N-oxide.

Experimental Section

Melting points and boiling points are uncorrected. The starting pyridine N-oxides were either commercially available or prepared according to literature procedures. In the latter case, the physical constants of the materials were in agreement with those reported in the literature. Gas chromatographic studies were performed with an F and M Model 810 Chromatograph (hydrogen flame detector) using a 4-ft, 3.8% SE 30 on 80–100 mesh Diatoport S column.

3-Nitro-2,6-lutidine N-oxide was prepared from 3-nitro-2,6-lutidine[6] by treatment with 30% hydrogen peroxide in acetic acid, according to the method of Ochiai.[7] Using this procedure the product was obtained in 64% yield, mp 101–102°.

Anal. Calcd for $C_7H_8N_2O_3$: C, 49.99; H, 4.79; N, 16.66. Found: C, 50.12; H, 4.54; N, 16.50.

General Procedure for the Reduction of Pyridine N-Oxides. A. Dioxane Solvent.—A slow stream of sulfur dioxide was introduced into a refluxing solution containing 0.1 mole of the N-oxide in 100 ml of dioxane for 3 hr (see ref 5). The solution was cooled and solvent was removed at aspirator pressure. The residue was made alkaline by the addition of 20% potassium carbonate solution and the product was removed by ether extraction. The ether extract was dried over potassium carbonate, filtered, and evaporated to yield the product. The product was purified by either distillation or recrystallization. The results are reported in Table I.

B. Water Solvent.—A slow stream of sulfur dioxide was introduced into a refluxing solution containing 0.1 mole of N-oxide in 100 ml of water for 3 hr. The solution was cooled and made alkaline by the addition of solid potassium carbonate. The product was removed by ether extraction. The ether extract was treated as in A to yield the product.

C. Aqueous Sodium Bisulfite.—A solution of 0.1 mole of the N-oxide and 0.2 mole of sodium bisulfite in 100 ml of water was refluxed for 6 hr. The solution was allowed to cool and made alkaline by the addition of solid potassium carbonate. The product was isolated by ether extraction and purified by either distillation or recrystallization. Unreacted starting material could be recovered by extraction of the aqueous layer with chloroform. Using this procedure the amounts of recovered starting material in the cases examined were as follows: 4-methoxy-2-picoline N-oxide, 10%; ethyl 6-methylnicotinate N-oxide, 25%; 6-acetamdo-2-picoline N-oxide, 28%; 5-ethyl-2-picoline N-oxide, 0%. Yield data are reported in Table II.

(6) Aldrich Chemical Co., Inc.

(7) E. Ochiai and R. Sai, *J. Pharm. Soc. Japan*, **65B**, 18 (1945).

5H-1,4-Benzodiazepin-5-ones from Substituted *o*-Aminobenzamides

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A previous attempt by us to prepare 5H-1,4-benzodiazepin-5-ones by cyclodehydration of substituted *o*-amino-N-(2-hydroxyalkyl)benzamides resulted in the formation of 2-oxazolines.[1] This observation was independently substantiated by Field and co-workers.[2] We now wish to report a successful synthesis of this type of benzodiazepinone starting from *o*-aminobenzamides substituted in such a way as to preclude the possibility of oxazoline formation. The reaction scheme is given in Chart I.

Treatment of *o*-benzylaminobenzamide (Ia) with ethylene oxide in acetic acid at room temperature afforded *o*-[benzyl(2-hydroxyethyl)amino]benzamide (IIa). The product was demonstrated by a melting point comparison to be different from the isomeric *o*-benzylamino-N-(2-hydroxyethyl)benzamide prepared from N-benzylisatoic anhydride and 2-hydroxyethylamine. Replacement of the hydroxy group in IIa with a chloro group was accomplished by mild treatment with thionyl chloride to minimize the possibility of dehydrating the carbamoyl group to a nitrile group.[3] Cyclodehydrochlorination of the resulting product (IIIa) with sodium hydride in benzene proceeded smoothly to afford 1-benzyl-1,2,3,4-tetrahydro-5H-1,4-benzodiazepin-5-one (IVa) in good yield.

