

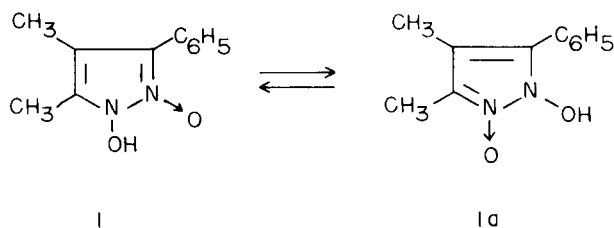
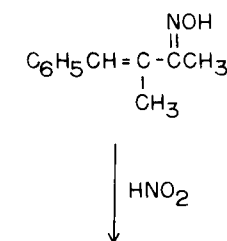
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The Synthesis and Some Reactions of an *N*-Hydroxypyrazole-*N'*-oxide (I)

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Sir:

It has been found that nitrosation of 3-methyl-4-phenyl-3-buten-2-one oxime produces the novel heterocycle, 1-hydroxy-3-phenyl-4,5-dimethylpyrazole-2-oxide (3). The structure of this material

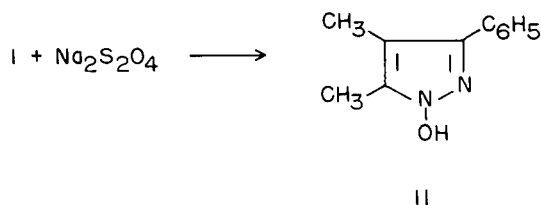


of I measured in dioxane solution containing perchloric acid was 6.4.

(3) Chelate compounds consisting of two equivalents of ligand per metal atom have been obtained with Zn^{II} , Ni^{II} , Co^{II} , and Cu^{II} . All these materials were readily prepared by mixing aqueous solutions of the appropriate metal salt and the sodium salt of I.

(4) Reduction products.

Reduction of I with aqueous sodium hydrosulfite produced a white solid, $\text{C}_{11}\text{H}_{12}\text{N}_2\text{O}$, m.p. 167-168°, whose n.m.r. spectrum [8.0 τ , (CH_3), 2.6 τ (C_6H_5), 1.5 τ (OH)] and infrared spectrum (5) (broad absorption in 3 μ region) are compatible with structure II. This compound appears to be the first *N*-hydroxy-



has been inferred from the following data:

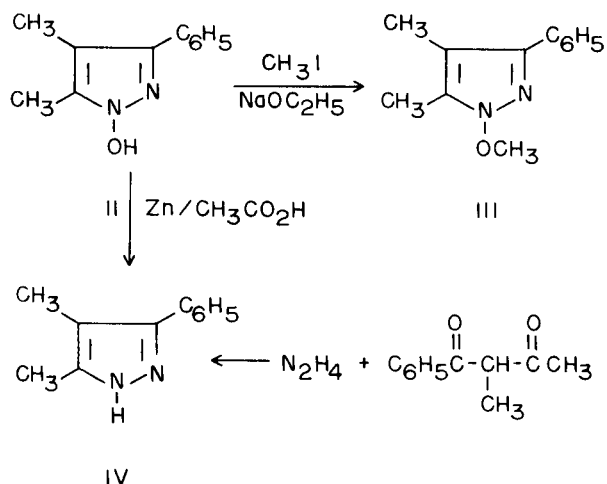
(1) A highly polar structure is indicated by a high melting point (200°) and very limited solubility in most organic solvents except dimethyl sulfoxide and dimethylformamide. The infrared spectrum of I showed weak, very broad absorption in the region of 3.7-4.3 μ (4) and very broad, structureless absorption, similar to that of many salts, in the region of 5-7 μ . The ultraviolet spectra of I and its sodium salt in ethanol were nearly superimposable indicating also the salt-like nature of I.

(2) Lack of n.m.r. absorption due to a single C-H proton combined with solubility in dilute base which can be accounted for by the highly delocalized anion which is produced from structure I. The pK_a

pyrazole reported. (Whether this is a 5-methyl derivative as pictured or a 3-methyl derivative has not been determined.)

