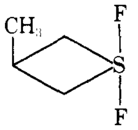
electronegativity rules[21,22] and the restriction against diapical linkage of five-membered rings, this compound presents a rare opportunity to study the relative importance of steric and ring strain effects[22] in determining conformations of sulfuranes. The ^{19}F NMR of **2** (which shows equivalent CF_3 groups on the ring) is compatible with diequatorial structure **2** or with a rapid equilibrium between **10a** and **10b**. The latter is considered highly unlikely since no peak broadening is seen in the 94.1-MHz ^{19}F NMR spectrum, even at −90°. Neither was the low-field aromatic ^1H NMR doublet, previously mentioned as being highly characteristic of an apical-equatorial bridged arylsulfurane, present in the NMR, although it would be expected for structures **10a** or **10b**. We also reject the zwitterionic structure **11** on the basis of the solubility of **2** in nonpolar solvents such as CCl_4 and upon the basis of analogies with other sulfuranes for which x-ray structures are available.[2c,d,j]

The apparent preference for the diequatorial five-membered ring fusion in **2** is at first glance surprising, in view of contrasting experience in phosphorane chemistry. Although a few structures are known in which four- and six-membered rings link equatorial positions of phosphoranes,[22b,23] these are all cases in which the great difference in apicophilicities pushes two fluoro or alkoxy ligands into the apical position with the two less electronegative carbon ligands of the ring being forced into the diequatorial geometry. A similar difference in apicophilicity would tend to favor the diequatorial disposition of the four-membered ring in sulfurane **12**.[24]



12

The preference for the diequatorial linkage in sulfurane **2** can be rationalized by reference to the smaller bond angles in the equatorial plane which have been reported for sulfuranes[2c,d,j,25] (104.4–108.1°) relative to the near 120° of the three bond angles in the equatorial plane of phosphorane analogues.[26] It is less clear why a recently prepared monocyclic tetrakisalkoxysulfurane should have an equatorial-apical five-membered ring.[9]

Acknowledgment. This research was supported in part by a grant from the National Science Foundation (MPS 71-03222) and in part by Fellowships for G.W.A. from Abbott Laboratories, the Phillips Petroleum Co., and the Dow Chemical Co.

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(5) Satisfactory elemental analyses for C and H (within 0.4%) were obtained for this and other new compounds of this study unless otherwise noted. ^1H NMR (CCl_4) δ 2.41 (s, 3, CH_3), 6.98 and 7.31 (AB pattern, 2, J_{AB} = 8 Hz), 7.25 (broad s, 1, proton ortho to fluoroalkyl group); ^{19}F NMR (CCl_4) doublet 76.6 ppm upfield from $CFCl_3$, J_{HF} = 1 Hz); mass spectrum (70 eV) *m/e* (rel intensity) 288 (51.9, $M\cdot^+$), 219 (100, M − CF_3), 150 (52.8), 121 (30.4); ultraviolet 255 nm (ϵ 11000), 300 (1500), 383 (62).

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(7) Authentic sulfinate **5** was prepared by the *tert*-butyl hypochlorite oxidation of **4** in CCl_4 (61% yield). It is a white, crystalline, air-stable solid mp 64–65°; ^1H NMR ($CDCl_3$) δ 2.56 (s, 3, CH_3), 7.58 (broad s, 1, proton ortho to fluoroalkyl group), 7.62 and 7.80 (AB pattern, 2, J_{AB} = 8 Hz); ^{19}F NMR ($CDCl_3$) 2 quartets 75.21 and 76.05 ppm upfield from $CFCl_3$, *J* = 9 Hz; mass spectrum (70 eV) *m/e* (rel intensity) 304 (100, $M\cdot^+$), 237 (58.3); 235 (31.8, M − CF_3), 166 (74.1); ir ($CHCl_3$) 3042 (w), 2938 (w), 1600 (m), 1311 (s), 1279 (s), 1242 (s), 1177 (s), 1063 (s), 979 (s).

