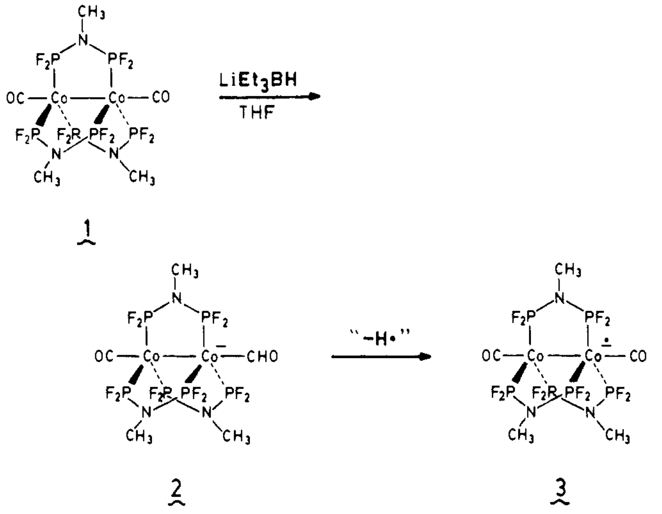
a known one-electron reducing agent. When **1** was treated with a stoichiometric amount of cobaltocene, the resulting green colored solution displayed an IR spectrum identical with that obtained from a solution containing decomposed **2**. Finally, a well-resolved EPR spectrum centered at $g = 2.025$ was recorded for **3** in agreement with published data.[18] The overall sequence of events is illustrated below.



The direct observation of **3** as the sole organometallic product from **2** is important as it represents the first reported paradigm of a stable paramagnetic species formed from a formyl C–H bond scission process. Moreover, **3** is of further general interest as it may be considered as a mixed-valence d^9–d^{10} complex that exhibits complete electron delocalization over both cobalt centers as required for a class III charge-transfer complex.[19] The fate of the formyl derived hydrogen atom is not known at this time, and attempts to retard the decomposition of **2** by using hydrogen atom donors such as 9,10-dihydroanthracene and tri-*n*-butyltin hydride have been unsuccessful.

We believe that the formation of the radical anion **3** (relative to other decomposition pathways) may be related to its intrinsic stability. In comparison to other known formyl complexes that decompose via a formyl C–H bond scission manifold, **3** affords the only chemically and electrochemically stable radical anion.[20] The stability of the resulting radical anion is important as it undoubtedly modulates the sequence of subsequent chemical events. Redox instability has been shown to drive the radical product of formyl decompostion in a chain propagating fashion to the corresponding metal-hydride product.[7,21] However, once formed **3** remains inert, a feature which is attributed to the redox stabilization associated with the ancillary fluorophosphine ligands.[22]

Formyl-trapping experiments and the reactions of **1** with other reducing agents, along with additional examples of cluster stabilized radical anions produced from formyl decomposition, will be reported in due course.

Acknowledgment. We thank Don Ellington for assistance with the NMR spectra and the UNT faculty research program and Robert A. Welch Foundation for financial support.

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Dioxetane Formation at a Double Bond Adjacent to Bridgehead Nitrogen: Rapid Reaction between Neostrychnine and Singlet Oxygen in a Polar Protic Medium. Evidence Against the Intermediacy of an Open Zwitterion

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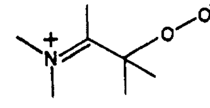
The mechanisms of reaction of $O_2(^1\Delta_g)$ with organic/biological substrates have been the subjects of considerable research effort over the last two decades.[1] Electron rich olefins, enol ethers, enamines, etc., react to give dioxetanes which can cleave to carbonyl fragments.[2-4] Much of the mechanistic discussion[5] has centered around the importance of charge-transfer interactions between the reactants and whether zwitterionic species such as **1** are intermediates on the pathway to dioxetane. Evidence for the intermediacy of open zwitterionic species has been claimed on the basis of trapping experiments in polar media where a nucleophile, most commonly, although not always, methanol as solvent, has scavenged a substrate/$O_2(^1\Delta_g)$-derived intermediate. The substrate has been either an indole[6] or an enol ether.[7] On the other hand, we have presented evidence which indicates that the reactions of such molecules with $O_2(^1\Delta_g)$ proceed via complexes which are formed rapidly and reversibly.[8] These latter species, exciplexes, must also be considered as possible precursors of both dioxetanes and the products of trapping.



