ultraviolet, mass,[15] and proton spectra as well as by the ability of genipin to produce an ineffaceable blue color when applied to skin.[16] An identical series of reactions also served in the transformation of triol **7b** to racemic genipin (**2**).

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(15) Mass spectra were measured in the laboratory of Professor K. Biemann, Massachusetts Institute of Technology.

(16) C. Djerassi, J. D. Gray, and F. A. Kincl, *J. Org. Chem.*, **25**, 2174 (1960).

(17) National Institutes of Health Postdoctoral Fellow, 1966–1967.

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Luminescence of Iridium(III) Chelates with 2,2′-Bipyridine and with 1,10-Phenanthroline

Sir:

Very few complexes of transition metal ions having a partly filled d shell are luminescent in fluid solutions. One notable exception is the tris(1,10-phenanthroline)-ruthenium(II) ion; this species and several other Ru(II) chelates with some similar ligands were first reported to luminesce by Brandt and co-workers.[1,2] Paris and Brandt[1] assigned the bands in the absorption spectrum of the tris(2,2′-bipyridine)ruthenium(II) ion and concluded that the emission accompanied a ligand-to-metal charge-transfer ($\pi^* \rightarrow d$) transition. Later, weak absorption bands at 539 mμ (18.550 kK) and at 664 mμ (15.050 kK) were reported for the latter species and led to reassignment of the luminescence as fluorescence associated with a ligand-field ($^1T_1 \rightarrow {}^1A_1$) radiative transition.[3] More recently other workers have concluded that there is no compelling reason to assign the luminescence of the tris(2,2′-bipyridine)ruthenium(II) ion to a ligand-field transition; indeed, there are several sound reasons against such an assignment.[4]

The present work describes luminescence from fluid solutions of the analogous iridium(III) chelates: tris(2,2′-bipyridine)iridium(III) ion, $[Ir(bipy)_3]^{3+}$, and tris(1,10-phenanthroline)iridium(III) ion, $[Ir(phen)_3]^{3+}$. The group theoretical classification of these chelates is D_3. The metallic ion is in an octahedral environment; moreover, these species are diamagnetic: the metallic ion has the low-spin d^6 configuration and geometry analogous to the ruthenium(II) chelates. The emission appears to accompany charge-transfer transitions from the ligand to the metal ion ($\pi^* \rightarrow d$), *i.e.*, similar in kind to that assigned by Paris and Brandt for the luminescence of the Ru(II) chelates.[1]

The ultraviolet–visible absorption spectra for the Ir(III) species are shown in Figure 1. The absorption spectrum of 2,2′-bipyridine in concentrated sulfuric acid is included in Figure 1 because the diprotonated form most nearly approximates chelated 2,2′-bipyridine with respect to the energies of the intraligand ($\pi^* \leftarrow \pi$) transitions. Assignments of the absorption bands are given in Table I.

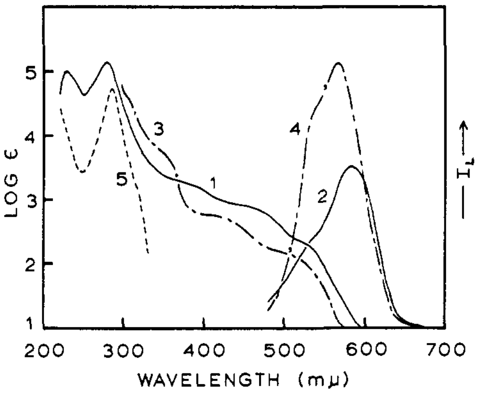

Figure 1. Absorption and luminescence spectra: (1) $[Ir(bipy)_3]^{3+}$ absorption spectrum in DMF; (2) $[Ir(bipy)_3]^{3+}$ luminescence spectrum in DMF, 370-mμ excitation; (3) $[Ir(phen)_3]^{3+}$ absorption spectrum in DMF; (4) $Ir(phen)_3{}^{3+}$ luminescence spectrum in DMF, 475-mμ excitation; (5) 2,2′-bipyridine absorption spectrum in concentrated H_2SO_4. I_L = luminescence intensity (in arbitrary units and corrected for variation of detector response with wavelength).

