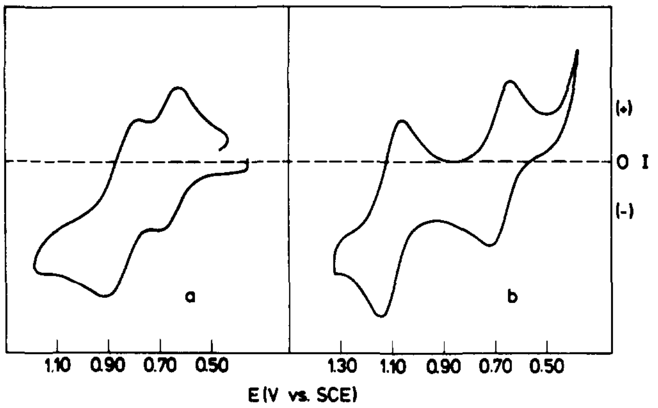
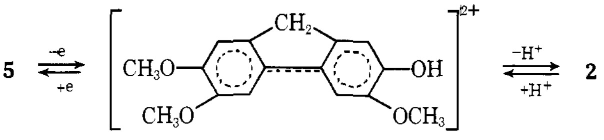


Figure 1. Cyclic voltammograms of **1** in (a) dichloromethane-TFA (3:1) and (b) dichloromethane-TFA-CF_3SO_3H (45:3:2). Supporting electrolyte is n-Bu_4NBF_4 (0.2 M). Voltage sweep rate is 150 mV/sec.

being reversible and the second quasi-reversible indicating a coupled chemical step. In the same medium, one-electron coulometric oxidation of **1** gave the cation radical (**5**) which could also be prepared by adding small amounts of CF_3SO_3H to solutions of **1** in TFA. The ESR spectra of **5** produced electrochemically and chemically were identical. Solutions of **5** prepared electrochemically could be quantitatively converted back to **1** by cathodic reduction. One-electron oxidation of **5** gave **2** which is stable in dichloromethane-TFA (3:1). The cyclic voltammogram of **1** in dichloromethane-TFA-CF_3SO_3H (45:3:2) is shown in Figure 1b. In this case, at low voltage sweep rates (40 mV/sec) both redox couples appear to be reversible. However, at higher sweep rates the peak separation of the second couple became greater, once again implicating a coupled chemical reaction. Thus we can conclude that the second couple corresponds to oxidation of **5** to the dication (**10**) which is in equilibrium with **2**. This is also indicated by the fact that solutions of **2** prepared by two-electron oxidation of **1** in the latter medium are not stable, presumably because of the greater reactivity of **10.**



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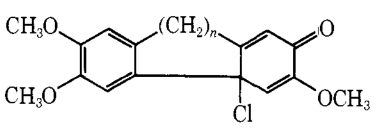
Examination of molecular models of the bridged biphenyls, **1**, **7**, and **8**, showed that the aromatic rings of **1** are forced to lie in the same plane while the preferred conformations of **7** and **8** are such that planes of the rings are ~20 and ~60° to one another. Since the most stable conformation of the cation radicals is one in which both rings lie in the same plane,[6] the greater the interplanar angle between the biphenyl rings in the substrates the greater the energy difference between cation radical and substrate. The latter is clearly reflected by the ease of oxidation: **1** (+0.70 V), **7** (+0.85 V), and **8** (+1.01 V). A further manifestation of forced planarity in the ions derived from **1** is the reactivity of **2** as compared to **9a** and **9b.** Chloride ion is oxidized by **2** while chlorination of **9a** and **9b** is observed to give cyclohexadienones **11.** Reaction of **2** or **9b** with water is accompanied by demethylation to give the orthoquinones **12** while H_2O acts as a base toward **9a** producing the phenanthrene.[7] Thus, the increased conjugation in **2** makes the aromatic system far less susceptible to nucleophilic attack. One might ask why **2** is less reactive toward nucleophiles but still undergoes an electron transfer reaction with Cl^-. If we consider the respective transition states we see that nucleophilic attack on the phenoxonium ion involves considerable change in geometry while planar **2** reverts to planar **1** after electron transfer which is accompanied by a minimal change in geometry. Preliminary results also indicate that **5** is much less acidic than the cation radicals derived from **7** and **8.**



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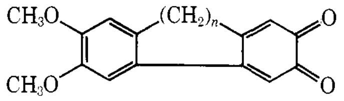

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The only previous report of stable phenolic cation radicals and phenoxonium ions concerned those derived from the α-tocopherol model compound.[8] The ions from **1** appear to be far less reactive. Further work is in progress on these unusual systems.