Apart from the aromatic protons, the nmr spectrum of IVa in deuteriochloroform revealed the presence of the benzylic CH_2 protons (singlet at δ 4.45). A single exchangeable lactam proton was noted as a broad singlet at δ 8.05. The four CH_2 protons of the diazepine ring appeared as a compact multiplet, centered at δ 3.38, that collapsed to a singlet on deuteration of the sample. The development of this singlet was somewhat unexpected, since an apparent magnetic equivalence is thereby indicated for the protons of the two chemically nonequivalent CH_2 groups. On protonation of IVa with trifluoroacetic acid in benzene, however, the chemical shifts for the two CH_2 groups of the diazepine ring became distinctly separated from each other, a triplet appearing δ 3.25 and a multiplet at 2.80. The triplet was assigned to the CH_2 protons adjacent to the quaternized nitrogen, and the multiplet to the CH_2 protons adjacent to the lactam nitrogen. On treatment with sodium deuterium oxide the two methylene patterns merged to a singlet.[4]

The structure of IVa was confirmed unequivocally by the following experiments. Reduction with lithium aluminum hydride ($LiAlH_4$) afforded 1-benzyl-2,3,4,5-

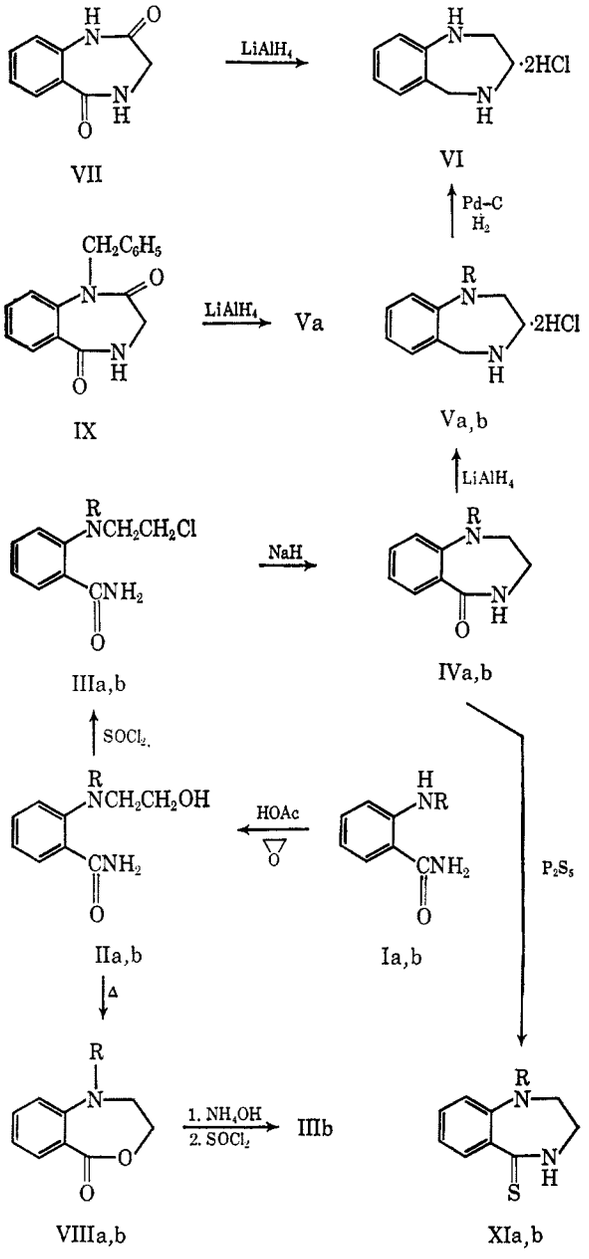
(1) A. A. Santilli and T. S. Osdene, *J. Org. Chem.*, **30**, 2100 (1965).

(2) G. F. Field, W. J. Zally, and L. H. Sternbach, *ibid.*, **30**, 2098 (1965).