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(15) Anal. Calcd for $C_{28}F_{18}H_{16}SO_3$: C, 43.42; H, 2.08. Found C, 42.75; H, 2.26 (the analysis was difficult because of the extreme water sensitivity of **2**). ^1H NMR (CCl_4) δ 2.63 (s, 3, CH_3), 7.28 (broad s, 10, hexafluorocumyl groups), 7.61 (broad s, 3, trisubstituted ring); ^{19}F NMR (CCl_4) broad quartets, 70.1 and 72.7 ppm upfield from $CFCl_3$ (broad q, 6 each, CF_3 groups of OR_F), 71.4 ppm (broad s, 6, ring CF_3); mass spectrum (70 eV) *m/e* (rel intensity) 705 (0.02, M − CF_3), 697 (0.01, M − Ph), 531 (15.5, M − OR_F), 227 (100, $PhC(CF_3)_2+$), field ionization mass spectrum *m/e* (rel intensity) 774 (0.1, $M\cdot^+$), 551 (0.2), 532 (100, M + H − OR_F).

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(20) ^1H NMR (C_6D_6) δ 0.78 (s, 3, CH_3), 0.86 (s, 3, CH_3), 0.98 (s, 3, CH_3), 1.07 (s, 3, CH_3), 1.86 (s, 3, $ArCH_3$), 6.87 (broad d, 1, proton para to fluoroalkyl group, *J* = 8 Hz), 7.6 (broad s, 1, proton ortho to fluoroalkyl group), 8.13 (d, 1, proton ortho to sulfur); ^{19}F NMR (CCl_4) 2 quartets 75.35 and 76.23 ppm upfield from $CFCl_3$, *J* = 9 Hz; mass spectrum (70 eV) *m/e* (rel intensity) 405 (0.3, M + H), 389 (2.06, M − CH_3), 335 (1.95, M − CF_3), 219 (100).

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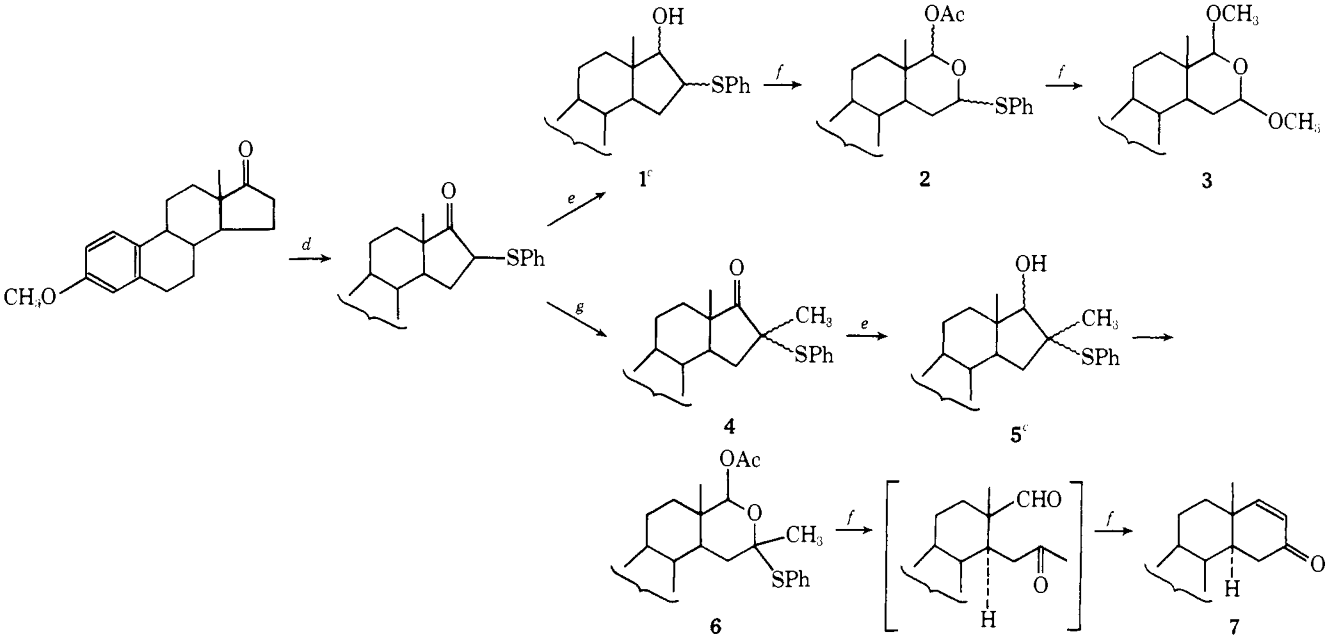
New Synthetic Reactions. New Approach to (Alkylative) Oxidative Ring Cleavage