References and Notes

(1) O. Hammerich and V. D. Parker, *Electrochim. Acta*, **18**, 537 (1973).
(2) A. Ronlan, O. Hammerich, and V. D. Parker, *J. Am. Chem. Soc.*, **95**, 7132 (1973).
(3) V. D. Parker, *Chem. Commun.*, 610 (1969).
(4) The propane gave only the bridged biphenyl while the ethane gave a mixture of the corresponding phenanthrene and dihydrophenanthrene.
(5) All potentials are for oxidation or reduction at a platinum electrode and are referred to the saturated calomel electrode.
(6) A. Ronlán, J. Coleman, O. Hammerich, and V. D. Parker, *J. Am. Chem. Soc.*, **96**, 845 (1974). In order to have the most effective overlap of orbitals on the carbons where the rings join, the ions must assume a planar conformation.
(7) Details of the product studies will appear later.
(8) U. Svanholm, K. Bechgaard, and V. D. Parker, *J. Am. Chem. Soc.*, **96**, 2409 (1974).

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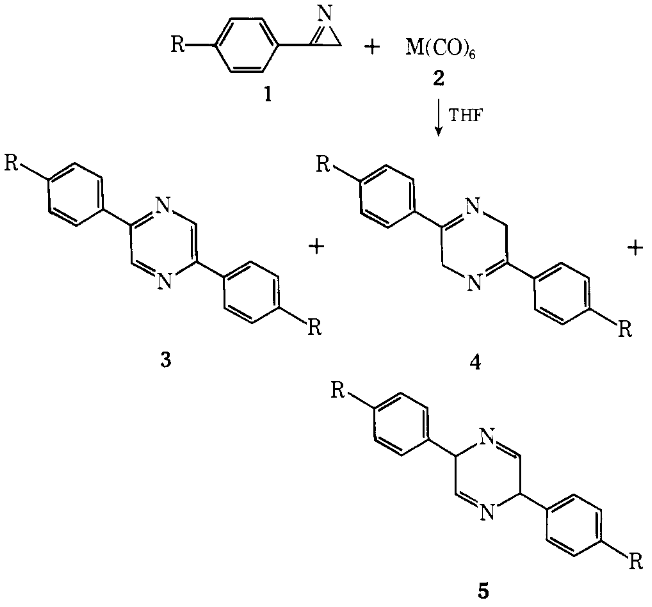
Group 6 Metal Carbonyl Induced Dimerization of Azirines

Sir:

There has been considerable recent interest in metal carbonyl effected ring-cleavage reactions of small ring systems such as 2-vinyloxiranes[1] and benzvalene.[2,3] In addition, diiron enneacarbonyl [$Fe_2(CO)_9$] can induce photolytic-type rearrangement of santonin using nonphotolytic conditions.[4] These results led to a study of the effect of metal carbonyls on 2-aryl azirines, a three-membered ring heterocycle which has been extensively investigated in terms of thermal[5] and photolytic[6] ring cleavage. We now wish to report that group 6 metal hexacarbonyls, $M(CO)_6$ (M = Cr, Mo, W), causes dimerization of 2-aryl azirines to dihydropyrazines and pyrazines under very mild conditions.

Reaction of 2-phenylazirine (**1**, R = H)[7] with an equimolar amount of molybdenum hexacarbonyl (**2**, M = Mo) in anhydrous tetrahydrofuran (THF) at room temperature for 24 hr (N_2 atmosphere) gave[8] 2,5-diphenylpyrazine (**3**, R =

