

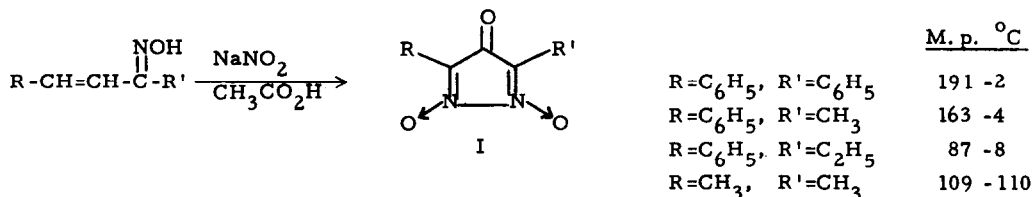
3,4-DIAZACYCLOPENTADIENONE OXIDES.  
 DERIVATIVES OF A NEW HETEROCYCLIC SYSTEM<sup>1</sup>.

Jeremiah P. Freeman<sup>2</sup> and Donald L. Surbey

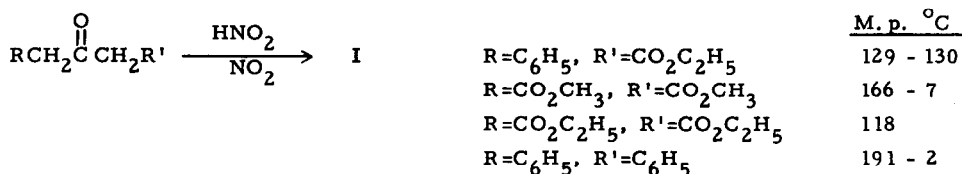
Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556

(Received in USA 7 August 1967)

The reaction of  $\beta$ -alkyl or aryl- $\alpha,\beta$ -unsaturated oximes with nitrous acid yields a mixture of the corresponding 3,4-diazacyclopentadienone dioxides I, and their oximes. For example, treatment of benzalacetone oxime in acetic acid with sodium nitrite solution rapidly produced an orange precipitate which was washed with methylene chloride and then recrystallized from dimethylformamide-methanol to yield the oxime of I,  $R=C_6H_5$ ,  $R'=CH_3$ , m. p. 218-219°, in 73% yield. Silica gel chromatography of the methylene chloride washes yielded ketone I,  $R=C_6H_5$ ,  $R'=CH_3$  in 9% yield. The yield of I could be increased to 40% by carrying



out the reaction under oxygen. Some compounds of this class are also available from the oxidative nitrosation of certain ketones. This latter reaction was discovered by Henry and



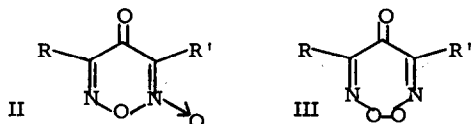
von Pechmann (1) while the former was investigated by Ponzio and his co-workers (2) following earlier studies by Harries (3).

The structure of these compounds, previously assigned six-(4) and seven-(1-3) membered ring structures, is based upon four lines of evidence. First, the n. m. r. spectrum of the dimethyl derivative, I,  $R=R'=CH_3$ , contains only a single sharp signal at 7.88 $\tau$  showing that the two groups are in identical environments (5). Thus the six-membered ring structure II is ruled out. Secondly, the bright yellow to orange-red colors of these

<sup>1</sup> We are indebted to the Donors of the Petroleum Research Fund of the American Chemical Society for support of this research.

<sup>2</sup> Alfred P. Sloan Fellow.

compounds<sup>3</sup> cannot be explained by the seven-membered ring structure III nor is the thermal stability of these compounds compatible with the peroxide structure. Thirdly, reduction



leads to pyrazole derivatives which are directly related to structure I. Finally, two of the compounds of type I have been synthesized from a five-ring precursor.