Sir:

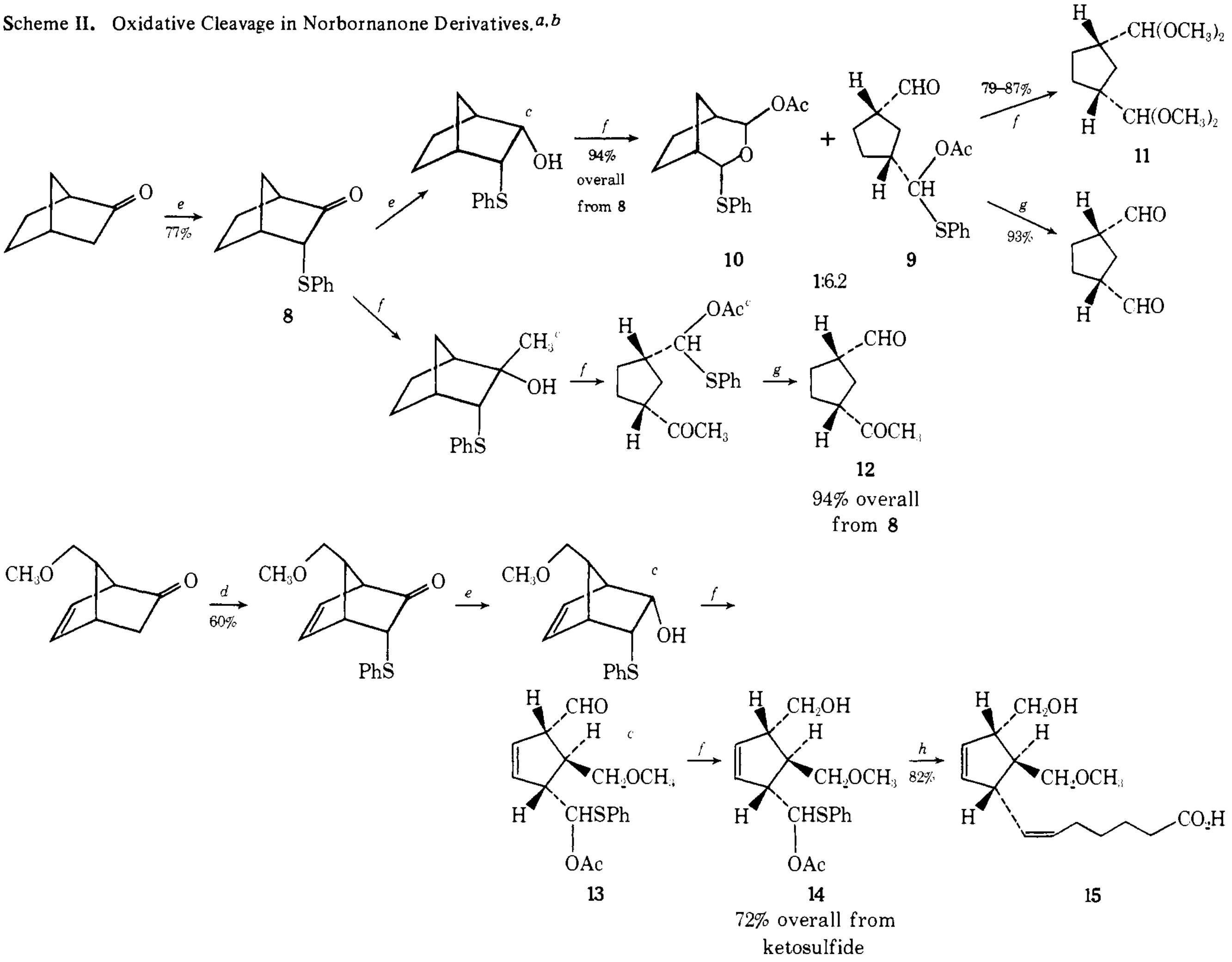
The utility of cyclic compounds for control of stereochemistry in organic synthesis as well as, to a lesser extent, the modification of ring size depends upon the ability to selectively cleave rings. Methods which involve generation of vicinal oxygen substitution (e.g., by oxidation of an olefin or ketone) are common.[1-4] The selective sulfenylation of polyfunctional compounds[5,6] suggests the desirability of replacing oxygen substituents with thio groups in many oxidative processes.[7]