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Information of pertinence to the above problem could, in principle, be available from the reactions of $O_2(^1\Delta_g)$ with relatively electron rich olefins for which formation of species of type 1 would be highly unfavorable for steric reasons; i.e., the immonium double bond would be at a bridgehead. With such considerations in mind we have examined the chemical reactivity of $O_2(^1\Delta_g)$ toward neostrychnine (**2**), a molecule in which the enamine nitrogen is indeed located at a bridgehead. This accounts for the very low pK_a of this molecule, 3.8,[9,10] and suggests that species of type **3**,

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(10) The corresponding value for strychnine (Δ^{19}-isomer of **2**) is 7.4.[9] The corresponding values for the closest available six-membered ring analogues, 1,4,5,6-tetrahydro-1,2-dimethylpyridine and 1,2-dimethylpiperidine, are 11.43 and 10.26, respectively (cf. ref 11 and references therein).

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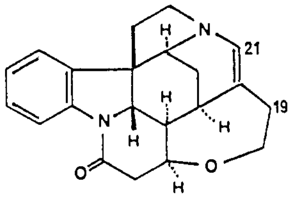

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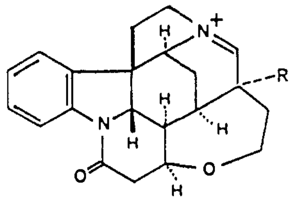

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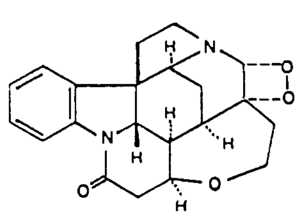

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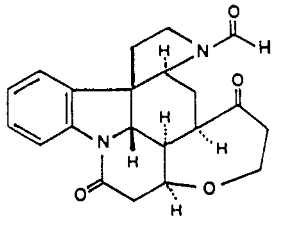

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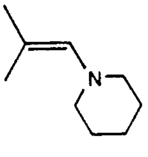
as anticipated, are highly unfavored. The neostrychnine employed in this work was prepared by Raney nickel treatment of strychnine[12] and fully characterized.[13]

An oxygen-bubbled solution of neostrychnine (3×10^{-3} mol L^{-1}) and methylene blue (10^{-4} mol L^{-1}) in methanol (100 mL) was irradiated at room temperature through Pyrex with a 100-W medium-pressure mercury arc. After 2 h, clean conversion to a single product was complete. No reaction was observed in the absence of light or oxygen. Isolation by preparative TLC (acetone/hexane, 7:3 on silica gel) and crystallization from methanol gave the *N*-formylketone **5** in 75% isolated yield, mp 206–212 °C. Spectral data[14] were in complete agreement with this structure. The molecule contains an additional two oxygens relative to neostrychnine and exhibits identical *N*-acylarylamine absorption in the ultraviolet. Two new infrared carbonyl stretching bands at 1654 cm^{-1} (*N*-formyl) and 1715 cm^{-1} (ketone) are apparent. In the 300 MHz PMR spectrum the one proton singlet at δ 5.73 due to the C(21) enamine proton in the substrate **2** has been replaced by two singlets at δ 8.26 and 8.38 (2:1) corresponding to the rotational isomers of the *N*-formyl grouping. Clearly the product is characteristic of normal enamines[15] indicating the intermediacy of the dioxetane **4**.[16]