Reduction of I by stirring for 30 min. at room temperature with zinc in acetic acid produced the corresponding 4-hydroxypyrazoles, IV, in yields from 40-86%. This sequence



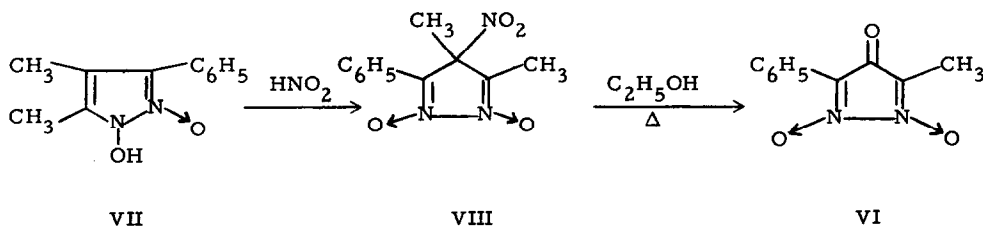
of reactions constitutes a reasonable convenient synthesis of this class of compounds which have been hitherto relatively inaccessible. The structure of these compounds rests on their elemental analyses, spectral properties, and independent synthesis in three cases. (7)

When the milder reductant sodium dithionite was employed, 1,4-dihydroxypyrazoles, V,

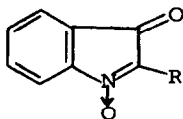


could be isolated. Their structure is based upon elemental analysis, spectral properties, and their reduction with zinc and acetic acid to the 4-hydroxypyrazoles.

The synthesis of VI (I, R=C<sub>6</sub>H<sub>5</sub>, R'=CH<sub>3</sub>) has been effected independently. Treatment of 1-hydroxy-3-phenyl-4,5-dimethylpyrazole-2-oxide, VII (8) with nitrous acid produced a nitro compound believed to have structure VIII which upon heating in ethanol yielded VI.<sup>4</sup>



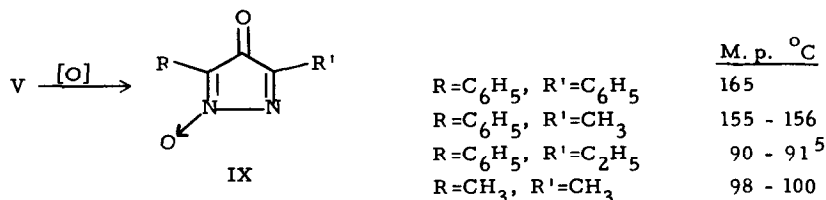
<sup>3</sup> These colors and high melting points are reminiscent of the isotogens which also contain a similar chromophore (6).



<sup>4</sup> These experiments were carried out by J. J. Gannon, Jr. in these Laboratories.

The details of this process are not clear but the sequence supports the five-ring structure for I. Synthesis of I,  $R=R'=C_6H_5$  has been effected in a similar way.

Compounds of type V, which are white crystalline solids, upon standing in the air or when treated with oxidizing agents such as Fremy's salt, were converted to deeply colored compounds whose structure is proposed as 3,4-diazacyclopentadienone monoxides, IX. The structure of these compounds was inferred from their elemental analyses, their infrared



spectra (absence of adsorption in the  $3\mu$  region and appearance of a carbonyl band at  $1700\text{ cm}^{-1}$ ), their deep colors,<sup>3</sup> and their ready reduction back to V. The similarity of behavior of compounds of type V and IX to a hydroquinonequinone system was further heightened by the ready one-electron reduction of IX to stable free radicals analogous to the semi-quinones.

Efforts to remove the N-oxide functions of I to obtain the parent diazacyclopentadienone system have so far been unsuccessful. Only tars were obtained with triphenylphosphine in benzene while the same reagent in ethanol reduced I to a mixture of IV and V. Compounds of type V in which  $R=CO_2R$  resist oxidation and compounds of type IX containing carbalkoxy groups have not been obtained. The chemistry of these novel heterocycles is currently under investigation.

#### REFERENCES

1. P. Henry and H. vonPechmann, Ber., 26, 997 (1893).
2. G. Ponzio, Gazz. chim. ital., 66, 479 (1936); G. Longo, ibid., 66, 815 (1936).
3. C. Harries and H. Tietz, Ann., 330, 237 (1904).
4. H. Wieland, Ann., 424, 112 (1921).
5. R. K. Harris, A. R. Katritzky, S. Øksne, A. S. Bailey and W. C. Patterson, J. Chem. Soc., 197 (1963); J. P. Freeman, J. Org. Chem., 28, 2508 (1963).
6. P. Pfeiffer, Ber., 45, 1819 (1912).
7. F. Sachs and A. Röhmer, Ber., 35, 3307 (1902).
8. J. P. Freeman and J. J. Gannon, Jr., J. Heterocyclic Chem., 3, 544 (1966).

<sup>5</sup>

A crystalline dimer has also been isolated but it reverts to monomer in solution.