Scheme I. Oxidative Cleavages in the Estrone Methyl Ether Series.[a,b]



[a] All new compounds have satisfactory spectral properties and elemental composition.[b] Yields represented in text are not optimized and are for pure compound isolated by chromatography and or crystallization. [c] Normally not purified but carried directly onto next step. [d] LICA, THF–HMPA 3:1, PhSSPh, 25°, 1 hr. [e] $NaBH_4$, C_2H_5OH, 25°, 15 hr. [f] See text. [g] NaH, THF, CH_3I, room temperature (15 hr), 55° (1 hr).

Scheme II. Oxidative Cleavage in Norbornanone Derivatives.[a,b]



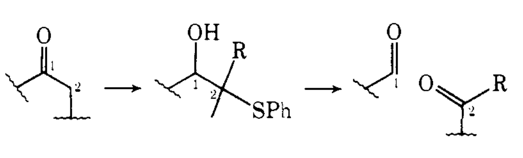
[a] All new compounds have satisfactory spectral properties and elemental composition. [b] Yields are not optimized and are for isolated pure compounds. [c] Normally not purified but carried directly onto next step. [d] See Scheme I, footnote d. [e] See Scheme I, footnote e. [f] See text. [g] $HgCl_2$, 3:1 CH_3CN/H_2O, reflux, 3.5 hr. [h] $Ph_3P^+CH_2(CH_2)_4CO_2HBr^-$, n-C_4H_9Li, THF, 0° to generate Wittig reagent then 25° (3 hr) and reflux (18 hr) for addition.

The difficulty in realizing such an approach is the facility of oxidation of sulfides to sulfoxides and/or sulfones. In this paper we wish to report the successful development of such a selective ring cleavage method initiated by the chemospecific sulfenylation of ketones and involving an oxidative cleavage employing lead tetraacetate.[8] The novelty of the cleavage is underscored by the fact that β-mercapto alcohols[9] and monoethers of vicinal diols do not cleave with this reagent.[2,10,11] This method has the further advantage of providing a differentiation of the two incipient carbonyl groups.

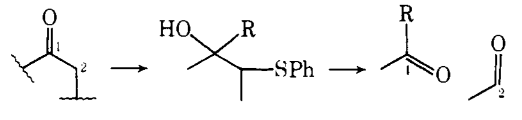
The approach is illustrated utilizing estrone methyl ether as an example (see Scheme I). The sulfenylated estrone methyl ether, obtained in 94% yield, was reduced to a stereoisomeric mixture of alcohols in 75% yield.[7a] Treatment of the thioalcohol **1** with 1.2 equiv of lead tetraacetate (LTA) in a 4:1 (v/v) mixture of anhydrous toluene-glacial acetic acid at 0° led to smooth conversion to a cyclic hemithioacetal acetate **2.**[12] Conversion to the cyclic hemiacetal **3**[12] proceeds quantitatively upon refluxing in methanol in the presence of 1 equiv of iodine (3 hr). The overall isolated yield of **3** from **1** is 81%.

The flexibility of the β-ketosulfides as synthetic intermediates enhances their use in this role. For example, methylation[13] (86% yield) followed by reduction and cleavage as before gave the related cyclic hemithioacetal acetate **6**[12] in 91% yield. Treatment of crude **6** with methanolic potassium hydroxide at 25° (20 hr) led, via in situ hydrolysis to the keto aldehyde, to the cyclohexenone **7**[12] (63% overall from alcohol **5**). This alkylative oxidative cleavage serves as a ring enlargement concomitant with a 1,3-carbonyl transposition.

