only reduced by the dihydropyridine coenzyme model and not by ethanol. Other as yet undefined groups in the enzyme must then be postulated to function in the activation of substrate and in the activation of indole to permit the reverse reaction. Further studies are in progress; in particular, the effect of substituents on the phenyl group of the indolenine on the rate of reduction will be investigated.

Acknowledgment. We wish to thank Dr. D. P. Hollis for his assistance in obtaining the nmr spectra.

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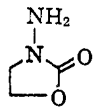
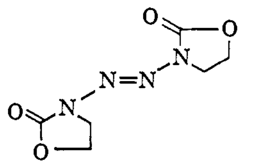
Stereospecific Oxidation of a 1,1-Disubstituted Hydrazine *via* Metal Ion Coordination. A New Approach to Isomeric Azo Compounds

Sir:

2-Tetrazenes, substituted amino derivatives of azo compounds, are capable of existing in the *cis* and *trans* forms, but to date only single isomeric products have been reported.[1–3]

We wish to report the first example of a tetrazene synthesis which affords both the *cis* and *trans* isomers. This has been accomplished by the stereospecific oxidation of the 1,1-disubstituted hydrazine, 3-amino-2-oxazolidinone (I), which results in the formation of either the *trans* (II) or *cis* (III) 3,3′-azobis(2-oxazolidinone), depending on the specific oxidizing agent used.


I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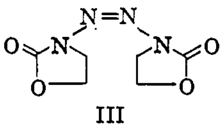
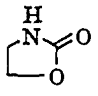

III


IV

Thus oxidation of I with bromine in aqueous solution, or with potassium iodate in concentrated nitric acid, or with potassium bromate in 6 *N* HCl at 5°, affords compound II, mp 298–299° (from acetonitrile), in 76, 82, and 86% yield, respectively. *Anal.* Calcd for $C_6H_8N_4O_4$: C, 36.01; H, 4.03; N, 27.97; mol wt, 200. Found: C, 36.31; H, 4.19; N, 28.06; mol wt,[4] 197.

Reaction of I with excess yellow mercuric oxide in either dry dioxane or tetrahydrofuran for several days at room temperature affords a new isomer, compound III, mp 170–171[5] (from dioxane), in 50% yield. Found: C, 36.11; H, 4.12; N, 27.91; mol wt, 199 (thermistor vapor pressure method in acetonitrile). In addition, compound II (10%) was also isolated by extraction of the mercuric oxide cake with hot acetonitrile.

The infrared spectra of compounds II and III were as expected (*e.g.*, carbonyl bands at 1765 and 1770 cm^{-1}, respectively), while the Raman spectra[6] showed –N=N– stretching frequencies at 1479 and 1474 cm^{-1}, respectively. The ultraviolet spectrum[7] of II, devoid of fine structure, contained bands at 272 mμ (ϵ 17,880) and a shoulder at 252 mμ (ϵ 9960); compound III gave bands at 290 mμ (ϵ 3840) and 217 mμ (ϵ 5980). Examination of the nmr spectrum[8] [hot $(CD_3)_2SO$] of each compound showed a pair of triplets, as would be expected on the basis of their structures. Compound II showed absorption centered at τ 3.99 ($-OCH_2-$) and at 4.58 ($-N-CH_2-$), while III absorbed at τ 3.85 ($-O-CH_2-$) and 4.50 ($-N-CH_2-$). The slight difference in chemical shift tends to confirm that these two compounds are isomeric in nature and not crystal modifications of each other.

The mass spectrometric fragmentation behavior of II and III were essentially identical. A change was observed in the position of the mass peaks during the analysis. Neither compound showed any parent ion when heated to 250°; however, peaks with *m/e* up to 390 were noted. The peak present at *m/e* 87 (assigned a relative abundance of 100%) was used to determine the relative concentration of the observed peaks; thus, for compounds II and III, respectively, *m/e* 85 (5, 26); *m/e* 59 (68, 66); *m/e* 44 (92, 99). The compounds decomposed mainly to carbon dioxide, nitrogen, and ethylene.

The densities of II and III were determined using density gradient columns and found to be 1.64 ± 0.01 and 1.159 ± 0.001, respectively, indicating a higher packing order for II due to greater symmetry. The higher order of symmetry for II was also indicated by the relative simplicity of its infrared spectrum.

