

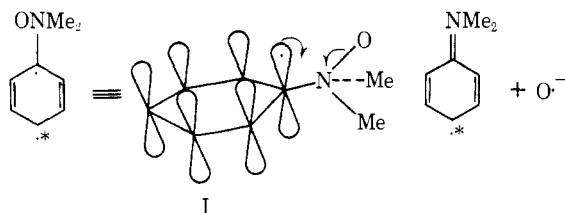
Communications to the Editor

Nitrogen Photochemistry. Excited State Theory Predictions and Amine Oxides

Sir:

We now wish to report that *N,N*-dialkylaromatic amine *N*-oxides undergo conformationally dependent, homolytic, β cleavages in accord with predictions of the benzene excited state theory.¹ Recently *N,N*-dimethylaniline and *N,N*-dimethylnaphthylamine *N*-oxides have been shown to undergo deoxygenation when the longest wavelength, Π , Π^* transition of each is activated.² The amine portion appears in the form of mono- and dimethylaromatic amines. The oxygen principally is found in the form of water when the solvents are methanol and 2-propanol. The only rearrangement product detected is a minor yield of 2-hydroxy-*N,N*-dimethylaniline from the irradiation of *N,N*-dimethylaniline *N*-oxide.

On applying the concepts of the recently proposed excited state resonance theory to the amine oxides, several predictions result. As illustrated below, these are (1) the bond rupture is angular dependent, (2) homolytic, and (3) the oxygen leaves as the oxygen radical anion or its conjugate acid, the hydroxy radical. Of the six possible diene orientations, the diene represented by structure I is of lowest ener-



gy and is a major contributor to the resonance hybrid because of the radical stabilizing ability of the nitrogen substituent.

In order to test the angular dependence prediction, three amine oxides, which have the N-O bond in the plane of the aromatic rings to be activated by light, II-IV, were synthesized.³ The amines were converted to the amine oxides by perbenzoic acid.⁴ Table I lists the quantum yield of starting material disappearance for compounds II-IV together with the quantum yields of product formation for the nonrigid reference compounds, *N,N*-dimethylaniline and *N,N*-dimethylnaphthylamine *N*-oxides. The angular dependence prediction is verified in a most remarkable way. Of the small amounts of irradiation products which are formed from II-IV, not much if any of the parent amines could be found.

In regard to the second prediction, the bond rupture is now proven to be homolytic since the amine oxides undergo

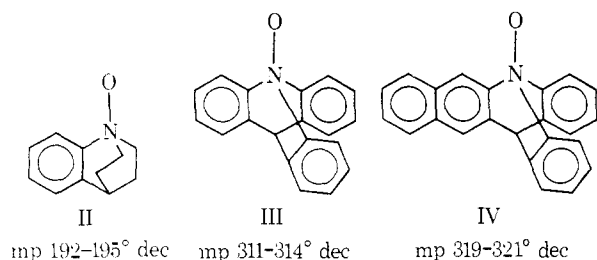
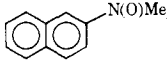
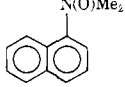


Table I. Quantum Yields of Amine Oxide Irradiations

Compound	Filter window, nm ^a	Quantum yield ^d
C ₆ H ₅ N(O)Me ₂	239-264 ^b	0.32
C ₆ H ₅ N(O)(CH ₂) ₅	245-267 ^b	0.30
	262-285 ^c	0.47
	261-280 ^c	0.15
II	238-265 ^b	0.02
III	260-276 ^c	0.04
IV	303-330 ^d	0.02

^a Wavelength range of greater than 1% transmittance. ^b The filter solution is composed of NiSO₄·6H₂O saturated in water, CoSO₄·7H₂O saturated in water, and 3 mg of cation X/ml of water.⁵ ^c The filter solution is composed the same as that of footnote *b* except that the concentration of cation X is reduced to 1 mg/ml and CCl₄ in cyclohexane is added (1:1 v/v) as a second filter solution.⁵ ^d The filter solution is composed of CoSO₄·7H₂O (1.5 M), 3 × 10⁻³ M K₂CrO₄ and used in conjunction with Pyrex glass.⁵ ^e The method of Parker and Hatchard⁶ was used to measure light intensity. The solutions of the amine oxides in methanol were deoxygenated with nitrogen. The mono- and dimethylaniline appearance and the disappearance of the bicyclic amine *N*-oxides were determined by uv spectral changes. The quantum yield error is ±10% except for the 0.02-0.04 values where it is *ca.* ±100%.

