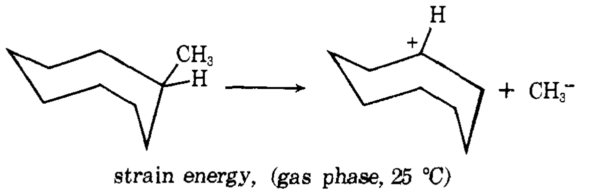
effects by Roberts[20] has shown that these shifts occur after the rate determining step. The solvolysis of cyclooctyl tosylate must be a limiting k_c process.

Some years ago Brown suggested that the solvolysis of medium ring derivatives was accelerated by relief of angle strain (I-strain).[21] Molecular mechanics calculations (Schleyer-Engler force field)[22] on the ionization of cyclooctane (with CH_3^- acting as a leaving group model, eq 2)[23] indicate that relief of strain may in fact facilitate ionization; other acyclic and monocyclic substrates show positive δ strain values.[25] Thus the rate acceleration of cyclooctyl tosylate predicted from the σ_t* correlation must result from relief of strain.



(2)

strain energy, (gas phase, 25 °C)
13.86 kcal/mol 10.80 kcal/mol

δ strain = −3.06 kcal/mol

In summary, strained secondary substrates can solvolyze without nucleophilic solvent assistance, even when there are no obvious barriers to nucleophilic approach, if the relief of ground-state strain upon reaction is sufficient to provide a competitive pathway.

Acknowledgment is made to the National Aeronautics and Space Administration and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research, and to P. v. R. Schleyer for critical comments.

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Preparation and Properties of Monolayer Films of Surfactant Ester Derivatives of Tris(2,2′-bipyridine)ruthenium(II)$^{2+}$

Sir:

There is intense interest in the photochemical properties of the tris(2,2′-bipyridine)ruthenium(II) cation, $(Ru^{II}(bpy)_3)^{2+}$.[1] It has recently been reported[2] that a substituted complex, $\{(bpy)_2Ru^{II}[bpy(COOC_{18}H_{37})_2]\}^{2+}(ClO_4^-)_2$ (where the substituents are in the 4,4′ positions of the bipyridine ligand), I, when incorporated in monolayer assemblies can efficiently catalyze the photodecomposition of water by visible light. We have found that during the preparation and handling of I, facile ester interchange and hydrolysis occurs under certain conditions. Further, the monolayer characteristics of I (vide infra) differ from those stated in ref 2. Accordingly, we believe that the reported photolysis observations involved a structure more complex than originally supposed, and careful characterization is required to obtain well-defined assemblies for further study.

The synthetic route to I[3] involves the esterification of 4,4′-dicarboxy-2,2′-bipyridine with *n*-octadecanol and subsequent reaction with $(bpy)_2Ru^{II}Cl_2$ in ethanol. Incomplete esterification, partial saponification during product workup, or ester interchange during the ligand insertion reaction can lead to alternate products. Most of a number of preparations we have examined have contained varying amounts of *n*-octadecanol, together with components of the type $\{[bpy]_2Ru^{II}[bpy(COOR_1)(COOR_2)]\}^{2+}$, where $R_1 = R_2 = H$ (II); $R_1 = C_{18}H_{37}$, $R_2 = H$ (III); or $R_1 = C_{18}H_{37}$, $R_2 = C_2H_5$ (IV). These separations have been accomplished by reverse phase (4 mm i.d. × 30 cm μBondapak/C_{18}) high pressure liquid chromatography employing a linear solvent gradient (50% aqueous THF/100% THF, both 0.015 M $MeSO_3H$, 0.5% HOAc). Under these conditions, I is chemically stable and is well separated from II, III, IV, and the dioctadecyl ester ligand (V), all of which are detected by their ultraviolet absorbancies at 254 and 280 nm. *n*-Octadecanol is detected by differential refractive index using 25% aqueous THF without $MeSO_3H$ and HOAc.