Hydrogenolysis[9] of III with platinum oxide catalyst at 50° in absolute ethanol resulted in the formation of 2-oxazolidinone (IV) in 75% yield. Compound II yielded only starting material under essentially similar reaction conditions, probably due to its generally poor solubility characteristics in the solvents tested.

Convincing evidence of the isomeric nature of the two compounds was obtained by the ultraviolet light catalyzed transformation of III to II in the crystal state. The isomerization proceeded to about 40% conversion in 8 hr and the product isolated (from acetonitrile) was identical in every way with II.

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[1] H. Wieland, "Die Hydrazine," Verlog von Ferdinand Enke, Stuttgart, 1913, pp 32–39.

[2] C. G. Overberger and B. S. Marks, *J. Am. Chem. Soc.*, **77**, 4104 (1955); C. G. Overberger, *Record Chem. Progr.*, **21**, 21 (1960).

[3] W. R. McBride and H. W. Kruse, *J. Am. Chem. Soc.*, **79**, 572 (1957).

[4] An X-ray molecular weight was obtained because of the poor solubility of this compound in the usual solvents used for molecular weight determinations.

[5] Extreme care should be exercised in handling this cmpound as it explodes violently, especially at its melting point.

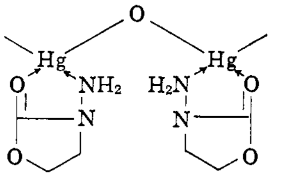
[6] Determination of the Raman spectrum of tetramethyl-2-tetrazene showed –N=N– absorption at 1480 cm^{-1}.

[7] Ultraviolet spectra were all determined in acetonitrile. Tetramethyl-2-tetrazene in ethanol gave bands at 277 mμ (ϵ 8828) and 250 mμ (ϵ 4849); see W. E. Bull, J. A. Seaton, and L. F. Audrieth, *J. Am. Chem. Soc.*, **80**, 2516 (1958).

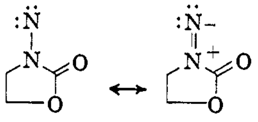
[8] Chemical shifts are recorded in τ values: G. V. D. Tiers, *J. Phys. Chem.*, **82**, 1151 (1958); internal standard $(CH_3)_4Si$.

[9] See, for example, C. Paal and W. N. Yao, *Ber.*, **63**, 57 (1930). They report the hydrogenolysis of tetraphenyltetrazene with palladium catalyst to diphenylamine.

On the basis of the above data, we conclude that compound II is the *trans* isomer and III the *cis* isomer. The mechanism by which III is formed lends support to these assignments, since only with yellow mercuric oxide has it been found possible to isolate the *cis* compound. It is believed that there is a high degree of steric control involved with this unique polymeric[10] oxidant in that it is able to form a highly ordered stereospecific intermediate chelate, of which one possible form is suggested by structure V. Under these conditions, the oxidation and coupling of molecules of I occur while they are held in the *syn* position, resulting in the formation of the *cis* azo structure. With the other oxidants, the uncomplexed aminonitrene (diazene)[11-14] intermediate species VI is probably formed, which due to the lack of any induced stereochemistry collapses by dimerization to the thermodynamically favored *trans* structure.



V



VI

These observations suggest a whole new approach to stereospecific oxidation of 1,1-disubstituted hydrazines. The possibility of designing hydrazines with suitable ligands for complexation and oxidation with yellow mercuric oxide offers the potential of tailor-making a variety of new isomeric azo compounds.

Acknowledgments. This research was supported by the Advanced Research Projects Agency, Propellant Chemistry Office, and was monitored by the Bureau of Naval Weapons, RMMP, under Contract NOrd 18728. We are indebted to N. B. Colthup for assistance in interpretation of the infrared and Raman spectra, J. E. Lancaster for assistance in interpretation of the nmr spectra, and T. E. Mead for the mass spectrographic determinations.

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Received January 17, 1966

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(10) The crystal structure of yellow HgO is an infinite planar zig-zag chain in which the Hg-O-Hg angle is 109° and the O-Hg-O angle is 179°; see D. Grdenić, *Quart. Rev.* (London), **19**, 316 (1965), for leading references.