(3) An attempt to prepare the tosylate ester of IIa was unsuccessful. The compound proved to be surprisingly unreactive to tosyl chloride in pyridine.

(4) S. Shiotani and K. Mitsuhashi [*J. Pharm. Soc. Japan*, **84**, 656 (1964)] reported a singlet at δ 3.04 (four protons) for the protons of the two chemically nonequivalent CH_2 groups bridging the nitrogen atoms in 2,3,4,5-tetrahydro-1H-1,4-benzodiazepine.

CHART I



a, R = $C_6H_5CH_2$
b, R = CH_3

tetrahydro-1H-1,4-benzodiazepine dihydrochloride (Va). Reductive hydrogenolysis of the latter product with palladium on carbon afforded the previously reported 2,3,4,5-tetrahydro-1H-1,4-benzodiazepine dihydrochloride (VI), prepared as described by Uskoković and co-workers[5] from the reduction of 3H-1,4-benzodiazepin-2,5(1H,4H)-dione (VII). In similar fashion Va was prepared alternatively by the $LiAlH_4$ reduction of the previously reported 1-benzyl-3H-1,4-benzodiazepine-2,5(1H,4H)-dione (IX).[5] The samples prepared by the two methods were identical.

In one experiment an attempt to distill IIa resulted in lactonization. The product thus afforded was 1-benzyl-2,3-dihydro-4,1-benzoxazepin-5(1H)-one (VIIIa). A carbonyl band at 5.80 μ in the infrared spectrum of the product was assigned to the lactone group. In the nmr spectrum, the benzylic CH_2 protons and the CH_2 protons adjacent to the O atom of the oxazepine ring were observed as a multiplet centered at δ 4.37 (four protons). The CH_2 protons adjacent to the ring N atom appeared upfield as a multiplet at δ 3.39.

1-Methyl-1,2,3,4-tetrahydro-5H-1,4-benzodiazepin-5-one (IVb) was prepared by the same reaction sequence used for the synthesis of IVa. The intermediate *o*-[(2-hydroxyethyl)methylamino]benzamide (IIb), isolated as an oil, was not characterized but was converted directly to *o*-[(2-chloroethyl)methylamino]benzamide (IIIb), which in turn was cyclized to IVb with sodium hydride in benzene. The reduction of IVb with $LiAlH_4$ afforded 2,3,4,5-tetrahydro-1-methyl-1H-1,4-benzodiazepine, isolated as the dihydrochloride (Vb).

When *o*-methylaminobenzamide (Ib) was allowed to react with ethylene oxide at steam bath temperature for several hours, the product thus formed was 2,3-dihydro-1-methyl-4,1-benzoxazepin-5(1H)-one (VIIIb), identified by comparison with an authentic sample prepared from methyl N-methylanthranilate and ethylene oxide as previously described by Kiprianov.[6] More recently Uhlig, Gentschew, and Martin[7] described the preparation of VIIIb as a by-product in the reaction of N-methylanthranilic acid with 2-bromoethanol. Everett and co-workers[8] described the formation of a related benzoxazepine derivative from the reaction of methyl anthranilate with ethylene oxide at elevated temperature. Treatment of VIIIb with ammonium hydroxide resulted in cleavage of the oxazepine ring. The product (an oil) thus formed was shown to be IIb by the fact that on reaction with thionyl chloride a solid derivative was obtained which was identical with IIIb.

The reaction of IVa and IVb with phosphorus pentasulfide in pyridine afforded 1-benzyl-1,2,3,4-tetrahydro-5H-1,4-benzodiazepine-5-thione (XIa) and 1-methyl-1,2,3,4-tetrahydro-5H-1,4-benzodiazepine-5-thione (XIb), respectively.

Attempts to debenzylate IVa *via* reductive hydrogenolysis under a variety of conditions failed. The reaction of IVa with 30% aqueous hydrobromic acid in acetic acid also failed to give the debenzylated product.