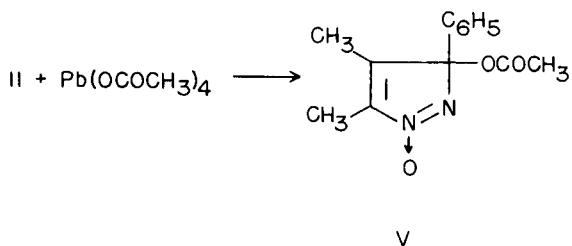
Compound II is amphoteric. It forms a methyl ether III [n.m.r. spectrum: 7.89 τ ($\text{C}-\text{CH}_3$), 7.79 τ ($\text{C}-\text{CH}_3$), 5.93 τ (OCH_3), 2.45 τ (C_6H_5)] upon treatment with methyl iodide in the presence of sodium ethoxide.

Reduction of I or II with zinc in acetic acid yielded 3-phenyl-4,5-dimethylpyrazole (IV) identical to a sample independently synthesized from 3-methyl-4-phenylbutane-1,3-dione (6). These reactions are summarized as follows. The ultraviolet spectra of



compounds II, III, and IV are virtually superimposable supporting the suggestion that they all contain a pyrazole nucleus. Their infrared and n.m.r. spectra also are similar.

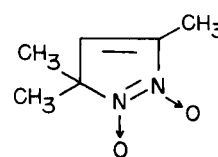
The hydroxypyrazole II is readily oxidized. At a platinum electrode in dry acetonitrile it is oxidized at 0.6 V. (vs. Ag° , 0.1 M silver perchlorate reference electrode). (When this oxidation is carried out in the cavity of an e.p.r. spectrometer, a complex, but resolved spectrum was obtained indicating the presence of a free radical species. It is believed without further proof that a nitroxide radical was formed (7).) When the oxidation was carried out with lead tetraacetate, an acetoxy compound, $\text{C}_{13}\text{H}_{14}\text{N}_2\text{O}_3$, m. p. 106° , was obtained which is assigned structure V.



The infrared spectrum of V shows strong bands at 1748 cm^{-1} and 1490 cm^{-1} consistent with an α,β -unsaturated azoxy compound (8) containing an

ester function. Its n.m.r. spectrum indicates that two methyl groups are weakly coupled to each other consistent with a structure having two such groups *cis* to each other on an aliphatic double bond. Also the phenyl group appears as a sharp singlet indicating that it is now attached to a saturated center. This oxidation is reminiscent of the oxidation of Δ^2 -pyrazolines to 3-acetoxy- Δ^1 -pyrazolines with lead tetraacetate (9).

The nitrosation product (I) had previously been assigned the structure of an acyclic nitrimine without proof (10). The similarities of some of the properties of I with pernitrosomesityl oxide (VI) (8), the nitrosation product of mesityl oxide oxime, originally suggested the structure of I.



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REFERENCES

- (1) Acknowledgement is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for support of this research.
- (2) National Science Foundation Summer Fellow, 1965.
- (3) It is not known whether this compound is inter- or intramolecularly hydrogen bonded, but in either case rapid proton exchange would inter-convert it with its isomer Ia. A similar situation exists with pyrazoles themselves.
- (4) The infrared spectrum of 1-hydroxyimidazole-3-oxide, a compound similar to I, is reported to show no OH absorption; J. B. Wright, *J. Org. Chem.*, **29**, 1620 (1964).
- (5) A. R. Katritzky and A. P. Ambler in "Physical Methods in Heterocyclic Chemistry", A. R. Katritzky, Ed., Academic Press, New York, N. Y., 1963, Vol. II, p. 235.
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- (7) We are indebted to Dr. Kenneth J. Martin of the Rohm and Haas Co., Redstone Research Laboratories for this experiment.
- (8) J. P. Freeman, *J. Org. Chem.*, **27**, 1309 (1962).
- (9) J. P. Freeman, *ibid.*, **29**, 1379 (1964).
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