We have found that substantially pure I can be obtained by avoiding contact of either I or its precursor V with alkaline solution. The preparation of I used for this report contains:[4] <0.5 mol % (II + III + IV), <0.5 mol % V, <0.5 mol % *n*-octadecanol and 2.6 mol % $[bpy]_2Ru^{II}[bpy(COOC_{18}H_{37})$

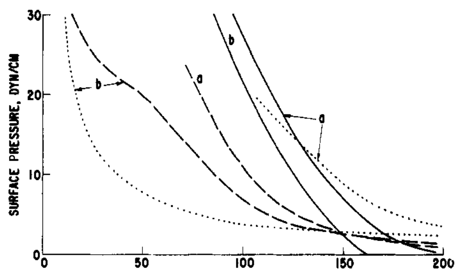

Figure 1. Surface pressure-area curves for I(—), III (- - -), and IV (• • •) on 0.1 M HCl (a) or 2.5 × 10^{-4} M $CdCl_2$ + 5 × 10^{-5} M $NaHCO_3$, pH 6.8 (b). Spread from $CHCl_3$ solution, 23 ± 1 °C, compression at 23 Å^2 molecule^{-1} min^{-1}

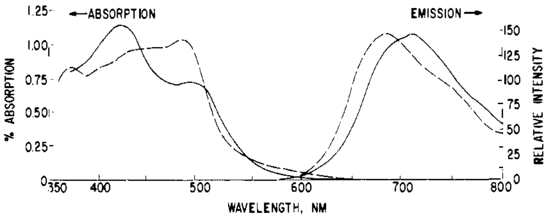

Figure 2. Absorption and corrected emission (λ_{ex} 440 nm) spectra of I as a single monolayer on both sides of hydrophobic glass slides coated with five layers of cadmium arachidate (—, transferred from 2.5 × 10^{-4} M $CdCl_2$ + 5 × 10^{-5} M $NaHCO_3$ at Π = 30 dyn/cm) and in $CHCl_3$ solution (- - -, absorption scaled, ϵ^{482} = 1.3 × 10^4; emission arbitrarily matched in peak height, Φ_L = 0.18 in solution).

$(COOC_{16}H_{35})]^{2+}$ which resulted from an impurity of *n*-hexadecanol in the octadecanol used for esterification. Unfortunately, the difficulty in separating octadecanol and III or IV from I makes elemental analysis of limited value in characterization; i.e., a mixture of octadecanol and III can have the same analysis as pure I. We have obtained samples of III[5] and IV[6] by preparative LC of portions of I treated with alkaline 10% aqueous THF or EtOH, respectively.

In acidic 20% aqueous THF solutions, I-IV are indistinguishable spectroscopically, possessing absorption maxima at 485 and 425 nm of the same extinction and emission maximum at 718 nm of the same intensity. In neutral 20% aqueous THF solutions, the carboxyl groups of II and III are ionized as evidenced by an immediate, substantial enhancement and blue shift of the emission spectra (II: 647 nm, 4.0× increase; III: 690 nm, 1.5× increase) and a corresponding 10-20% increase in extinction and shift in the absorption spectra (II: 457 nm, 430 (sh); and III: 472 nm, 435 (sh)). In alkaline 20% aqueous THF, I, IV, and also III undergo hydrolysis with the development of similar spectral shifts which finally are identical with ionized II.

While II is water soluble, I, III, and IV all form insoluble monolayers on aqueous subphases. At subphase pH > 7.5, the films shrink with time (faster at higher pH; the process is complete within 1 min on 1 M NaOH), reaching a stable limiting area of 20 Å^2 per stearyl residue in the molecule.[7] On neutral and acidic subphases, the films are stable: typical Π-*A* curves are shown in Figure 1.[8] For I, these curves are reversible without hysteresis on all subphases examined; the same is true for III and IV on HCl and $NaClO_4$ solutions, but films on $CdCl_2$/pH 6.8 solution exhibit hysteresis on compression-expansion cycling, which we have not yet examined in detail. The observed areas for III and IV on this subphase are also so small (<20 Å^2/molecule) that their significance is uncertain.