(11) W. H. Urry, H. W. Ruse and W. R. McBride, *J. Am. Chem. Soc.*, **79**, 6568 (1957), ref 3; W. R. McBride and E. M. Bens, *ibid.*, **81**, 5546 (1959).

(12) C. G. Overberger, *Record Chem. Progr.*, 21, 21 (1960); C. G. Overberger, N. P. Marullo, and R. G. Hiskey, *J. Am. Chem. Soc.*, **83**, 1374 (1961); C. G. Overberger and L. P. Herin, *J. Org. Chem.*, 27, 2423 (1962).

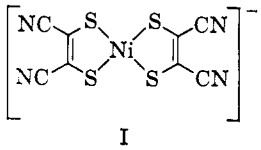
(13) L. A. Carpino, A. A. Santilli, and R. W. Murray, *J. Am. Chem. Soc.*, **82**, 2728 (1960).

(14) D. M. Lemal, F. Menger, and E. Coats, *ibid.*, **86**, 2395 (1964), and references therein.

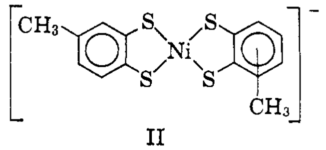
Concerning Cation-Stabilized Anion Free Radicals

Sir:

The occurence and the paramagnetic resonance properties of cation-stabilized free radicals are now well documented in the literature.[1-4] In many cases thus far studied the complexed metal ion has a closed-shell configuration, so that extensive mixing of metal and ligand orbitals in the wave function of the unpaired electron is unlikely. It has recently been suggested[5] that several planar anionic complexes, bis(maleonitriledithiolato)nickel (Ni(mnt)$_2^-$, I), bis(toluene-3,4-dithiolato)nickel (Ni(tdt)$_2^-$, II), and glyoxalbis(2-mercaptoanil)nickel (Ni(gma)$^-$, III), are all most appropriately described as containing diamagnetic d^8 Ni(II) with the unpaired electron localized on the ligands. This description was based on the asserted close similarity among the g tensors of these species.[5] Such a suggestion is at variance with the large g-value anisotropy observed for the complexes[6,7] and the demonstration[7] that the Ni(III) d^7 configuration is pragmatically useful in interpreting the oriented single crystal epr properties of Ni(mnt)$_2^-$. The postulated lack of involvement of metal orbitals in the unpaired electron wave functions of these complexes has prompted our extensive paramagnetic resonance investigation of III and related systems. From the point of view of paramagnetic resonance, the ultimate validity of the above postulate hinges upon what is the expected g tensor for a system unambiguously described as a cation-stabilized free radical. Significant deviations of g values from that of a free electron spin (g = 2.0023) may be expected from extensive involvement of sulfur orbitals in the wave function.[8]



I



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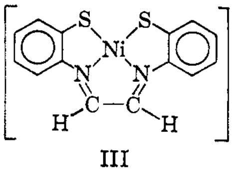

III

We have interpreted the g and hyperfine tensor of I in terms of a b$_{3g}$ ground-state wave function, which is roughly 50% delocalized over the π system of the ligands.[7] The spin-orbit coupling was assumed to be entirely caused by the nickel atom, and the contribution of sulfur was not considered. Hückel molecular orbital calculations on I[9] predict considerably less metal

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(1) I. M. Brown and S. I. Weissman, *J. Am. Chem. Soc.*, 85, 2528 (1963).

(2) D. R. Eaton, *Inorg. Chem.*, 3, 1268 (1964).

(3) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *J. Am. Chem. Soc.*, 86, 2799 (1964).

(4) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, 4, 55 (1965).

(5) E. I. Steifel, J. H. Waters, E. Billig, and H. B. Gray, *J. Am. Chem. Soc.*, 87, 3016 (1965).

(6) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *ibid.*, 85, 2029 (1963).

(7) A. H. Maki, N. Edelstein, A. Davison, and R. H. Holm, *ibid.*, 86, 4580 (1964).

(8) W. G. Hodgson, S. A. Buckler, and G. Peters, *ibid.*, 85, 543 (1963); J. J. Windle, A. K. Wiersma, and A. L. Tappel, *J. Chem. Phys.*, 41, 1996 (1964). The latter authors find g values as large as 2.06 for alkyl sulfide radicals. It is probable, however, that the spin is essentially localized on the sulfur atom in these radicals.