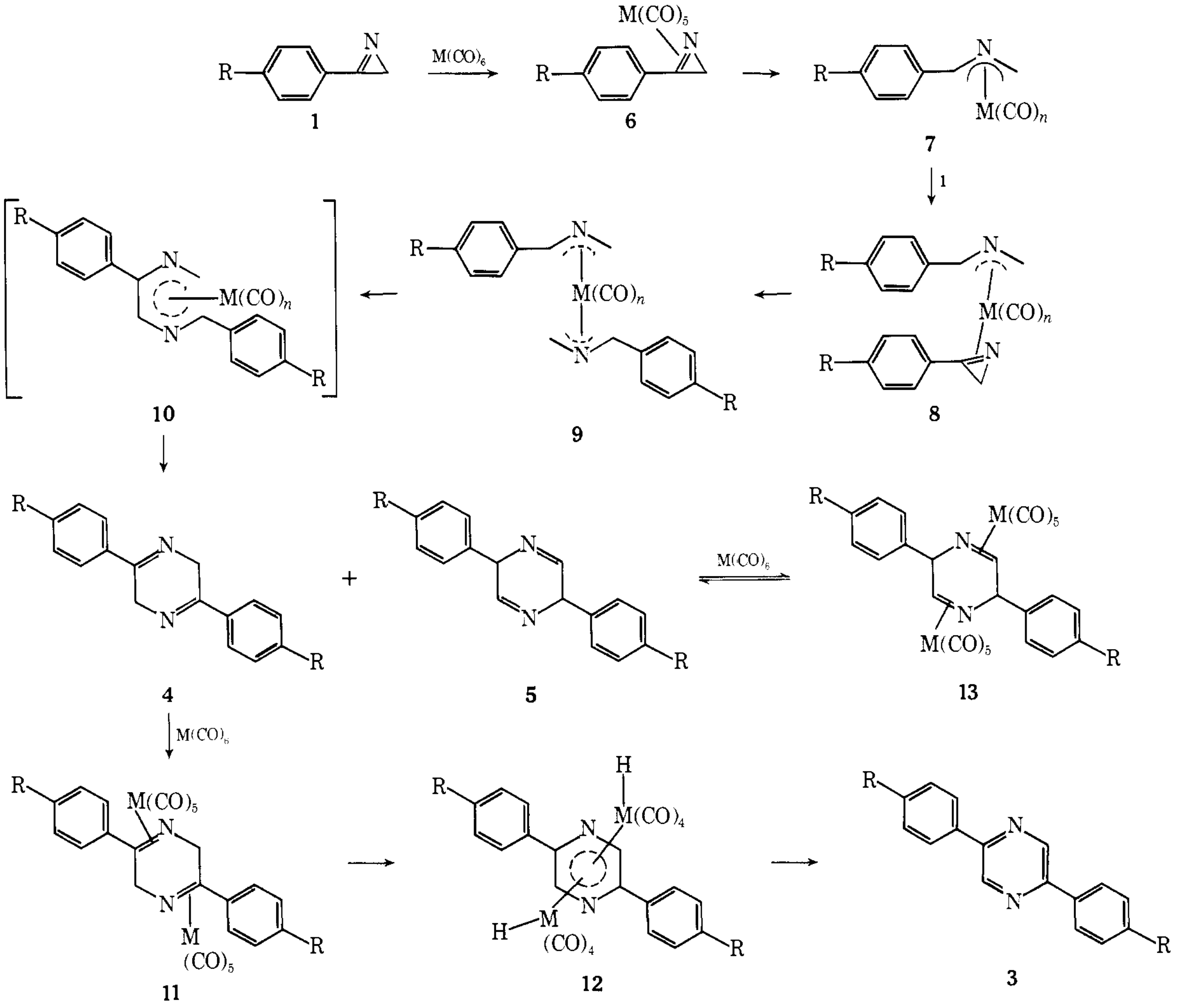
H, mp 196–198°,[9] 20.4% yield), 2,5-diphenyl-3,6-dihydropyrazine (**4**, R = H, 10.1%), and 3,6-diphenyl-3,6-dihydropyrazine (**5**, R = H, 13.2%). The products were characterized on the basis of analytical data[10] and infrared, nuclear magnetic resonance, and mass spectral results. Stirring a THF solution of **1**, R = H, for 2 days (N_2 atmosphere) did not give **3–5**, R = H.