Application of this method to several norbornanones (Scheme II) provides further illustration of the flexibility of the sequence. Sulfenylation of norbornanones leads to the endo isomers as the major or exclusive product as a result of kinetic protonation of the enolate of the β-ketosulfide during work-up.[14] Reduction and cleavage of the endo isomer **8** leads smoothly to the desired ring cleaved products **9**[12] and **10.**[12] Treatment of **9** and/or **10** with iodine in refluxing methanol produced the same bisacetal **11.**[12] Alternatively, hydrolysis gave *cis*-cyclopentan-1,3-dicarboxaldehyde (semicarbazone mp 203°).[15] Thus, isomerization via enolization does not occur. Addition of methyllithium to **8** followed by oxidative cleavage gives keto aldehyde **12.**[12] By controlling the timing of alkylation and cleavage, different orientations in the alkylative oxidative cleavage may be obtained as exemplified by eq 1 and 2. How the mechanism of this reaction relates to the oxidative cleavage of diols is uncertain at present.[16]



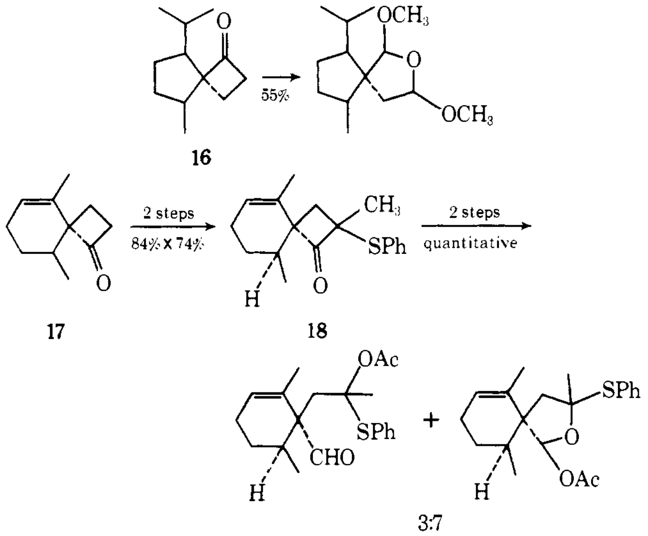
(1)



(2)

The fact that the carbon α to the carbonyl group in starting material becomes a carbonyl group in a protected form in the product allows selective manipulations. The product **13** of oxidative cleavage starting from 7-*anti*-methoxymethylnorborn-5-en-2-one[17] was reduced to the alcohol **14**[12] with sodium borohydride in ethanol (0°, 1 hr). The hemithioacetal could be used directly in subsequent carbonyl additions in the presence of a nucleophile to liberate the unprotected functional group. Direct Wittig reaction of **14** led to the desired olefin **15.**[12] This example also illustrates the compatibility of the method with a rather sensitive double bond. Such a sequence may have application in the stereocontrolled synthesis of cyclopentanoid sesquiterpenes and prostanoid derivatives.

As anticipated, this route works equally well in the case of cyclobutanones **16**[18] and **17.**[19] It is interesting to note that methylation of the sodium enolate (generated with NaH) of the α-phenylthiocyclobutanone derived from **17** gave mainly O-alkylation but the lithium enolate (generated with n-C_4H_9Li) gave the desired product of C-alkylation **18.** Extension of this method to cyclohexanones has so far been unsuccessful.[20]



16

17

18

This approach has several useful features. The regioselectivity is controlled by the regioselectivity of the sulfenylation and will frequently complement other methods of cleavage of cycloalkanones such as the Baeyer–Villager oxidation.[1–3] Controlled variation of the alkylation pattern because of the versatility of the sulfenylated ketones gives great flexibility in developing carbon skeletons. The chemospecificity allows other functional groups sensitive to many oxidizing agents such as alcohols and olefins to be present without complications. By choice of the timing of alkylation and cleavage, the method also constitutes a novel modification of ring size.

Acknowledgment. We wish to thank the National Science Foundation and the National Institutes of Health for their generous support of our programs.

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(20) In these cases, only starting material is recovered. This result suggests a chemospecific cleavage of a cyclopentanone or cyclobutanone in the presence of cyclohexanones or acyclic ketones is possible.
(21) Camille and Henry Dreyfus Teacher Scholar Grant Recipient, 1970–1975.