Experimental Section[9]

***o*-Benzylaminobenzamide** was prepared by heating under reflux for 20 min a stirred mixture of 13.6 g of anthranilamide, 12.6 g of benzyl chloride, and 4.0 g of sodium hydroxide in 250 ml of water. After removal by filtration the crystalline product amounted to 17.4 g, mp 160–167°. Recrystallization from methanol gave 11.3 g of product, mp 171–173° (lit.[10] mp 171–172°).

***o*-[Benzyl(2-hydroxyethyl)amino]benzamide (IIa).**—To a stirred solution of 35 ml of ethylene oxide in 200 ml of glacial acetic acid was added 25.9 g of *o*-benzylaminobenzamide. The reaction mixture was stirred at room temperature for 72 hr, concentrated to one-half the original volume in a rotary evaporator, and basified with 10% sodium hydroxide solution. An oil

(5) M. Uskoković, J. Iacobelli, and W. Wenner, *J. Org. Chem.*, **27**, 3606 (1962).

(6) A. Kiprianov, *Ukr. Khim. Zh.*, **1**, 644 (1925); *Chem. Abstr.*, **21**, 2467 (1927).

(7) E. Uhlig, M. Gentschew, and A. Martin, *Chem. Ber.*, **98**, 983 (1965).

(8) J. L. Everett, J. J. Roberts, and W. C. J. Ross, *J. Chem. Soc.*, 2386 (1953).

(9) Melting points were taken in capillary tubes (Thomas–Hoover melting point apparatus) and are corrected. Infrared spectra were determined in potassium bromide disks on a Perkin-Elmer Model 21 spectrophotometer. Nmr spectra were determined in deuteriochloroform (tetramethylsilane internal standard) on a Varian A-60 spectrophotometer. The protonation experiment with IVa was carried out in benzene with trifluoroacetic acid.

(10) W. L. F. Armarego [*J. Chem. Soc.*, 2697 (1961)] prepared this amide by the reaction of N-benzylisatoic anhydride with ammonia. A mixture melting point of the samples prepared by the two methods showed no depression.

separated which crystallized on cooling to afford 33.4 g of product. The analytical sample, mp 136–137°, from ethyl acetate, gave λ_{max}^{KBr} 6.22 μ (C=O) and 9.44 μ (OH deformation), with no amide II band.

Anal. Calcd for $C_{16}H_{18}N_2O_2$: C, 71.09; H, 6.71; N, 10.36. Found: C, 70.90; H, 6.50; N, 10.13.

o-Benzylamino-N-(2-hydroxyethyl)benzamide.—To 0.6 g of 2-hydroxyethylamine in 25 ml of ethanol was added 2.5 g of N-benzylisatoic anhydride. The reaction mixture was heated for a few minutes on a hot plate and taken to dryness *in vacuo*. The residual oil was dissolved in 40 ml of 2 *N* hydrochloric acid and filtered, and the filtrate was basified with 2 *N* sodium hydroxide solution. An oil precipitated which on cooling gave 1.5 g of a solid. Recrystallization from ethyl acetate–petroleum ether (bp 30–60°) gave 0.3 g of product: mp 80–82°, λ_{max}^{KBr} 6.15 μ (C=O) and 6.50 μ (amide II).

Anal. Calcd for $C_{16}H_{18}N_2O_2$: C, 71.09; H, 6.71; N, 10.36. Found: C, 70.79; H, 6.36; N, 10.38.

o-[(2-Hydroxyethyl)methylamino]benzamide (IIb).—To an ice-cold, stirred solution of 60 ml of ethylene oxide in 250 ml of glacial acetic acid was added 30 g of *o*-methylaminobenzamide.[11] The reaction mixture was stirred for 2 hr at ice-bath temperature and for 72 hr at room temperature, concentrated to one-half its original volume in a rotary evaporator, basified with 10% sodium hydroxide solution, and extracted with ether (five 500-ml portions). The ether extracts were combined, dried over magnesium sulfate, filtered, and evaporated to dryness, yielding 36 g of an oil. The oil was redissolved in 150 ml of chloroform and the solution was dried over magnesium sulfate, filtered, and evaporated to dryness, leaving 35.9 g of product, λ_{max}^{film} 6.05 μ (C=O) and 9.75 μ (OH deformation).