The azirine **1**, R = H, reacted with Cr(CO)$_6$ (**2**, M = Cr), under identical conditions to that described for Mo(CO)$_6$, to give **3**, R = H (17.2%), and **5**, R = H (16.8%), but not **4**, R = H. Compounds **3**, R = H (29.2%), and **5**, R = H (13.4%), were also formed using W(CO)$_6$ (**2**, M = W), a reaction time of 7 days being used here since only trace product formation occurred after 24 hr. Exposure of the methoxy substituted azirine **1**, R = OCH_3, to Mo(CO)$_6$ gave the pyrazine **3**, R = OCH_3 (19.1%), and the dihydropyrazine isomers **4**, R = OCH_3 (16.5%), and **5**, R = OCH_3 (8.0%). Similar reaction of 2-(4′-methylphenyl)azirine (**1**, R = CH_3) with Mo(CO)$_6$ afforded **3**, R = CH_3 (18.0%), **4**, R = CH_3 (14.6%), and **5**, R = CH_3 (21.0%). 1,3-Diazabicyclo[3.1.0]hex-3-enes, produced by irradiation of **1**,[6] were not detected in any of the metal carbonyl reactions.

A possible mechanism for the azirine–M(CO)$_6$ reaction is outlined in Scheme I. The initial step probably involves π-complexation (**6**), although formation of the isomeric N-donor ligand complex cannot be ruled out. Ring-opening of **6** would give **7** which can then react with more azirine to afford **8**. Cleavage of the azirine ring of the latter would give **9**. Coupling of the organic ligands in **9** would result in generation of the dihydropyrazines **4** and **5** (possibly via **10**). Dehydrogenation of **4** to **3** can then occur via the π-complex **11**. Abstraction of an allylic hydrogen by each of the metals of **11** would give the bis-π-allylhydrometal tetracarbonyl complex **12**, which can then collapse to the pyrazine **3**. Treatment of a mixture of **4**, R = H, and **5**, R = H, with Mo(CO)$_6$ in THF gave **3**, R = H, along with recovered **5**, R

Scheme I



= H. Similarly, when a THF solution of pure 3,6-diphenyl-3,6-dihydropyrazine (**5**, R = H) was stirred with $Mo(CO)_6$ in THF for 3 days, **5** R = H, was recovered unchanged. Clearly, the pyrazine **3** is formed from **4** but not **5**, perhaps because it would be sterically more difficult for the metal carbonyl groups to abstract the allylic hydrogens in **13** than in **11.** The formation of **13,** if any occurs, would thus be reversible. The failure to observe any 2,3-diarylpyrazines, or their dihydro derivatives, in any of these reactions may be due to steric effects in coupling of the two organic ligands in **9.**

An investigation of the reactions of azirines, and related systems, with other metal carbonyls is currently in progress.

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(7) A. G. Hortmann, D. A. Robertson, and B. K. Gillard, *J. Org. Chem.*, **37,** 322 (1972).
(8) The usual work-up conditions were as follows. The reaction mixture was filtered and the filtrate was flash evaporated under reduced pressure. Crystallization of the flash evaporation residue from benzene gave the pyrazine **3**. The dihydropyrazines, **4** and **5**, were separated by column chromatography on neutral alumina [activity grade III] using benzene-chloroform as the eluant. Yields are of products of ≥97% purity. Yields of analytically pure materials were considerably less.
(9) L. Wolff, *Chem. Ber.*, **20,** 432 (1887).
(10) Satisfactory (±0.4%) analytical data were obtained for all compounds.
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Steady-State Considerations in the Electron-Transfer Quenching of the Tris(2,2′-bipyridine)ruthenium(II) Luminescence

Sir:

Recent studies have shown that electron transfer provides an efficient mechanism for the quenching of tris(2,2′-bipyridine)ruthenium(II) luminescence by certain metal complexes and organic molecules.[1-4] Direct evidence for an electron-transfer quenching mechanism is provided by the detection of $Ru(bipy)_3{}^{3+}$ and the reduced quencher both in flash experiments on reversible systems[2] and after the continuous irradiation of irreversible systems.[1,3,4] Indirect evidence for electron-transfer rather than energy-transfer quenching mechanisms can also be obtained in suitable systems from relative rate and spectroscopic considerations.[3] Another approach that might be used to distinguish between these mechanisms is the measurement of the degree of oxidation (or reduction) of the sensitizer under steady-state conditions. To the best of our knowledge this method has not been used previously, and in this paper we report a measurement of the steady-state concentrations of $Ru(bipy)_3{}^{3+}$ and Fe^{2+} produced in the irradiation of $Ru(bipy)_3{}^{2+}$ in the presence of Fe^{3+} ions. The back electron-transfer reaction between $Ru(bipy)_3{}^{3+}$ and Fe^{2+} is sufficiently slow that the concentration of these products attains appreciable steady-state values (Scheme I). In this scheme $Ru(bipy)_3{}^{3+}|Fe^{2+}$ and $Ru(bipy)_3{}^{2+}|Fe^{3+}$ represent the ground-state precursor and successor complexes, respectively, and energy transfer quenching (k_{en}) leading to $Ru(bipy)_3{}^{2+}|{}^*Fe^{3+}$ is not shown.[5] In terms of this scheme[7] the steady-state concentrations [X] of $Ru(bipy)_3{}^{3+}$ or Fe^{2+} ions in a sample of given $Ru(bipy)_3{}^{2+}$(D) and Fe^{3+}(Q) concentrations is given by