While I requires an area of 85 Å^2/molecule (at 30 dyn/cm), rather than 40 Å^2 as found by Sprintschnik et al., mixtures obtained in some preparations can have smaller area requirements; we have obtained one such mixture[9] whose Π-*A* curve matches closely that obtained by Sprintschnik *et al.*[3]

Absorption and emission spectra[10,11] of monolayers of I transferred to hydrophobic slides coated with five layers of cadmium arachidate are shown in Figure 2, in comparison to I in $CHCl_3$ solution. The excitation spectrum in solution reproduces the corresponding absorption trace. Upon immersion of these slides in 3× distilled water, the absorption spectrum exhibits slight changes in maxima (410, 495 nm) and extinction (ca. 25% increase which may be due entirely to optical path changes), while the luminescense is reduced by ca. 20-60% and is blue shifted ca. 5-10 nm. We have not found that the luminescence is "almost entirely quenched" upon immersion into water or that it is recoverable upon heating under vacuum (<1 Torr/35 °C for 15 h) as reported by Sprintschnik et al.

We have also failed to observe gas evolution on illumination of slides coated with monolayers of I and immersed in water;[12] however, after this exposure the coating was found to be degraded or lost (no visible absorption or emission was detectable). We also note that the evolution of gas bubbles is an inherently insensitive test, since saturation of even a layer of water 0.5 mm thick requires the production of more than 100 molecules of H_2 for each active catalyst molecule.

In view of the complexities of the synthesis and irreproducibility in forming monolayer assemblies, we do not consider these experiments a critical test of the observations of Sprintschnik et al. They do, however, indicate some precautions which must be observed in order to obtain well-defined assemblies for such an examination.

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(4) Anal. Calcd for $C_{68}H_{96}N_6Cl_2RuO_{12}$: C, 59.99; H, 7.11; N, 6.17; Cl, 5.21; Ru, 7.42. Found: C, 60.01; H, 7.19; N, 6.08; Cl, 5.24; Ru, 7.56. IR (KBr) 3040, 3060, 2925, 2860, 1725, 1270, 1245, 1090, 720 cm^{-1}. ^{1}H NMR (100 MHz, $CDCl_3$) (δ 0.89 (t, 2.5 Hz), 1.28 (broad s), 1.86 (mult); 70 H), 4.34 (t, 3.0 Hz, 4 H), (7.44, 7.76, 8.00, 8.51, 8.90 (all mult), ca. 23 H). UV-visible ($CHCl_3$) 287 nm (ϵ 5.8 × 10^4), 312 (sh, 3.4 × 10^4), 365 (9.8 × 10^3), 405 (sh, 9.1 × 10^3), 430 (sh, 1.1 × 10^4), 482 (1.3 × 10^4). Spectrographic analysis indicates no other transition metal elements present (<1-10 ppm).

(5) IR (KBR) 3400, 3070, 2915, 2815, 1720, 1600, 1300, 1235, 1075, 720, cm^{-1}. UV-visible ($CHCl_3$) 291 nm (4.8 × 10^4), 310 (sh, 2.5 × 10^4), 355 (sh, 7.6 × 10^3), 398 (sh, 6.3 × 10^3), 438 (sh, 1.1 × 10^4), 465 (1.2 × 10^4).

(6) Anal. Calcd for $C_{52}H_{64}N_6Cl_2RuO_{12}$: C, 54.9; H, 5.7; N, 7.4; Found: C, 54.3; H, 5.8; N, 6.9. IR (KBr) 3050, 2915, 2850, 1720, 1598, 1310, 1250, 1080, 723 cm^{-1}. ^{1}H NMR (100 MHz, CD_2Cl_2) (δ 0.96 (t, 3 Hz, 1.36 (broad s), 1.52 (t, 3.5), 1.81 (mult), 38 H), (4.43 (t, 3 Hz), 4.50 (q, 3.5), 4 H), (7.53, 7.80, 8.04, 8.12, 8.51, 8.98 (all mult), 22 H). UV-visible ($CHCl_3$) 288 nm (ϵ 5.4 × 10^4), 312 (sh, 3.1 × 10^4), 364 (9.2 × 10^3), 405 (sh, 8.7 × 10^3), 430 (sh, 1.1 × 10^4), 481 (1.2 × 10^4).