o-[Benzyl(2-chloroethyl)amino]benzamide (IIIa).—To 50 ml of thionyl chloride at ice-bath temperature was added, with stirring, 10.1 g of IIa. The reaction mixture was stirred for 30 hr at room temperature and the excess thionyl chloride was removed by evaporation *in vacuo* at room temperature. The residue was washed with ethyl acetate and dissolved in 150 ml of water. The resulting solution was filtered and the filtrate was basified with 10% sodium hydroxide solution, giving 6.1 g of product. Recrystallization of a portion of the product from benzene–petroleum ether (bp 30–60°) afforded an analytical sample, mp 82–83°, λ_{max}^{KBr} 6.00 μ (C=O).

Anal. Calcd for $C_{16}H_{17}ClN_2O$: C, 66.55; H, 5.93; Cl, 12.28; N, 9.70. Found: C, 66.75; H, 5.85; Cl, 12.57; N, 9.86.

o-[(2-Chloroethyl)methylamino]benzamide (IIIb).—To 220 ml of thionyl chloride at ice-bath temperature was added, with stirring, 35.9 g of IIb. The reaction mixture was stirred for 6 hr at ice-bath temperature and for 12 hr at room temperature. The solution was evaporated to dryness *in vacuo*, maintaining the temperature below 25°. The resulting solid was washed with petroleum ether (bp 30–60°) and dissolved in 300 ml of water. Basification of the resulting solution with 10% sodium hydroxide solution gave a solid which amounted to 24.1 g, mp 87–93°. A portion recrystallized from cyclohexane afforded an analytical sample: mp 93–94.5°, λ_{max}^{KBr} 6.03 μ (C=O).

Anal. Calcd for $C_{10}H_{13}ClN_2O$: C, 56.47; H, 6.16; Cl, 16.67; N, 13.17. Found: C, 56.29; H, 6.39; Cl, 16.5; N, 13.43.

1-Benzyl-1,2,3,4-tetrahydro-5H-1,4-benzodiazepin-5-one (IVa).—To a stirred suspension of 0.6 g of sodium hydride (50% mineral oil dispersion) in 50 ml of dry benzene was added 2.9 g of IIIa. The reaction mixture was heated under reflux for 1 hr and kept for 12 hr at room temperature. The solvent was removed *in vacuo*. The residue was triturated with 50 ml of petroleum ether (bp 30–60°) and filtered. The filter cake was washed with 25 ml of water to remove sodium chloride. The product (2.3 g) was recrystallized from benzene–petroleum ether (bp 30–60°) to afford a product: mp 140–142.5°; λ_{max}^{KBr} 6.05 μ (C=O); δ^{CDCl_3} 3.38 (compact m, 4, $N(CH_2)_2N$), 4.45 (s, 2, CH_2Ar), 8.05 (s, 1, CONH) ppm; $\delta_{CF_3CO_2H}^{C_6H_6}$ 2.80 (m, 2, lactam NCH_2), 3.25 (t, 2, quaternized NCH_2) ppm; $\delta_{2.\ NaOD}^{1.\ C_6H_6\text{-}CF_3CO_2H}$ 2.74 (s, 4, NCH_2CH_2N) ppm.

Anal. Calcd for $C_{16}H_{16}N_2O$: C, 76.16; H, 6.39; N, 11.10. Found: C, 76.02; H, 6.05; N, 10.85.

1,2,3,4-Tetrahydro-1-methyl-5H-1,4-benzodiazepin-5-one (IVb).—To a stirred suspension of 4.0 g of sodium hydride (50% mineral oil dispersion) in 150 ml of dry benzene was added dropwise a solution of 16.2 g of IIIb in 20 ml of dry benzene. The reaction mixture was heated under reflux for 3 hr and cooled to room temperature, and 25 ml of benzene saturated with water was added. The benzene solution was washed with water (three 100-ml portions) and evaporated, yielding 3.5 g of material, mp 166–169°. An additional 2.0 g of product (mp 165–169°) was recovered from the water layer by extraction with chloroform (two 250-ml portions). Recrystallization of the combined fractions from benzene afforded 5.2 g of product: mp 167–168°, λ_{max}^{KBr} 6.03 μ (C=O).