the typical radical reactions of producing acetone from 2-propanol and giving phenol from benzene. When *N,N*-dimethyl-1-naphthylamine *N*-oxide was irradiated in 2-propanol under nitrogen, 50-60% of acetone was formed at 2-3% conversion. In benzene with 5% 2-propanol as a cosolvent, the nonamine photoproducts from *N,N*-dimethyl-1-naphthylamine *N*-oxide are 5% phenol and 6% acetone.

Pertaining to the third prediction, the nature of the oxygen-containing products, the ortho-meta-para substitution patterns on aromatics and the relative reactivity toward aromatics strongly suggest that the oxygen reactive species in the irradiated amine oxide solutions is the hydroxy radical. The H-O bond dissociation energy is 119 kcal/mol so the hydroxy radical can abstract a hydrogen atom to produce water in any solvent used in this study, and water is the principal product in the media tried.² However, when *N,N*-dimethyl-2-naphthylamine *N*-oxide (2-DMNO) is irradiated in the presence of anisole and chlorobenzene, phenols are also produced and the ortho:meta:para ratios of the product phenols are 68:4:28 and 46:27:27, respectively, which is in fair accord with the known ortho:meta:para ratios of phenols produced when the hydroxy radical is formed by another method, *i.e.*, 84:0:16⁷ and 42:29:29⁷ respectively. Furthermore, the relative rates of reaction of 2-DMNO with anisole, benzene, and chlorobenzene are 3:1:0.6, respectively, which compares favorably with the same, known relative rates of reaction of these aromatics with the hydroxyl radical, *i.e.*, 6.35:1:0.55.⁷

Whether OH· or O⁻ is produced initially from the amine oxide excited state depends on the stage which protonation occurs. The deoxygenation step should be aided by the presence of acid. Then the amine oxide would be protonated prior to bond fission and no charge separation would be re-

quired. Consequently, 2-DMNO was irradiated in three solutions: methanol, 0.5 M acetic acid in methanol, and 0.5 M KOH in methanol. The same products were formed 1.3 times faster in the acid solution compared to the other two as shown by uv analysis of the reaction mixture at 347 nm, a naphthylamine chromophore. Though the rate difference is not great, this indicates that $O^{\cdot-}$ is first formed which, with its respectable basicity ($pK_a = 11.9$), protonates shortly thereafter.

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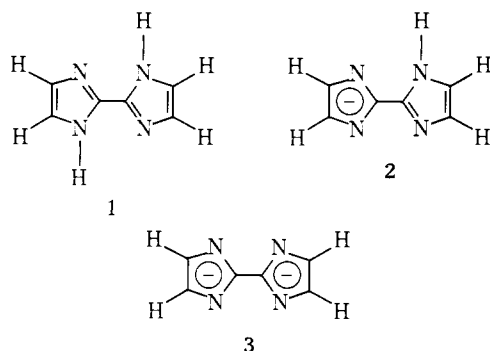
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Rhodium(I) and Iridium(I) Complexes of Anions of 2,2'-Biimidazole

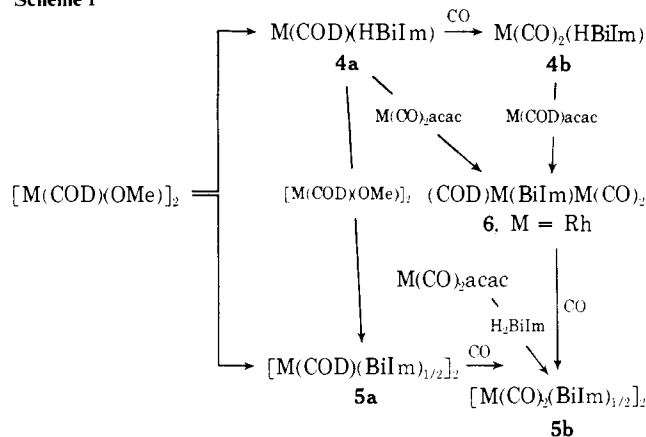
Sir:

Organic and inorganic substances which possess highly anisotropic conduction, dielectric, and optical properties arise from the crystallization of planar, sterically compact molecules or ions which possess delocalized electrons and accessible, stable oxidation states. Examples of organic materials are the salts of tetracyanoquinodimethan (TCNQ)¹ and salts of tetrathiofulvalene (TTF).² Inorganic salts are typified by the platinum mixed-valence salt $K_2Pt(CN)_4Br_{0.3} \cdot 3H_2O$ ³ and the iridium complex $Ir(CO)_3Cl_{1.1}$.⁴ These materials and their properties have been reviewed.⁵

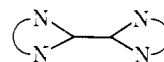
The purpose of this study was to explore combinations of compact delocalized ligands and 4d and 5d transition metals in an effort to obtain new materials which may possess unusual physico-chemical properties. This communication describes the synthesis and characterization of new rhodium(I) and iridium(I) complexes derived from the conjugated ligand 2,2'-biimidazole (H_2BiIm), **1**.



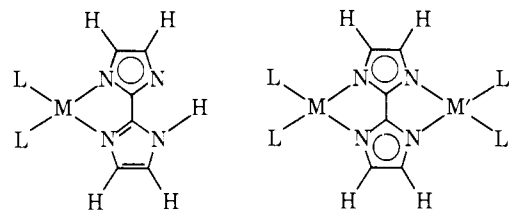
Scheme I



The coordination properties of H_2BiIm and its anionic derivatives, **2** and **3**, have not been thoroughly examined. Since the synthesis of H_2BiIm in 1859 by Debus,⁶ only complexes of Cu(II),⁷ Ni(II),^{7,8} Co(II),⁷ and Fe(II)⁷ which contain coordinated neutral biimidazole have been prepared. The coordination geometry of the nickel complex $[Ni(H_2BiIm)_2(H_2O)_2](NO_3)_2$ has been determined by an X-ray crystallographic study.⁸ The addition of hydroxide ion to aqueous solutions of these complexes resulted in the precipitation of insoluble complexes believed to contain the monoanion $HBIIm$, **2**.⁷ The syntheses described below result in tractable mononuclear products of the $HBIIm$ and homo- and heterodinuclear products of the hitherto unknown dianion $BiIm$, **3**. We believe the latter products represent the first examples of dinuclear complexes containing the tetracoordinate bisamidine or tetraza linkage



The selective production of derivatives of **2** and **3** is illustrated in Scheme I.⁹ The reactions are driven by the use of strong bases¹⁰ OMe^- and $acac^-$ ($acac^-$ = acetylacetonate ion). The rhodium and iridium complexes abstract a pyrrole proton from H_2BiIm forming the homogeneous reaction product $MeOH$ or $Hacac$.¹¹ The reactions were carried out under argon in dry, deaerated solvents with nearly quantitative yields.



4a, L = $(COD)_{1/2}$.

1,5-cyclooctadiene

b, L = CO

M = Rh, Ir

5a, LL' = $(COD)_{1/2}$

b, LL' = CO

M = M' = Rh, Ir or

M = Rh, M' = Ir

Bright yellow crystals of air stable $Rh(COD)(HBIIm)$, **4a**, are obtained by treating $[Rh(COD)(OMe)]_2$ with 2 mol of H_2BiIm in refluxing methylene chloride for 30 min. Lustrous orange needles of air stable $Rh(CO)_2(HBIIm)$, **4b**, form when carbon monoxide is passed through a benzene solution of **4a** readily displacing the diene. The corresponding **4a** and **4b** (M = Ir) are light orange and black, respectively, and are air stable. Two infrared carbonyl absorptions in solutions of **4b** (M = Rh 2079 (s), 2011 (s); M = Ir 2068 (s), 2000 (s)) are consistent with a cis dicarbonyl structure.