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Photophysical Evidence for "d–d" Emissions from Homobischelated Complexes of Iridium(III)

Sir:

The pathways for energy transfer processes which begin with excitation and terminate with luminescence, photochemistry, and heat production in transition metal complexes have been explored by a variety of techniques. Photophysical evidence accumulated from studies of complexes of Rh(III), Ru(II), Ir(III), and Os(II) at 77 K has led to the formulation of the following postulate.[1,2] "In the absence of photochemistry from upper excited states, emission from a transition-metal complex with an unfilled d shell will occur from the lowest electronic excited state in the molecule or from those states which can achieve a significant Boltzmann population relative to the lowest excited state."[1] This postulate was formulated on the basis of the observation of luminescence quantum yields of Rh(III), Ru(II), and Os(II) complexes which were found to be independent of excitation wavelength.[1,2] However, in no case did the studies at 77 K include excitation of states of orbital parentage different from that of the emitting state (i.e., at all the excitation wavelengths employed in these studies the quantum yield for "d–d" emission from Rh(III) complexes was measured following excitation into higher "d–d" bands and the quantum yield for $d\pi^*$ emission from Ru(II) and Os(II) complexes was measured following excitation into higher $d\pi^*$ bands).

Recent photophysical evidence from studies of heterobischelated complexes of Ir(III)[3–5] and heterotrischelated complexes of Rh(III)[6] indicates that the emissions of these complexes originate from several thermally nonequilibrated levels at 77 K, contrary to the generalization quoted above. These results have led us to propose the following selection rules for radiationless transitions in Ir(III) complexes: $d\pi^* \leftrightsquigarrow d\pi^*$, $\pi\pi^* \leftrightsquigarrow \pi\pi^*$, $d\pi^* \not\leftrightsquigarrow \pi\pi^*$. These rules imply that there is a tendency for retention of orbital parentage in the radiationless pathways which lead from one electronically excited level to another in the charge-transfer and ligand-localized manifolds of levels. We have found these rules to be particularly rigid when the energy gaps between excited states of different orbital parentage are small ($<300\ \mathrm{cm^{-1}}$) and when these states are localized in different areas of the molecular framework.[7] For larger energy gaps the rules still appear to describe the preferred pathways for energy degradation in heterobischelated Ir(III) complexes,[4,5] though they may be somewhat less rigid.

Since no "d–d" emissions have been reported in these complexes, their role in the electronic energy transfer pathways in Ir(III) complexes has not been deduced from photophysical studies. However, studies of the photochemistry of iodoammine complexes of Rh(III) have led to the conclusion that the low lying charge-transfer-to-metal (CTTM) and "d–d" excited states do not interconvert efficiently.[8] Furthermore, recent photochemical results[9] indicate that chloride aquation of homobischelated Ir(III) complexes (e.g., $\mathrm{[IrCl_2(phen)_2]Cl}$) takes place from a "d–d" level. These results suggest that a thermally controlled deactivation process of the emitting levels leads to population of the reactive "d–d" level in the temperature region between 8 and 65°C, although the emitting levels are presumed to be of the same orbital parentage as those observed at −196°C.

In order to investigate further the role of "d–d" levels in the deactivation pathways of Ir(III) complexes, we have undertaken a study of the time-resolved emission spectra of several homobischelated complexes of Ir(III) in the temperature region between −196 and 0°C. In this communication we report the results of this study for two homobischelated complexes of Ir(III) whose photochemistry in fluid solutions has been reported.[9]

The complexes, *cis*-dichlorobis(1,10-phenanthroline)iridium(III) chloride, $\mathrm{[IrCl_2(phen)_2]Cl}$, and *cis*-dichlorobis(5,6-dimethyl-1,10-phenanthroline)iridium(III) chloride, $\mathrm{[IrCl_2(5,6\text{-}mephen)_2]Cl}$, were prepared by the method of Broomhead and Grumley[10] and were purified by repeated recrystallization from dilute HCl followed by column chromatography on Sephadex LH-20. Solutions of the complexes (10^{-4} *M*) in glycerol (Matheson Coleman and Bell spectroquality) were prepared and stored in the dark at 0°C when not in use. Low temperature baths were used to attain temperatures between −196 and 0°C.[11] Time-resolved emission spectra were obtained with apparatus described in a previous publication[4] which utilizes a pulsed nitrogen laser for excitation at 337 nm. All spectra were corrected for the wavelength dependence of the photomultiplier-monochromator combination. Corrected steady-state luminescence spectra were recorded with a Hitachi MPF-3A spectrophotofluorimeter using 337-nm excitation. Photolysis of the complexes was found to lead to a luminescent product under prolonged laser excitation at 337 nm, particularly at temperatures above −41°C. However, the time-resolved