Anal. Calcd for $C_{10}H_{12}N_2O$: C, 68.16; H, 6.86; N, 15.90. Found: C, 68.01; H, 6.74; N, 15.85.

1-Benzyl-2,3,4,5-tetrahydro-1H-1,4-benzodiazepine Dihydrochloride (Va). Method A.—To a stirred suspension of 2.3 g of lithium aluminum hydride ($LiAlH_4$) in 150 ml of dry tetrahydrofuran was added a warm solution of 5.0 g of IVa in 125 ml of tetrahydrofuran. The reaction mixture was heated under reflux for 2 hr. The excess reducing agent was decomposed by the dropwise addition of a 50% aqueous tetrahydrofuran solution followed by 30 ml of 10% sodium hydroxide solution. The reaction mixture was filtered and the filtrate was dried over magnesium sulfate and evaporated to dryness, giving 4.2 g of an oil. The oil was dissolved in 40 ml of 20% ethanolic hydrogen chloride solution, and 80 ml of acetone was added, resulting in the deposition of a crystalline salt (2.5 g), mp 134–140°. Recrystallization from ethanol–acetone gave a product with mp 134–136.5°, λ_{max}^{KBr} 4.2 μ (broad salt bands).

Anal. Calcd for $C_{16}H_{20}Cl_2N_2 \cdot H_2O$: C, 58.36; H, 6.73; Cl, 21.5; N, 8.51. Found: C, 58.75; H, 6.69; Cl, 21.0; N, 8.79.

Method B.[12]—The reduction of 3.5 g of 1-benzyl-3H-1,4-benzodiazepine-2,5(1H,4H)-dione (IX)[5] with 3.0 g of $LiAlH_4$ and subsequent conversion to the dihydrochloride as in method A afforded a product (0.5 g) with mp 134–136°. A mixture melting point of the two samples gave no depression, and their infrared spectra were identical.

2,3,4,5-Tetrahydro-1H-1,4-benzodiazepine Dihydrochloride (VI) *via* Debenzylation of Va.—A suspension of 2.1 g of Va and 0.2 g of 10% palladium–charcoal catalyst in 100 ml of ethanol was hydrogenated by shaking in a Parr apparatus for 5 hr. The reaction mixture was filtered and the filtrate was evaporated to dryness on a rotary evaporator. The residual oil was dissolved in 10 ml of methanol into which was bubbled hydrogen chloride gas. Acetone was added to the point of turbidity. The solution was cooled and scratched, yielding 0.65 g of product: mp 237–239° dec (lit.[5] mp 243–244°), λ_{max}^{KBr} 3.87–4.23 μ (broad salt bands). A mixture melting point of the product with the authentic sample gave no depression, and their infrared spectra were identical.

2,3,4,5-Tetrahydro-1-methyl-1H-1,4-benzodiazepine Dihydrochloride (Vb).—To a stirred suspension of 1.5 g of $LiAlH_4$ in 500 ml of tetrahydrofuran was added 1.0 g of IVb. The reaction mixture was heated under reflux for 2 hr and a saturated solution of sodium sulfate (50 ml) was added to decompose the excess of reducing agent. The reaction mixture was filtered and the filtrate was evaporated to dryness. The oily residue was dissolved in 50 ml of chloroform and the solution was dried over magnesium sulfate, filtered, and evaporated to dryness, affording 0.9 g of an oil. The dihydrochloride salt, prepared from a 20% methanolic hydrogen chloride solution as above, amounted to 0.5 g, mp 188–190°. Recrystallization from methanol–acetone afforded a sample with mp 187–188°, λ_{max}^{KBr} 3.85–4.23 μ (broad salt bands).