In addition, under identical conditions, the rate for *chemical* reaction of **2** with $O_2(^1\Delta_g)$ was essentially the same (slightly less than a factor of 2 lower) as that for the simple unstrained model **6** which gives exclusively *N*-formylpiperidine and acetone under the same conditions.[17] There is no doubt[8,19] that, at the temperature of our experiments, reaction of both **2** and **6** involves pre-equilibrium formation of an exciplex followed by "slow" product formation. Were that irreversibly formed product a zwitterion of type **1**, one would, for reasons already emphasized, anticipate a very significant reduction in the rate constant for chemical reaction of **2** relative to that of **6**. Since no such difference is observed we are forced to the conclusion that it is possible, in a *polar protic* medium such as methanol, for $O_2(^1\Delta_g)$ to react to give dioxetanes via a mechanism which does not involve the intermediacy of open zwitterions.[20]



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(13) This material[12] was twice recrystallized from ethanol, mp 224–225 °C (lit. 228 °C[12]): λ_{max} (ethanol) 252 (12 400), 279 (4240), 288 (3300); ν_{max} (Nujol) 1680 (s); δ ($CDCl_3$) 8.06 (d, 8 Hz, 1 H), 7.27 (m, 2 H), 7.08 (t, 8 Hz, 1 H), 5.73 (s, 1 H), 4.2–1.3 (17 H); *m/z* (%) 334 (100), 277 (28), 220 (11), 167 (23), 144 (16), 130 (16), 115 (14), 107 (21).

(14) λ_{max} (ethanol) 253 (12 500), 278 (3740), 288 (2920); ν_{max} (Nujol) 1715 (s), 1674 (s), 1654 (s); δ ($CDCl_3$) 8.38 (s, 0.3 H), 8.26 (s, 0.7 H), 8.14 (d, 8 Hz, 0.7 H), 8.12 (d, 8 Hz, 0.3 H), 7.35–6.80 (3 H), 4.4–1.7 (17 H); *m/z* (%) 366 (100), 337 (10), 294 (98), 220 (50), 180 (36), 168 (57), 123 (50), 130 (71), 115 (59).

(15) Foote, C. S.; Dzakpasu, A. A.; Lin, J. W.-P. *Tetrahedron Lett.* **1975**, 1247.

(16) The α-face of the molecule is by far the less hindered, hence the stereochemistry shown in **4**. This would certainly be correct if $O_2(^1\Delta_g)$ were "delivered" via an $N(b)/O_2(^1\Delta_g)$ complex.

(17) The relative rates of chemical reaction in methanol were essentially the same with either methylene blue or 2-acetonaphthone as sensitizer. Reactions were monitored by GLC with a 3.8 m by 0.22 mm (i.d.) vitreous silica capillary column coated with cross-linked methyl silicone BP-1(OV-1), 0.25 μm thickness, 0.15 kg cm^{-2} (hydrogen). For **2** and **5**: injection block 300 °C, isothermal at 270 °C, external standard stigmasterol. For **6** and *N*-formylpiperidine: injection block 150 °C, programmed at 50 °C (4 min) to 170 °C (10 °C min^{-1}), internal standard octan-1-ol. Overall rate constants for quenching of $O_2(^1\Delta_g)$ in methanol were determined by time-resolved IR emission spectroscopy as described.[18] These rate constants, 1.0×10^8 L mol^{-1} s^{-1} for **2** and 2.0×10^8 L mol^{-1} s^{-1} for **6**, were in the same ratio as the rates of chemical quenching. These data together with those of Foote and coworkers[15] indicate that both **2** and **6** are essentially exclusively chemical quenchers of $O_2(^1\Delta_g)$.

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(20) Clearly, some degree of electron donation from N(b) into the double bond of **2** must occur. Equally clearly, the inherent conjugative "electron-donating ability" of the activating group cannot be the dominant factor in controlling rate constants for chemical reaction.

A New Model for the Oxygen-Evolving Complex in Photosynthesis. A Trinuclear μ_3-Oxo-Manganese(III) Complex Which Contains a μ-Peroxo Group

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Oxidation of water by the photosynthetic process in plants is believed to involve a cluster of four (or three) manganese atoms.[3] Recently much effort has been devoted to the isolation of multinuclear manganese complexes, which it is hoped, will provide useful models for the oxygen-evolving complex in plants.[4-15] These

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(1) Victoria University of Wellington.

(2) Chemistry Division, D.S.I.R.

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