Table I. Absorption Band Assignments for 2,2′-Bipyridine and 1,10-Phenanthroline Chelates of Ir(III)

Compound	λ_{max}, mμ[a]	Log ε[b]	Assignment
2,2′-Bipyridine[c]	285	4.83	$\pi^* \leftarrow \pi$
$[Ir(bipy)_3]^{3+}$ [d]	235	4.89	$\pi^* \leftarrow d$
	284	5.08	$\pi^* \leftarrow \pi$
	370 (s)	3.2	$\pi^* \leftarrow d$
	480 (s)	2.8	$\pi^* \leftarrow d$
	515 (s)	2.3	$\pi^* \leftarrow d$
$[Ir(phen)_3]^{3+}$ [d]	<300	>4.7	$\pi^* \leftarrow \pi$
	310 (s)	4.4	$\pi^* \leftarrow \pi$
	350 (s)	3.7	$\pi^* \leftarrow d$
	430 (s)	2.7	$\pi^* \leftarrow d$
	520 (s)	2.1	$\pi^* \leftarrow d$

[a] s = shoulder. [b] ε is molar absorptivity. [c] Solvent, concentrated H_2SO_4. [d] Solvent, dimethylformamide.

Jørgensen attributed bands in the range 285–345 mμ in the absorption spectra of 20 Ir(III)–pyridine complexes to ($\pi^* \leftarrow d$) charge-transfer transitions.[5] Spectral studies of the tris(ethylenediamine)iridium(III) ion, $[Ir(en)_3]^{3+}$, in solution show the lowest energy singlet $d^* \leftarrow d$ ($^1T_1 \leftarrow {}^1A_1$) transition at 249 mμ and the lowest energy triplet ($^3T_1 \leftarrow {}^1A_1$) transition at 302 mμ.[6] Both 2,2′-bipyridine and 1,10-phenanthroline are placed above ethylenediamine in the spectrochemical series.[7] Therefore, in $[Ir(bipy)_3]^{3+}$ and $[Ir(phen)_3]^{3+}$ the splitting of the several ligand field states will be larger than in $[Ir(en)_3]^{3+}$, and more energy will be required to effect the $^1T_1 \leftarrow {}^1A_1$ and $^3T_1 \leftarrow {}^1A_1$ transitions. The energy required for a ligand-field transition in the 2,2′-bipyridine and 1,10-phenanthroline chelates of Ir(III) is estimated as approximately equal to the energy necessary for an intraligand ($\pi^* \leftarrow \pi$) transition and thus is greater than that for a charge-transfer ($\pi^* \leftarrow d$) transition. The luminescence of these Ir(III) chelates is therefore assigned to a $\pi^* \rightarrow d$ transition.

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(1) J. P. Paris and W. W. Brandt, *J. Am. Chem. Soc.*, **81**, 5001 (1959).

(2) H. Veening and W. W. Brandt, *Anal. Chem.*, **32**, 1426 (1960).

(3) G. A. Crosby, W. G. Perkins, and D. M. Klassen, *J. Chem. Phys.*, **43**, 1498 (1965).

(4) R. A. Palmer and T. S. Piper, *Inorg. Chem.*, **5**, 864 (1966); see footnote 88 at end of paper.

(5) C. K. Jørgensen, *Acta Chem. Scand.*, **11**, 166 (1957).

(6) C. K. Jørgensen, *ibid.*, **10**, 500 (1956).

(7) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, Oxford, 1962, p 109.