Anal. Calcd for $C_{10}H_{16}Cl_2N_2$: C, 51.07; H, 6.86; Cl, 30.15; N, 11.91. Found: C, 50.78; H, 6.90; Cl, 29.9; N, 11.88.

1-Benzyl-2,3-dihydro-4,1-benzoxazepin-5(1H)-one (VIIIa).—To 15 ml of ethylene oxide in 50 ml of glacial acetic acid was added 12.0 g of IIa. The mixture was stirred at room temperature for 12 hr and the excess acetic acid was removed *in vacuo* on a rotary evaporator. The residual oil was basified with 10% sodium hydroxide solution and dissolved in 30 ml of chloroform. The chloroform solution was dried over magnesium sulfate, filtered, and taken to dryness on a rotary evaporator. Distillation of the oily residue through a short semimicro Vigreux column afforded 3.1 g of a fraction which distilled at 210–250° (0.4 mm) and solidified to an amorphous mass. Recrystallization from methanol gave a sample: mp 115–117°; λ_{max}^{KBr} 5.80 μ (lactone C=O); δ^{CDCl_3} 3.39 (m, 2, CH_2N), 4.37 (m, 4, $C_6H_5CH_2N$, CH_2O) ppm.

Anal. Calcd for $C_{16}H_{15}NO_2$: C, 75.87; H, 5.97; N, 5.53. Found: C, 75.69; H, 5.81; N, 5.34.

1-Methyl-2,3-dihydro-4,1-benzoxazepin-5(1H)-one (VIIIb).—

(11) R. P. Staiger and E. B. Miller, *J. Org. Chem.*, **24**, 1214 (1959).

(12) The authors wish to thank Mr. Richard C. Reed for performing this experiment.

A mixture of 10.5 g of IIb and 21 ml of ethylene oxide in 50 ml of glacial acetic acid was allowed to react for 16 hr at steam-bath temperature in a pressure flask. The reaction mixture was concentrated to one-half the original volume and made basic to litmus by the addition of 10% sodium hydroxide solution. An oily residue was deposited which crystallized on cooling and scratching, giving 7.0 g of product, mp 70–74°. Recrystallization from heptane afforded 5.8 g of product, mp 74–77°. A second recrystallization from *n*-pentane raised the melting point to 79–80° (lit.[6] mp 81–82°). A mixture melting point of the product with the authentic sample gave no depression, and their infrared spectra were identical, λ_{max}^{KBr} 5.86 μ (lactone C=O).

Preparation of IIIb from VIIIb.—A suspension of 4.0 g of VIIIb in 30 ml of concentrated ammonium hydroxide was heated in a Parr bomb at 180° for 6 hr. The reaction mixture was filtered and the aqueous layer was extracted with chloroform (three 75-ml portions). The combined chloroform fractions were dried over magnesium sulfate, filtered, and evaporated to dryness, giving 0.7 g of an oil. This material was allowed to react for 2 hr with 30 ml of thionyl chloride at ice-bath temperature and allowed to stand at room temperature for 16 hr. The excess thionyl chloride, was removed, leaving an oily residue. The residue was dissolved in 100 ml of water and the reaction mixture was filtered. The filtrate was brought to pH 2 with 10% HCl and washed with chloroform (two 50-ml portions). The water layer was basified with 10% sodium hydroxide solution and extracted with chloroform (two 100-ml portions). The combined chloroform extracts were dried over magnesium sulfate, filtered, and evaporated *in vacuo*. An oily residue crystallized on standing. Recrystallization from cyclohexane gave 0.1 g of IIIb, mp 91–95°. A mixture melting point with IIIb prepared from IIb gave no depression, and the infrared spectra of the samples were identical.

