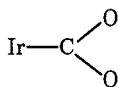
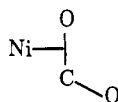


structures for **1** and for **3** and its congeners. The latter adducts may contain



configurations rather than the



grouping of **1**. Further research on the nature and reactivity of CO₂ adducts is in progress.

Acknowledgment. The author appreciates suggestions by Dr. G. W. Parshall concerning the interaction of CO₂ with transition metal complexes, and thanks Drs. Parshall and U. Klabunde for useful discussions.

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- (5) T. Herskovitz, to be submitted for publication.
- (6) Calcd for C₁₃H₂₂O₂P₄ClIr: C, 27.30; H, 5.64; O, 5.60; P, 21.66; Cl, 6.20; Ir, 33.60. Found: C, 27.65; H, 5.76; O, 5.42; P, 21.56; Cl, 6.44; Ir, 33.29.
- (7) With ¹³CO₂ these bands are at 1515 and 1220 cm⁻¹ while with C¹⁸O₂ they are at 1530 and 1200 cm⁻¹; IR data are from Nujol mulls.
- (8) H. D. Kaesz and R. B. Saillant, *Chem. Rev.*, **72**, 231 (1972).
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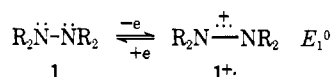
T. Herskovitz

Contribution No. 2453, the Central Research and Development Department Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898
Received December 6, 1976

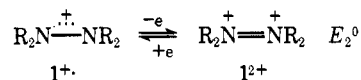
Isolation of 9,9'-Bis-9-azabicyclo[3.3.1]nonane Radical Cation Hexafluorophosphate, and Its Reversible Oxidation to the Dication

Sir:

Cyclic voltammograms for the oxidation-reduction of many tetraalkylhydrazines (**1**) show the wave shape expected for nearly reversible (rapid) electron transfer at room temperature, allowing convenient determination of the standard oxidation potential, E_1^0 , for these compounds.¹ Deprotonation of **1**⁺ would lead to its destruction, since the resulting α -hydrazinoalkyl radical would be more easily oxidized than **1**. Proton loss from **1**⁺ is clearly far slower than from alkylamine radical cations; alkylamines show irreversible cyclic voltammograms, attributed to rapid deprotonation of the radical cation.² Although many tetraalkylhydrazine radical cations persist for hours to days at millimolar concentrations, previous attempts at isolation of **1**⁺ salts, even in the cold, have led only to their decomposition. The cation radical lifetimes are distinctly shorter at high concentrations.³

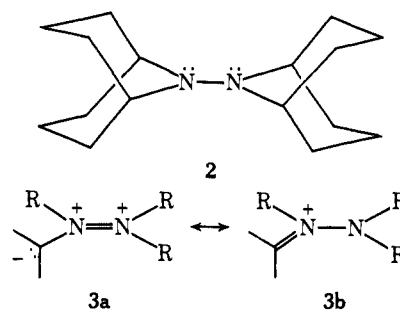


The structures of **1**⁺ are indicated by ESR studies⁴ to have nearly parallel spin-bearing orbitals on nitrogen, and low activation energies for bending at nitrogen; they have a "three electron π bond".⁵ Removal of the formally antibonding π electron might be expected to be relatively facile, and a second, irreversible oxidation wave with a peak potential above +1 V vs. SCE was observed for several examples of **1**, and attributed to removal of the second electron.⁵ The dication **1**²⁺, with its



adjacent positive charges, would be expected to deprotonate or react with nucleophiles very rapidly, so it is not surprising that the dication lifetime is short, making the second oxidation wave irreversible. We hypothesized that the reason for our failure to be able to concentrate **1**⁺ solutions without destruction of the radical cation is that **1**⁺ disproportionates to give the extremely reactive dication and basic hydrazine, leading to decomposition in spite of the low disproportionation constant.

