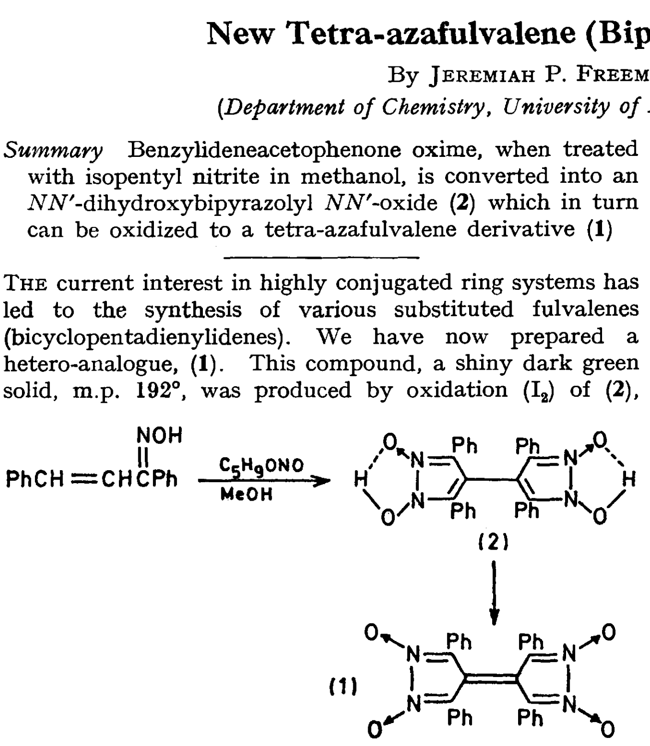
New Tetra-azafulvalene (Bipyrazol-4-ylidene) Derivatives

By Jeremiah P. Freeman and John F. Hansen

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

Summary Benzylideneacetophenone oxime, when treated with isopentyl nitrite in methanol, is converted into an *NN'*-dihydroxybipyrazolyl *NN'*-oxide (**2**) which in turn can be oxidized to a tetra-azafulvalene derivative (**1**)

The current interest in highly conjugated ring systems has led to the synthesis of various substituted fulvalenes (bicyclopentadienylidenes). We have now prepared a hetero-analogue, (**1**). This compound, a shiny dark green solid, m.p. 192°, was produced by oxidation (I_2) of (**2**), which in turn was obtained by treatment of benzylideneacetophenone oxime with isopentyl nitrite in methanol. The overall yield of (**1**) from the oxime was 45%.

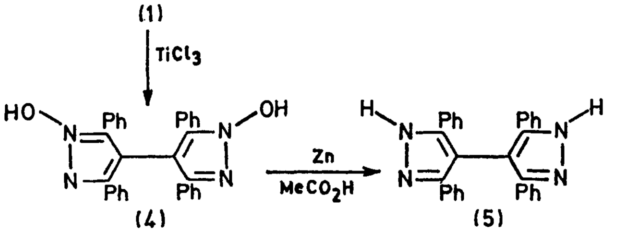


The structure of (**1**) rests upon its analysis and spectral properties and upon the structure of (**2**). Compound (**2**) was soluble in aqueous $NaHCO_3$ (*cf.* other *N*-hydroxypyrazole *N'*-oxides[1]) and was purified and stored as a dipotassium salt. It showed a molecular ion at *m/e* 502; its other chemical and spectral properties were similar to those previously reported[1] for compounds of this structure.†

Compound (**1**) showed the following spectral properties: λ_{max} 502; log ϵ 4·29 [similar to that of an isomeric tetra-azafulvalene system, 4,4',5,5'-tetraphenylbi-imidazol-2-ylidene[2] (λ_{max} 494; log ϵ 4·75)]; ν_{max} 1580 and 1550 cm^{-1}. It showed no molecular ion in its mass spectrum, but a prominent peak at *m/e* 440 ($M^+ - 60$; loss of 2 NO?) was observed.

Reduction ($TiCl_3$) of (**1**) produced a white solid, m.p. 286—289°, whose analysis and spectral properties were consistent with structure (**4**). This compound undergoes dimethylation, diacetylation, and ditosylation as expected. Further reduction of (**4**) yielded the bipyrazole (**5**), m.p. 328—331°. The structure of this latter compound follows from its analysis, stability in the mass spectrometer, acidic properties (solubility in base and formation of insoluble silver salt), and the formation of a diacetyl derivative.

The dihydroxybipyrazole (**4**) reacted with lead dioxide in acetonitrile to produce a deep magenta solution, but only (**4**) could be isolated from the solution. However, this solution exhibited a strong e.s.r. signal and acted as a moderate oxidant, oxidizing benzylic alcohols to the aldehydes. No information on the structure of the species is available.



It might be expected that the double bond character of the central C–C bond of compound (**1**) would be very low because of the severe interactions of the four '*ortho*' phenyl rings. For example, attempts to obtain fulvalenes with corresponding phenyl substituents were unsuccessful.[3] Because of its low solubility in suitable solvents, it has not yet been possible to obtain e.s.r. data to establish whether compound (**1**) is radical in character[4] or exists as in structure (**1**) but dilute solutions do show unresolved e.s.r. signals.

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† Compound (**2**) forms insoluble complexes with Cu^{II} and undergoes methylation to a dimethyl derivative, whose mass spectrum shows a molecular ion and whose n.m.r. spectrum includes a 6H singlet at δ 4·14 p.p.m.

[1] J. P. Freeman and J. J. Gannon, *J. Org. Chem.*, 1969, **34**, 194.

[2] U. Mayer, H. Baumgartl, and H. Zimmerman, *Tetrahedron Letters*, 1966, 5221.

[3] P. L. Pauson and B. J. Williams, *J. Chem. Soc.*, 1961, 4159.

[4] For a review of investigations of the diradical character of other bis-nitrones, see E. G. Rozantsev and V. D. Sholle, *Synthesis*, 1971, 190.