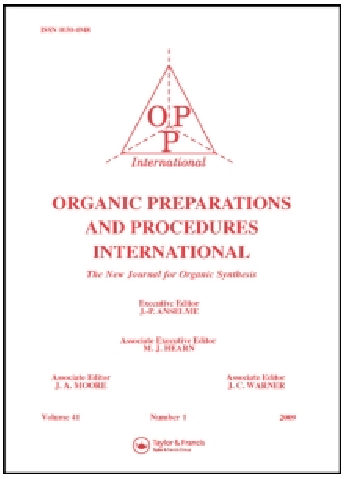

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SYNTHESIS OF THE ETHYLNITRONE OF ACETALDEHYDE

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REFERENCES

1. D. S. Rao and B. D. Tilak, J. Sci. Ind. Res., 13B, 829 (1954).
2. H. Wynberg, J. De Wit and H. J. M. Sinnige, J. Org. Chem., 35, 711 (1970).
3. M. Ahmed, J. Ashby, M. Ayad and O. Meth-Cohn, J. Chem. Soc., Perkin Trans. I, 1099 (1973).
4. D. S. Rao and B. D. Tilak, J. Sci. Ind. Res., 16B, 65 (1957). The product reported by Dann and Kokorudz [Chem. Ber., 91, 181 (1958)], was shown by us to be the benzo[1,2-b:4,3-b']dithiophene.
5. A. Kraak, A. K. Wiersema, P. Jordens and H. Wynberg, Tetrahedron, 24, 3381 (1968).

SYNTHESIS OF THE ETHYLNITRONE OF ACETALDEHYDE

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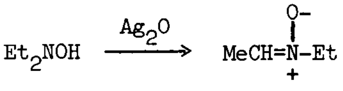
A useful synthesis of acetaldehyde ethylnitrone (N-ethylidenethylamine N-oxide), the first known primary N-alkylnitrone of a simple aliphatic aldehyde, was needed for identification purposes and further testing. This compound is an intermediate in the oxidation of N,N-diethylhydroxylamine (I),[1] which has been proposed as an atmospheric additive to inhibit photochemical smog formation.[2] Efforts to synthesize II by the condensation of acetaldehyde with N-ethylhydroxylamine or by the N-ethylation of acetaldoxime failed completely. Bubbling O_2 through I afforded a solution contaminated by ca. 2% of material with promising spectral properties, but whose separation without decomposition proved impossible. The nitrone (II) was ultimately prepared in essentially quantitative yield by the oxidation of DEHA with silver oxide:[3]



$$\mathrm{Et_2NOH} \xrightarrow{\mathrm{Ag_2O}} \mathrm{MeCH{=}\overset{O^-}{\underset{+}{N}}{-}Et}$$

I II

The product could be vacuum distilled without decomposition at room temperature into a receiver cooled in Dry Ice and was stable for prolonged periods below 0°. When left at room temperature under N_2, the colorless distillate turns yellow within hours and its ^1H NMR spectrum is complicated by the appearance of broad new peaks at δ 1.1 and 2.6, which are also characteristic of the yellow product isolated by vacuum distillation much above room temperature; they can be attributed to oligomer formation (conclusion derived by analysis of the mass spectra of aged samples of II).

Because of the geometrical constraints introduced by the double bond, the nitrone (II) can exist as *syn* or *anti* isomers. The NMR spectrum showed that one of these isomers amounts to about 95% of the product although the presence of the second isomer also is indicated from small absorptions at δ 1.8 (d) and 6.7 (q) ($J = 6$ Hz, ratio 3:1).

EXPERIMENTAL

Acetaldehyde ethylnitrone (II).- Redistilled N,N-diethylhydroxylamine (Aldrich, 2.23 g, 25 mmol) was dripped into a rapidly stirred suspension of dry silver oxide (11.6 g, 50 mmol) in 50 ml of anhydrous ether maintained at 0° under N_2. After 1 hr., the reaction mixture was filtered through Celite, dried over Na_2SO_4 and stripped of solvent at 10 torr to give quantitative yields of II which could be further purified by distillation at 25-30° (ca. 1 torr) into a receiver cooled in Dry Ice. The nitrone is extremely hygroscopic and even after drying and distillation, the product contains a small amount of water which can be minimized but not eliminated entirely by working under N_2 with oven-dried glassware. The structure proof for II is based primarily on its spectral properties.

IR (CCl_4) cm^{-1}: 3000 and 2950 (CH stretch), 1600 (C=N stretch), 1460 (sh), 1440-1420, 1380, 1360, 1340, 1250, 1190, 1140, 1100, 1040; MS (m/e): 87.0687 (P, 100%, calc. 87.0684), 72.0445 (P-Me, 25%, Calc. 72.0449), 71 (P-O, 25%), 59 (P-C_2H_4, 60%), 56 (P-Me-O, 60%); ^1H NMR ($CDCl_3$-TMS) δ: 1.40 (t, 3H, J = 7 Hz), 1.95 (d, 3H, J = 6 Hz), 3.85 (q, 2H, J = 7 Hz), 7.10 (q, 1H, J = 6 Hz); ^{13}C NMR ($CDCl_3$) ppm: 10.5 (methyl), 11.3 (methyl), 57.6 (CH_2, $J_{^{13}CH_3}$ = 141 Hz), 132.0 (vinyl CH, $J_{^{13}CH}$ = 179 Hz).

REFERENCES

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1. T. Caceres, E. Lissi and E. Sanhueza, Int. J. Chem. Kinetics, 10, 1167 (1978).
2. D. Schaal, K. Partymiller and J. Heicklen, Science Total Environ., 9, 209 (1978) and references therein.
3. E. G. Rozantsev, "Free Nitroxyl Radicals," Eng. trans. by B. J. Hazzard, p. 208, Plenum, New York, N. Y., 1970.

CONVENIENT SYNTHESIS OF 2-TRIMETHYLSILYLOXYPYRIDINES

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Hexamethyldisilazane is an efficient derivatizing agent for use in the gas chromatographic analysis of relatively non-volatile 2-(1H)-pyridones. Excellent yields of 2-trimethylsilyloxypyridines II were obtained in six cases examined (Table 1), by treatment of I with hexamethyldisilazane in