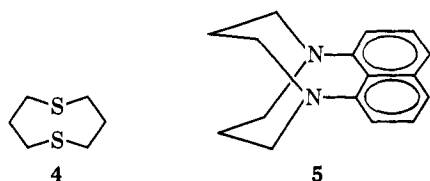
The bis-bicyclic tetraalkylhydrazine **2**⁶ was prepared by photolytic nitrogen expulsion from the tetrazene⁷ obtained by iodine oxidation⁸ of 9-amino-9-azabicyclo[3.3.1]nonane.⁹ The cyclic voltammogram of **2** shows two completely reversible one electron oxidation waves, $E_1^0 = -0.01$, $E_2^0 = +1.18$ V vs. SCE, in acetonitrile at room temperature, even at 20 mV/s



scan rates. The lifetime of **2**²⁺, even in the presence of the basic hydrazine, therefore exceeds several seconds. The geometrically imposed requirement that the α -CH bonds be perpendicular to the charge-bearing orbitals on nitrogen clearly has a huge effect on the rate of deprotonation, as anticipated on the basis that the deprotonated form is precluded from having iminium ion resonance stabilization as indicated in **3b**, a Bredt's rule effect. Because disproportionation of **2**⁺ would not lead to its immediate destruction, we attempted isolation of this cation. Oxidation of **2** with nitrosoum hexafluorophosphate¹⁰ in methylene chloride gave gas evolution, and solvent removal gave crude **2**⁺ PF₆⁻, which was recrystallized from methylene chloride-chloroform or ethanol to give light yellow air stable flakes, 283-286 °C dec.¹¹ The ESR spectrum of this solid (powdered, 10⁻⁴ m in KBr) consisted of a single broad line, 5.3 G peak-to-peak, and Faraday balance measurements give $\mu_{\text{eff}} = 1.82$ (at 5.92×10^3 G), close to the value of 3^{1/2} predicted for a doublet species with orbital moments quenched. Solutions are yellow (λ_{max} 345 nm, log ϵ 3.56 in 95% ethanol) and give the same intensity ESR spectrum as does electrochemical or chemical oxidation of **2** at the same concentration. The ESR spectrum consists of five broad lines in 1:2:3:2:1 ratio, $a(2N) = 13.15$ G, with a fine structure of many lines separated by about 0.2 G partially resolvable with difficulty.

The systems most comparable to **2**⁺ and **2**²⁺ in having one or two positive charges formally localized on adjacent heteroatoms are the mono- and dication of the eight-membered ring cyclic disulfide **4** reported by Musker, Wolford, and

Roush,¹⁰ and those of the bicyclic diamine **5** studied by Alder, Gill, and Goode.¹² The ions of both **4** and **5** differ from those of **2** in that the former have a σ bonding interaction between the heteroatoms, while $2^{+\bullet}$ and 2^{2+} are π ions.¹³



References and Notes

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- We thank the National Science Foundation for partial financial support of this work, and Professors Musker and Alder for communication of their results prior to publication.

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Sensitized Photooxygenation of 1-Methyl-3-vinylindoles

Sir:

The oxidations of indoles with molecular oxygen, including singlet oxygen (1O_2), have been extensively studied.¹ Most of them involve C_2 – C_3 ring cleavage or the formation of 3-hydroperoxidic intermediates. In the sensitized photooxygenation of vinyl-substituted aromatics, 1O_2 attacks on the side chain to give carbonyl compounds (1,2-cycloaddition) and/or allylic hydroperoxides ("ene" reaction),² or adds to a diene system comprised of the side chain and an aromatic double bond (1,4-cycloaddition).³ In this communication, we wish to report on the results of the reaction of 1-methyl-3-vinylindoles with 1O_2 . The characteristic features of our results are as follows: (a) 1O_2 can easily add to the vinylindoles with retention of stereochemistry to give dioxacarbazole-type 1,4-endoperoxides in aprotic solvents, while the photooxygenation in protic solvents yields 3-formyl-1-methylindole; (b) unusual fragmentation of the dioxacarbazole-type 1,4-endoperoxides occurs to afford two aldehydes through the supposed dioxetane intermediate. These observations suggest that the 1,4-endoperoxide might be an initial intermediate prior to the intermediary dioxetane in the oxidative double bond cleavage of the vinylindoles with 1O_2 in protic solvents.

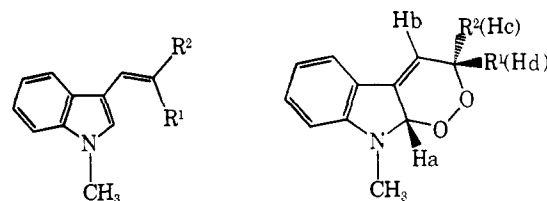
When the sensitized photooxygenation⁴ of 1-methyl-*trans*-3-styrylindole (**1a**)⁵ was carried out in *n*-hexane containing 10% dichloromethane, a 1,4-endoperoxide **2a** has precipitated as silky crystals in 96% yield, mp 99.0–100.5 °C.