(7) Gas chromatography confirms that when the process is complete, the remaining films are composed of octadecanol.

(8) For I, the curves on NaCl or Na_2SO_4 solutions, or pure water, resemble closely that on HCl. For all three compounds, $NaClO_4$ (to 1 M) produces a marked reduction in film compressibility, but with areas at 30 dyn/cm within ~10% of those observed on 0.1 M HCl.

(9) 37 mol % I, 55 mol % IV, 8 mol % octadecanol.

(10) A detailed description of the combined absorption and emission monolayer spectrometer is contained in General Electric Company Corporate Research and Development Report 75CRD162: S. J. Valenty, J. O. Fielding, and G. Jernakoff, Aug 1975, unpublished. All emission and excitation spectra are corrected; bandpass of both monochromators is 8.5 nm.

(11) Typically, absorption of monolayers of I on either hydrophilic glass or cadmium arachidate layers have the same maxima (±5 nm) and extinction (±2.0 × 10^{-4} OD/layer). By rinsing such slides with THF/$CHCl_3$ and subsequent LC analysis, we have demonstrated recovery of unchanged I; since

recovery is not yet quantitative, this observation is of uncertain significance.

(12) Experimental conditions: water previously boiled, two slides illuminated with GE H100 PSP44-4 Hg Lamp for 425 h.

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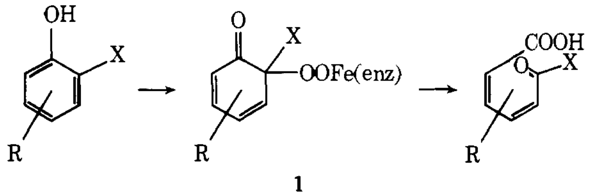
Novel Peroxycobalt(III) Complexes Derived from 4-Aryl-2,6-di-*tert*-butylphenols. A Model Intermediate of Dioxygenase Reaction

Sir:

Oxidative cleavage of phenolic rings by molecular oxygen, widely seen in nature, is one of the most interesting biological oxygenation reactions. Pyrocatechase and metapyrocatechase are the typical enzymes which catalyze the oxygenation of phenolic substrates leading to the oxidative cleavage of the aromatic rings.[1] These enzymes require ferric or ferrous ion as the cofactor, which is considered to participate in the reaction center.[2] α-Ketoperoxy complex (**1**) involving the metal ion at the reaction center of the enzyme has been postulated as a primary intermediate of the dioxygenase reaction for phenolic substrates.[3] Little is, however, known about such a peroxy complex of type **1**. We now wish to report the synthesis of peroxycobalt(III) complexes of type **1** by the oxygenation of 4-aryl-2,6-di-*tert*-butylphenol with Co(salpr) (salpr = bis(3-salicylideneaminopropyl)amine), a five-coordinated Co(II) Schiff's base complex.[4] This provides a model for the proposed intermediate of the dioxygenase reaction.