Spectra of these Ir(III) complexes were obtained in dimethylformamide (DMF) and in ethyl alcohol solution. Solutions were prepared by dissolving the solid chelates [$Ir(bipy)_3(ClO_4)_3$ was prepared as previously described;[8] $Ir(phen)_3(ClO_4)_3$ was prepared in an analogous manner] and also by heating the stoichiometric amounts of the ligand and the metal ion (from iridium chloride) in refluxing ethyl alcohol for 96 hr or in refluxing DMF for 48 hr. Wavelengths of maximum absorption and emission of these Ir(III) chelates did not depend on the method of preparation or on the solvent. Relative luminescence quantum yields for the chelates (in DMF) were about an order of magnitude less than quinine fluorescence in 0.1 *N* H_2SO_4; the intensity of $[Ir(phen)_3]^{3+}$ was approximately twice the intensity of $[Ir(bipy)_3]^{3+}$.

Acknowledgment. The authors are grateful to the National Science Foundation for financial support (Grant GP-5449).

[8] B. Martin and G. M. Waind, *J. Chem. Soc.*, 4284 (1958).

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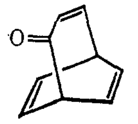
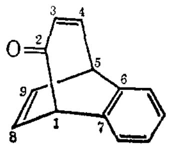
Reaction of Tropone with Benzyne. Formation and Photoisomerization of 6,7-Benzobicyclo[3.2.2]nona-3,6,8-trien-2-one

Sir:

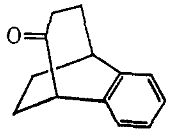
As a vinylog of norbornadiene the bicyclo[3.2.2]nona-2,6,8-triene system and its unknown keto derivative I ("homobarrelenone") have elicited recent synthetic interest.[1] We wish to report the practical one-step synthesis of 6,7-benzobicyclo[3.2.2]nona-3,6,8-trien-2-one (II) by thermal addition of benzyne to tropone, and describe herewith a photochemical rearrangement of this adduct.



I



II



III

The thermal decomposition of a suspension of ~40 mmoles of *o*-benzenediazoniumcarboxylate[2] in a solution of 38 mmoles of tropone[5] in anhydrous tetrahydrofuran at 36–37° under nitrogen for 17 hr produced after solvent removal a dark oil. Chromatography over magnesium silicate (benzene–ether) afforded a colorless crystalline adduct in 40% yield,[6,7] purified by sublimation under reduced pressure (50–60°, 0.10 mm) or recrystallization from hexane, mp 83–84°. Structure II is assigned on the basis of the following data: mass spectral data: *m/e* 182, 181, 154, 153, 152, 128; $\nu_{max}^{CCl_4}$ (cm^{-1}) 3070 (m), 3040 (m), 2970 (m), 1675 (s), 1630 (m), 1480 (m), 1455 (w), 1375 (m), 1320 (w), 1280 (w); $\lambda_{max}^{C_2H_5OH}$ (mμ) 225 (ϵ 5720), 263 (704), 351 (137); $\lambda_{max}^{C_6H_{12}}$ 210 (18,700), 225 (sh) (5620), 263 (743), 331 (sh) (69), 344 (113), 357 (151), 373 (136), 388 (sh) (64); nmr data ($CDCl_3$), see Table I.[8] *Anal.* Calcd for $C_{13}H_{10}O$: C, 85.70; H, 5.53; mol wt, 182. Found: C, 85.69; H, 5.41; mol wt, 188 (osmometric in $CHCl_3$).

