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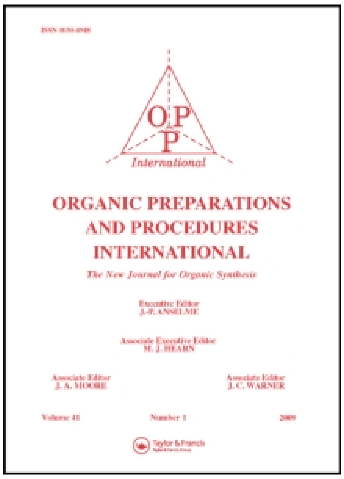

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4-PYRIDYLETHYLENE OXIDE

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4-PYRIDYLETHYLENE OXIDE

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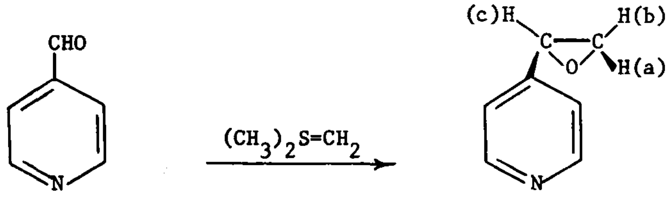
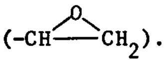
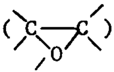
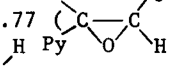
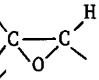
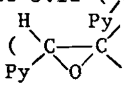


I

II

Dimethylsulfonium methylide is an excellent methylene transfer reagent which has been used to prepare a variety of epoxides from the corresponding saturated aldehyde or ketone.[1] In this paper this procedure is applied to an aldehyde containing a pyridine ring. Treatment of pyridine-4-carboxaldehyde (I) with dimethylsulfonium methylide gives the previously unknown 4-pyridylethylene oxide (II) as an unstable liquid which is isolated and purified as its picrate.[2] The free 4-pyridylethylene oxide was prepared by treating the picrate with aqueous sodium bicarbonate solution. The 4-pyridylethylene oxide decomposes slowly at room temperature and even decomposes at -10° to some extent.[3] The infrared spectrum (CS_2) showed no C=O or S=O bonds and showed absorption at 1155, 1275 and 825 cm^{-1}  $(-\mathrm{CH}\overset{\mathrm{O}}{\text{——}}\mathrm{CH}_2)$. The nmr spectrum ($CDCl_3$) showed three quartets at δ 2.77 (a, 1.0 H), 3.20 (b, 1.0 H), and 3.85 (c, 1.0 H) assigned as shown in structure I, and showed resonances at 7.0 and 8.6 ppm for the β- and α-protons of the pyridine ring respectively. Reduction of 4-pyridylethylene oxide with platinum oxide in ethanol gave as expected 4-ethanolpyridine. In addition to serving as a structure proof of II, this reaction shows that II has sufficient stability to be used as an intermediate in organic synthesis.

EXPERIMENTAL[4]

4-Pyridylethylene Oxide Picrate.--Into a 2 ℓ, 3-necked flask fitted with a mechanical stirrer, drying tube, and nitrogen inlet tube was placed 6.00 g (0.25 mole) of 50% sodium hydride in mineral oil. The mineral oil was separated from the sodium hydride by washing with ether and decanting the liquid phase. To the sodium hydride was added 175 ml of distilled dimethylsulfoxide, and the stirred mixture was heated under nitrogen at 60° until hydrogen ceased to be evolved. The solution was diluted with 175 ml of freshly distilled tetrahydrofuran and cooled in an ice-salt bath. To this cold (-10 to -15°) solution was added rapidly (2 min.) a solution of 51 g (0.25 mole) of trimethylsulfonium iodide[5] in 200 ml of dimethylsulfoxide. As soon as the trimethylsulfonium iodide was added, 21.4 g (0.20 mole) of distilled pyridine-4-carboxaldehyde[6] in 50 ml of tetrahydrofuran was added over a 2 min. period while the dimethylsulfonium methylide solution was maintained at -10 to -15°. The reaction mixture was left at ice-bath temperature for 5 min., allowed to warm to room temperature, diluted with 800 ml of water and extracted with ether. The ethereal extracts were dried (Na_2SO_4) and then a saturated solution of picric acid in ether was added until no further precipitation occurred. The solid was filtered and dried to give 16.2 g (23%) of crystals, mp 130-135°. The analytical sample prepared by recrystallization from methanol had mp 139-141°, ν_{max}^{KBr} 875 cm^{-1} (). The nmr spectrum (pyridine) showed a quartet at δ 2.77 ( cis to pyridine ring, 1.0 H), a quartet at 3.12 ( trans to pyridine ring, 1.0 H) and a quartet at 3.87 ppm (, 0.99 H).

