

ON THE RECENTLY REPORTED SYNTHESIS OF THE NITROXIDE,
2,2,3,3-TETRAMETHYLAZIRIDINE-1-OXYL

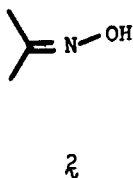
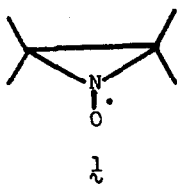
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Recently Luckhurst and Sundholm² claimed to have synthesized the interesting nitroxide 2,2,3,3-tetramethylaziridine-1-oxyl (1). ESR and chemical evidence was offered in support of their contention. Our continuing interest in nitroxide chemistry and in particular nitroxide 1 ³ owing to its relevance to the general problem of developing effective olefin spin labels has led us to re-examine Luckhurst's results. We wish to report that the colorless crystals, mp 58-60°, which were taken by Luckhurst and Sundholm to be nitroxide 1 are in fact acetone oxime (2).



The colorless crystals were prepared according to the published² procedure, *i.e.*, unpurified⁴ 2,3-(dihydroxylamino)-2,3-dimethylbutane (3)⁵ was allowed to stand at $\sim 25^\circ$ in air for several days. The solid changed into a paramagnetic oil (A) from which the colorless crystals, mp 58-60°, separated on further standing. Indeed, the crystals were found to be paramagnetic when ESR spectra were determined on samples which had not enjoyed further purification. However, recrystallization of the initially obtained colorless crystals from pentane afforded non-paramagnetic, readily sublimable colorless plates, mp 59-60°. This

last substance showed no melting point depression on admixture with authentic acetone oxime, mp 59-60°, ⁶ moreover, the infrared spectra of the two substances were identical.

Luckhurst² reports that "the product was purified for the electron resonance experiments by elution from an alumina column with toluene and for the mass spectrometry measurements by chromatography from a 10% polyethyleneglycol adipate/1% phosphoric acid column attached to the spectrometer." We find that the paramagnetic oil (A) is eluted from an alumina column with toluene. It is clear that Luckhurst's esr spectra were those of an as yet unidentified nitroxide (or nitroxides) present in the oil and not those arising from the colorless crystals. The mass spectral evidence cited also has no bearing since it was not demonstrated that the "major component" from the vpc trace was in fact paramagnetic and identical with the colorless crystals obtained earlier. The same criticism applies to the LAH reduction studies on the "dominant product."

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References

1. NDEA Predoctoral Fellow, 1966-1969; PRF Predoctoral Fellow, 1969-1970.
2. G. R. Luckhurst and F. Sundholm, Tetrahedron Letters, 675 (1971).
3. R. J. Dinerstein, Ph.D. Thesis, University of Oregon, June, 1971.
4. Our best sample of $\text{C}_6\text{H}_{16}\text{N}_2\text{O}_2$ showed mp 159-162° (CH_2Cl_2). Calc. for $\text{C}_6\text{H}_{16}\text{N}_2\text{O}_2$: C, 48.63; H, 10.88; N, 18.90. Found: C, 48.58; H, 11.02; N, 18.85. Material of this purity did not undergo rapid decomposition when exposed to air at 25° for several days. When stored under oxygen, however, without first changing into a liquid, the material slowly afforded crystals of acetone oxime which grew around the upper regions of the flask.
5. M. Lamchen and T. W. Mittag, J. Chem. Soc., 2300 (1966).
6. Matheson, Coleman and Bell, supplier.