The NMR spectrum⁶ of **2a** displayed a singlet at δ 2.86 (3 H, N-CH₃), and four multiplets centered at 5.56 (1 H, Hd), 5.86 (1 H, Ha or Hb) 5.92 (1 H, H_b, or H_a), and 7.0 (9 H, aromatic) ppm with their coupling constants: $J_{ab} = J_{ad} = J_{bd} = 2.6$ Hz. Other spectral characteristics of **2a** were as follows: IR (KBr) 1605, 1060, 1040, and 1022 cm^{-1} ; MS (m/e) 265 (M^+ , 25%), 160 (100). Anal. ($C_{17}H_{15}NO_2$): C, 76.99; H, 5.67; N, 5.17.

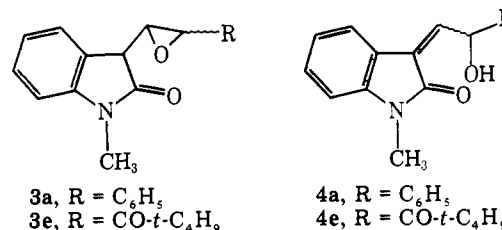
Similar photooxygenation of the *cis*-isomer **1b**⁵ afforded the stereoisomer **2b**^{7,8} as granules in 90% yield, mp 80–81 °C. The olefin **1a** gave no **2b**, whereas the isomer **1b** gave no **2a**. Consequently the 1,4-cycloaddition of 1O_2 to the vinylindoles **1** is a completely stereospecific process.

Similarly, 1-methyl-3-vinylindole (**1c**) was photooxygenated to give the corresponding peroxide **2c**⁹ as flakes in 71% yield, mp 80–82 °C. The irradiation of 1-methyl-3-(2-methylpropen-1-yl)indole (**1d**) gave also the 1,4-endoperoxide **2d**¹⁰ as an oil in quantitative yield.

Furthermore, a vinylindole bearing an electron-withdrawing substituent on the β -carbon of the side chain undergoes the 1,4-cycloaddition of 1O_2 . Thus 1-methyl-3-(2-pivaloylvinyl)indole (**1e**)¹¹ was photooxygenated¹² to give two oxindoles **3e**¹³ and **4e**¹⁴ in the yields of 43 and 24%, respectively. Under the reaction conditions, the corresponding 1,4-endoperoxide **2e** could not be obtained because of its easy isomerization to the oxindole **3e** (vide infra). The oxindole **4e** might be formed through a further isomerization of **3e**; in fact, **3e** was converted to **4e** quantitatively by prolonged treatment under the isolation conditions or in the presence of acid catalyst.



- 1a**, $R^1 = H$; $R^2 = C_6H_5$
1b, $R^1 = C_6H_5$; $R^2 = H$
1c, $R^1, R^2 = H$
1d, $R^1, R^2 = CH_3$
1e, $R^1 = H$; $R^2 = CO-t-C_4H_9$
2a, $R^1 = H$; $R^2 = C_6H_5$
2b, $R^1 = C_6H_5$; $R^2 = H$
2c, $R^1, R^2 = H$
2d, $R^1, R^2 = CH_3$
2e, $R^1 = H$; $R^2 = CO-t-C_4H_9$



- 3a**, $R = C_6H_5$
3e, $R = CO-t-C_4H_9$
4a, $R = C_6H_5$
4e, $R = CO-t-C_4H_9$

In contrast with the reaction in aprotic solvents, the sensitized photooxygenation of the vinylindoles **1** in protic solvents caused dramatic change of products.¹⁵ When the vinylindole **1a** was irradiated in ethanol or methanol, not the corresponding peroxide **2a** but 3-formyl-1-methylindole **5** was obtained together with benzaldehyde in more than 90% yield. The other vinylindoles **1b–d** were also converted to the aldehyde **5** in protic solvents. It should be noted that, in all cases examined, the indole **1** gave no products derived from a 1,2-addition of 1O_2 onto the C_2 – C_3 double bond or a 3-peroxidic intermediate.

The unexpected solvent effects on the sensitized photooxygenation of the vinylindole **1** could reasonably be interpreted by the following facts; the 1,4-endoperoxide **2a** was quantitatively decomposed into the formylindole **5** and benzaldehyde in alcohol ($\tau_{1/2} \approx 10$ min at room temperature) (path A), whereas, the peroxide **2a** was fairly stable in aprotic solvents such as benzene, chloroform, acetonitrile, and *n*-octane. It was easily isomerized into an oxindole **3a**¹⁶ when heated in solution