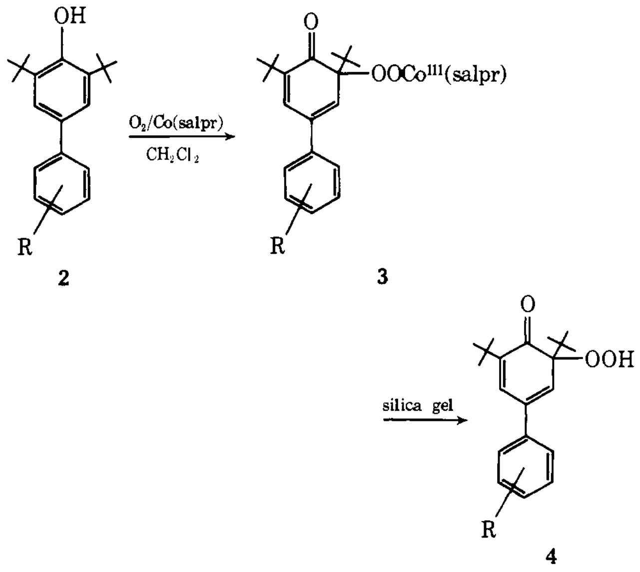


1

X = H or OH

When oxygen is bubbled through a solution of 4-aryl-2,6-di-*tert*-butylphenol (**2**) (0.5 mmol) and Co(salpr) (0.4 mmol) in CH_2Cl_2 (6 ml) at 0 °C the reaction is normally completed within 1 h. The reaction mixture is concentrated (3 ml) and diluted with petroleum ether (20–30 ml) to result in the precipitation of the unreacted Co(salpr). After removal of the precipitates by filtration, the filtrate is kept at −20 °C over night to give the α-ketoperoxycobalt(III) complex (**3**), black prisms.[5] The IR absorption at 1640 cm^{-1} for all complexes, **3**, is referred to the 2,4-cyclohexadienone structure.[6] The NMR spectra are all in good agreement with structure **3** (Scheme I). The signal of one of the *tert*-butyl groups in **3** shifts to considerably higher field compared to that of the corresponding hydroperoxides, **4** (Δ = 0.16–0.22 ppm), reflecting the coordination effect. The magnitude of coupling between the olefinic protones of **3** (J = 2.8 Hz) is characteristic of that between 3-H and 5-H in the 2,4-cyclohexadienone system.[7-9] Structure **3** was further confirmed by the fact that the filtration of a CH_2Cl_2 solution of **3** through a short column of silica gel affords the corresponding α-ketohydroperoxides, **4**, in nearly quantitative yield. Compound **4a** was identical with the sample obtained in the base-catalyzed oxygenation of **2a**.[7]

Scheme I



	a	b	c	d	e	f	g	h
R	4-OMe	3-OMe	2-OMe	4-Me	3-Me	2-Me	H	4-Cl

The NMR spectrum of the reaction mixture resulting from the oxygenation of **2** shows only signals for **2** and **3** but not for **4**, indicating that compound **3** is the sole product in the oxygenation. For the formation of **3**, 1.25 mol/mol of oxygen was taken up against **2** or Co(salpr) incorporated into **3**, and no hydrogen peroxide is detected in the reaction mixture, which shows neutral pH. The stoichiometry of this reaction is therefore depicted as follows:

$$\mathbf{2} + \text{Co(salpr)} + \tfrac{5}{4}O_2 \rightarrow \mathbf{3} + \tfrac{1}{2}H_2O$$

The solution of Co(salpr) in CH_2Cl_2 bubbled with oxygen at room temperature displays the typical ESR signals for the Co-O_2 (1:1) complex (eight lines, a_{Co} = 13 G).[10] Upon addition of a small amount of **2a** under interception of oxygen, the signals were diminished with simultaneous appearance of

Table I. Preparation and Physical Properties of **3**

Compd	Conversion[a] (%)	Yield (%)	Mp (°C)	NMR($CDCl_3$), δ (ppm) *t*-Bu		Me	C=CH[c]		Ar	IR (Nujol) (cm^{-1})
3a	80	100	131–132	0.83	1.23	3.80	5.85	6.89	6.7–7.6	1640
3b	83	100	123–125	0.82	1.21	3.83	6.00	—[d]	6.6–7.6	1640
3c	76	100	125–127	0.88	1.26	3.81	5.80	6.82	6.7–7.6	1640
3d	67	100	131–133	0.83	1.24	2.35	5.99	6.88	6.7–7.6	1640
3e	62	100	122–124	0.84	1.25	2.40	5.97	—[d]	6.7–7.6	1640
3f	70	100	125–126	0.85	1.25	2.16	5.45	6.63	6.7–7.6	1640
3g	72	100	118–119	0.83	1.24	—	6.03	—[d]	6.7–7.6	1640
3h	37[b]	100	126–127	0.87	1.25	—	5.97	6.88	6.7–7.6	1640

[a] Conversion of **2** to **3**: determined by the yields of the corresponding hydroperoxides **4** which were isolated by filtration of **3** through a short column of silica gel. [b] Determined by isolation of **3h**. [c] A pair of doublets with J = 2.8 Hz. [d] The signal is concealed behind the aromatic signals.