Table I. Nuclear Magnetic Resonance Data

Positional assignment[a]	Chemical shift, ppm from TMS	Coupling constants,[b] cps
5 (broad triplet)	4.19	$J_{5,4} = 8.4$ $J_{5,9} = 6.2$ $J_{5,8} = 1.5$ $J_{5,3} = 0.7$
1 (doublet of triplets)	4.59	$J_{1,8} = 6.5$ $J_{1,3} = 2.0$ $J_{1,9} = 1.5$
3 (doublet of quartets)	5.17	$J_{3,4} = 11.0$ $J_{3,1} = 2.0$ $J_{3,5} = 0.7$
8 (septet)	6.49	$J_{8,9} = 8.0$ $J_{8,1} = 6.5$ $J_{8,5} = 1.5$
9 (septet)	6.84	$J_{9,8} = 8.0$ $J_{9,5} = 6.2$ $J_{9,1} = 1.5$
4 (doublet of doublets)	7.15	$J_{4,3} = 11.0$ $J_{4,5} = 8.4$
Aromatics (4 H) (complex pattern)	~7.13	

[a] The positional assignments for hydrogens 8 and 9 were verified by spin decoupling measurements with hydrogens 1 and 5, respectively. [b] The reported *J* values determined from 100-cps sweep-width spectra are accurate to ±0.1 cps.

Chemical evidence for structure II was provided by its rapid uptake of 2 molar equiv of hydrogen in ethanol with palladium on carbon as catalyst to afford the tetrahydro derivative III as a colorless oil:[9] mass spectral data: *m/e* 186, 142, 130, 129, 128; $\nu_{max}^{CCl_4}$ (cm^{-1}) 3070 (w), 3025 (w), 2930 (s), 2870 (m), 1710 (s), 1490 (m), 1465 (m), 1430 (w); $\lambda_{max}^{C_2H_5OH}$ (mμ) 264 (ϵ 465), 271 (443), 292 (308); $\lambda_{max}^{C_6H_{12}}$ 259 (sh) (378), 264 (454), 272 (425), 282 (174), 292 (192), 301 (198), 311 (160), 322 (75); nmr (CCl_4) (ppm): 1.94 (6 H, multiplet), 2.14 (2 H, multiplet, $-CH_2C(=O)-$), 3.23 (1 H, broad multiplet, position 5), 3.47 (1 H, multiplet, position 1), 7.13 (4 H, singlet, aromatics). *Anal.* Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.57. Found: C, 84.06; H, 7.58.

The 1,4 addition of benzyne to tropone is consistent with the reported reaction of maleic anhydride and N-phenylmaleimide with tropone.[10] On the other hand, reaction of dimethyl acetylenedicarboxylate reportedly proceeds through the bicyclo[4.1.0]heptadienone valence tautomer.[11]

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[1] M. J. Goldstein and A. H. Gevirtz, *Tetrahedron Letters*, 4413 (1965).

[2] The benzyne intermediate was generated *in situ* according to the Friedman[3] modification of the Stiles[4] procedure.

[3] L. Friedman, private communication.

[4] M. Stiles, R. G. Miller, and U. Burckhardt, *J. Am. Chem. Soc.*, **85**, 1792 (1963).

[5] P. Radlick, *J. Org. Chem.*, **29**, 960 (1964).

[6] A second uncharacterized product, isolated from the hexane–benzene eluates, was shown to be a 2:1 benzyne–tropone adduct by mass spectrometry (*m/e* 258).[7]

[7] The chromatographic medium used was Florisil synthetic adsorbent, a product of the Floridin Co.

[8] The nmr spectra were recorded with a Varian A-60-A spectrometer equipped with a Model V-6058A spin decoupler. Mass spectral data were recorded on a Hitachi RMU-6D spectrometer. The infrared and ultraviolet data were taken on a Perkin-Elmer Model 337 grating spectrophotometer and a Cary Model 14 spectrophotometer, respectively. The A-60-A and RMU-6D spectrometers were purchased through a National Science Foundation major equipment grant to Brown University.

[9] Purified by short-path distillation at 130° (1.1 mm).

[10] J. Meinwald, S. L. Emerman, N. C. Yang, and G. Buchi, *J. Am. Chem. Soc.*, **77**, 4401 (1955).

[11] H. J. Dauben and T. J. Pratt, Abstracts of Papers, 153rd National Meeting of the American Chemical Society, Miami, Fla., April 10–14, 1967.