1-Benzyl-1,2,3,4-tetrahydro-5H-1,4-benzodiazepine-5-thione (XIa).—To a stirred suspension of 1.3 g of IVa in 10 ml of dry pyridine was added 1.3 g of phosphorus pentasulfide. The reaction mixture was heated under reflux for 2 hr, poured into 200 ml of boiling water, and cooled. An oil was deposited which crystallized on standing. Recrystallization from cyclohexane afforded 0.4 g of product: mp 119.5–120.5°, λ_{max}^{KBr} 3.18 μ (NH stretch) and 6.5 μ (S=CNH deformation).

Anal. Calcd for $C_{16}H_{16}N_2S$: C, 71.62; H, 5.96; N, 10.44; S, 11.95. Found: C, 71.66; H, 5.68; N, 10.67; S, 11.70.

1,2,3,4-Tetrahydro-1-methyl-5H-1,4-benzodiazepine-5-thione (XIb).—The product (0.7 g, mp 153–155°) was prepared, in the manner described for XIa, from 1.0 g of IVb and 1.0 g of phosphorus pentasulfide in 10 ml of dry pyridine. Recrystallization from ethanol afforded an analytical sample: mp 153.5–154°, λ_{max}^{KBr} 3.14 μ (NH stretch) and 6.62 μ (S=CNH deformation).

Anal. Calcd for $C_{10}H_{12}N_2S$: C, 62.45; H, 6.29; N, 14.57; S, 16.67. Found: C, 62.47; H, 6.11; N, 14.42; S, 16.70.

Acknowledgment.—The authors are grateful to Mr. William B. Edwards, III, for his technical assistance, to Dr. Gordon Ellis and staff for the microanalyses, to Mr. Bruce Hofmann and Dr. Charles Hetzel for their assistance with the infrared and nmr spectra, respectively, and to Dr. S. J. Childress for many helpful suggestions.

Autoxidation of Octene-1 with *t*-Butyl Hydroperoxide and Metal Acetylacetonates

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In the course of studies exploring the usefulness of *t*-butyl hydroperoxide as an epoxidizing agent,[1] the effect of small quantities of metal acetylacetonates was noted.[2] The catalytic effect of the metal acetylacetonate–*t*-butyl hydroperoxide system was also observed in the polymerization of styrene.[3] Throughout these studies it was generally observed that the systems under investigation were sensitive to oxygen.[2,3] It is known that olefins in the presence of free-radical sources readily absorb oxygen[4–7] and that metals in the presence of peroxides promote the production of free radicals,[6–9] as well as reaction intermediates which are not so well defined.[2,7,8,10] The metal-catalyzed oxidation of many organic substances,[6,7,9,11,12] and decomposition of peroxides[6,7,9,13,14] have been frequently studied. It has also been shown that some metal acetylacetonates are oxidized by molecular oxygen at elevated temperatures.[15] This preliminary study is an effort to evaluate the metal acetylacetonate–*t*-butyl hydroperoxide system in terms of its ability to initiate autoxidation (Table I). Comparison of these results is made with earlier work[2,3] done under comparable conditions in which olefin epoxidation, styrene polymerization, and peroxide decompositions were studied (Table II).

Consideration of Tables I and II leads to the conclusion that Al(III), Zr(IV), Ni(II), Zn(II), and TiO(II) acetylacetonates have little or no effect on *t*-butyl hydroperoxide under the mild conditions of these experiments. *t*-Butyl hydroperoxide itself, in the absence of the acetylacetonates, exhibits no catalytic effect on the autoxidation of octene-1 under these conditions. It is also clear that all the other metals for which data are available promote autoxidation when the hydroperoxide to metal acetylacetonate ratio is balanced such that the peroxide decomposition rate is less than the oxygen absorption rate. It has been shown that under conditions of high metal concentrations or long time intervals a steady-state autoxidation rate is reached which is independent of initiator concentration.[16,17] The meaning of this steady state is that the peroxide produced in the autoxidation is the sole significant chain initiator. A zero rate of oxygen absorption might mean that oxygen is being produced as rapidly from peroxide decomposition as it is absorbed by substrate autoxidation. As in the case of metal acetylacetonate–*t*-butyl hydroperoxide initiated styrene polymerization[3] an optimal concentration range must exist for autoxidation initiation by the same system.

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