Scheme I

$$\begin{tikzcd}
{}^*\mathrm{Ru(bipy)_3{}^{2+}} + \mathrm{Fe^{3+}} \arrow[r, "k_{el}"] \arrow[d, shift left, "k_0"] & \mathrm{Ru(bipy)_3{}^{3+}|Fe^{2+}} \arrow[r, shift left, "k_2"] \arrow[d, "k_1"] & \mathrm{Ru(bipy)_3{}^{3+}} + \mathrm{Fe^{2+}} \arrow[l, shift left, "k_{-2}"] \\
\mathrm{Ru(bipy)_3{}^{2+}} + \mathrm{Fe^{3+}} \arrow[u, shift left, "h\nu"] \arrow[r, shift left] & \mathrm{Ru(bipy)_3{}^{2+}|Fe^{3+}} \arrow[l, shift left] &
\end{tikzcd} \qquad (1)$$

$$k_{el}[{}^*D][Q] = \frac{k_1k_{-2}[X]^2}{k_2} \qquad (2a)$$

If the absorbance of the quencher at the excitation wavelength may be neglected and the absorbance of the donor is not too large, then the expression for the concentration of the excited donor in a 1-cm path length cell can be simplified from eq 8 of a previous paper[3] to give

$$[{}^*D] = \frac{2.3 \times 10^3 I^{in}A_D}{k_0 + k_q[Q]} \qquad (2b)$$

where $A_D = \epsilon_D([D_0] - [X])$, A_D and ϵ_D are the absorbance of $Ru(bipy)_3{}^{2+}$ (corrected for $Ru(bipy)_3{}^{3+}$ concentration) and its molar absorptivity, respectively, $[D_0]$ is the total ruthenium concentration in the presence of the quencher, $k_q = (k_{en} + k_{el})$, I^{in} is the incident light intensity, and the concentrations of the precursor and successor complexes have been neglected. Since the emission intensity (I^{em}) is proportional to [*D], the ratio of measured emission intensities (at constant incident light intensity) from a sample containing Q to that from a reference sample without Q is

$$\frac{I^{em}}{I_{ref}{}^{em}} = \frac{[{}^*D]}{[{}^*D]_{ref}} = \frac{\{[D_0] - [X]\}k_0}{[D]_{ref}\{k_0 + k_q[Q]\}} \qquad (2c)$$

Equations 2a and 2b can be combined to yield eq 3a which is an expression for the steady-state concentrations in

$$\left\{\frac{[X_1]}{[X_2]}\right\}^2 = \frac{I_1{}^{in}\{[D_0] - [X_1]\}}{I_2{}^{in}\{[D_0] - [X_2]\}} \qquad (3a)$$

a given sample at two different light intensities. Similarly, eq 3b is an expression for the emission intensities of a given

$$\frac{[D_0] - [X_1]}{[D_0] - [X_2]} = \left[\frac{I^{em}}{I_{ref}{}^{em}}\right]_1 \left[\frac{I^{em}}{I_{ref}{}^{em}}\right]_2^{-1} \qquad (3b)$$

sample relative to that of an unquenched reference sample at the two light intensities. Values of [X] as a function of light intensity can now be obtained by the simultaneous solution of eq 3a and 3b.

Emission intensity measurements were made on a Perkin-Elmer model MPF-4 fluorescence spectrophotometer equipped with a 150-W Xenon lamp. Incident light intensities were determined using ferrioxalate actinometry[8] and were successively reduced with neutral density filters. An