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Anal Calcd for $C_{13}H_{10}N_4O_8$: C, 44.57; H, 2.87; N, 16.00. Found: C, 44.69; H, 2.94; N, 15.96.

In a separate run the ethereal extracts were concentrated to give 14.8 g of a liquid that contained 4-pyridylethylene oxide and dimethyl sulfoxide as its major components. Attempts to purify this liquid by vacuum distillation or preparative gas chromatography were unsuccessful.

Generation of 4-Pyridylethylene Oxide (II) from Its Picrate.--A 7.00 g (0.02 mole) sample of 4-pyridylethylene oxide picrate was suspended in 50 ml of saturated sodium bicarbonate solution and 300 ml of water was added to dissolve the sodium picrate. The aqueous solution was extracted 5 times with 75 ml portions of ether. Concentration of the dried extracts afforded 2.09 g of liquid. This liquid was extracted with ether leaving a dark oil. The ethereal extracts were concentrated to give 1.63 g (76.2%) of a light yellow liquid. A VPC (DEGS) showed only one peak.

Reduction of 4-Pyridylethylene Oxide Using Platinum Oxide Catalyst in Ethanol.--4-Pyridylethylene oxide (1.21 g, 0.01 mole) in 80 ml of ethanol containing 0.50 g of platinum oxide was reduced at 2-5 atm until hydrogen ceased to be taken up. Concentration of filtered solution gave 1.15 g (93.5%) of 4-ethanolpyridine. A VPC (DEGS) showed only one peak equal in retention time to an authentic sample of 4-ethanolpyridine. The infrared spectrum was identical to the infrared spectrum of an authentic sample of 4-ethanolpyridine. Conversion to the picrate gave 2.44 g (69.5%) of picrate, mp 125-130°. Recrystallization from ethanol gave crystals, mp 128-131°. Reported[6] mp 134-135°. A mixture of this compound with an authentic sample of 4-ethanolpyridine picrate, mp 128-131°, was not depressed.

REFERENCES

1. E. J. Corey and M. Chaykovsky, J. Amer. Chem. Soc., 89, 1353 (1967); E. J. Corey and M. Jautelat, ibid, 89, 3912 (1967).

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2. The low yield of II-picrate (23%) obtained is probably due to some decomposition of II prior to the formation of its picrate which is stable (see footnote 5) and to the attack of dimethylsulfonium methylide on the pyridine ring. No starting aldehyde (I) was recovered.
3. A sample of 4-pyridylethylene oxide kept at -10° for one month had completely decomposed. Its picrate, however, has been kept stored at 0° for over a year without decomposition.
4. Melting points were determined on a Kofler hot stage microscope using a calibrated thermometer. Ir spectra were measured with a Perkin Elmer 221 Spectrophotometer; NMR spectra were recorded on a Varian Model A-60 spectrometer using TMS as an internal standard.
5. H. J. Emeléus and H. G. Heal, J. Chem. Soc., 1126 (1946).
6. The pyridine-4-carboxaldehyde was obtained from Aldrich Chemical Company, Inc.

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