and the rhenium was recovered (95%) with its oxidation state unchanged in the new carbonyl chloride $(Et_4N)_2[Re_2(CO)_6Cl_4]$.[9]

$$[Re_2(CO_6)_3H_3]^- + 4HCl \longrightarrow 3H_2 + [Re_2(CO)_6Cl_4]^{2-} + H^+$$

The same carbonyl chloride complex may be obtained from the reaction of the carbonyl alkoxides with alcoholic HCl.

The ir spectrum in the CO stretching region of the orange hydride in acetonitrile solution is virtually identical with the carbonyl alkoxide spectra: there are just two bands, both strong, with frequencies of 1995 and 1905 cm^{-1}. We therefore assign both of these bands as terminal ν(CO). Since there are no other ir bands in the 1700–2200-cm^{-1} region, where terminal ν(Re–H) absorptions are expected,[4] the ir spectra support the indication of the nmr spectrum that the three hydridic protons bridge the two rhenium atoms. The six CO groups are all terminal giving a structure analogous to the alkoxides for which two ir-active ν(CO)'s are expected. $[Re_2(CO)_6H_3]^-$, as we have formulated it, is electron deficient; *i.e.*, more bonding orbitals are available than electrons to fill them. The hydrogen bridges may be regarded as bent two-electron, three-center bonds. The M–H–M bridges in $[(C_5H_5)_2Mo_2H\{P(CH_3)_2\}(CO)_4]$,[14] $[HFe_3(CO)_{11}]^-$,[15] and $[HMn_3(CO)_{10}(BH_3)_2]$[16] have been described previously as bent two-electron, three-center bonds.

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[14] R. J. Doedens and L. F. Dahl, *J. Am. Chem. Soc.*, **87**, 2576 (1965).

[15] L. F. Dahl and J. F. Blount, *Inorg. Chem.*, **4**, 1373 (1965).

[16] H. D. Kaesz, W. Fellmann, G. R. Wilkes, and L. F. Dahl, *J. Am. Chem. Soc.*, **87**, 2753 (1965).

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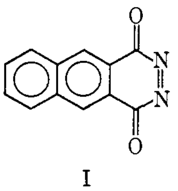
Received July 5, 1968

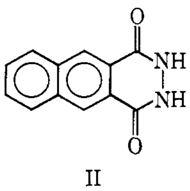
A Chemiluminescent Diazaquinone

Sir:

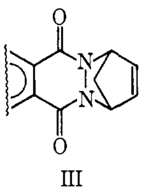
We have synthesized a relatively stable diazaquinone[1] (benzo[*g*]phthalazine-1,4-dione, I) which undergoes a chemiluminescent reaction relevant to the mechanism of the well-known chemiluminescence of cyclic aromatic hydrazides[2] such as 2,3-dihydrobenzo[*g*]phthalazine-1,4-dione (II)[3] and luminol (VII).



I



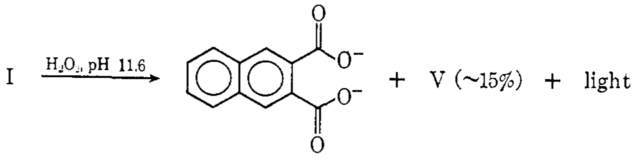
II



III

Addition of 0.5 equiv of chlorine to the monosodium salt of II suspended in 1,2-dimethoxyethane (glyme) at −50° yielded[4] a mixture from which maroon crystals of I were isolated after filtering and cooling at −80°: infrared (glyme) 1715 cm^{-1} (C=O);[1a] ultraviolet (glyme) 423 nm (log ϵ 3.5), 296 (4.0), 242 (4.8). *Anal.* Calcd for $C_{12}H_6N_2O_2$: C, 68.57; H, 2.88; N, 13.33. Found: C, 68.41; H, 2.92; N, 13.10. Structure I was corroborated by rapid formation of Diels–Alder adducts with butadiene or cyclopentadiene (*e.g.*, III).[1a] Unlike phthalazine-1,4-dione, which is a very unstable compound,[1a] crystalline I is stable for months at −20° and it persists for hours at room temperature in a dilute glyme solution.

Diazaquinone I reacts with alkaline hydrogen peroxide to give a bright violet chemiluminescence (eq 1). Chemiluminescence does not occur unless base and hydrogen peroxide are simultaneously present. The minor product V is apparently either hydrazide II or a labile dimer[1a] of II; addition of hemin to the reaction mixture converts V to IV with additional chemiluminescence.



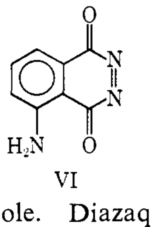
IV (~85%) (1)

In contrast, the reaction of hydrazide II with alkaline peroxide does not yield appreciable chemiluminescence unless hemin[5] or other peroxide-decomposing catalysts (or oxidizing agents) are added (eq 2).

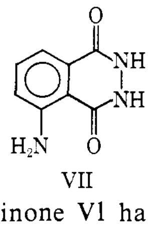
$$\text{II} \xrightarrow[\text{pH 11.6}]{H_2O_2,\ \text{hemin}} \text{IV } (>97\%) + \text{light} \qquad (2)$$

The chemiluminescence emission spectra[6] of I and II are identical, λ_{max} 358 nm, and they coincide with the fluorescence of 2,3-naphthalenedicarboxylate ion, IV, which is presumably the light-emitting species. The ratio of chemiluminescence quantum yields of I to II is difficult to measure because the reaction of I is too fast to allow effective mixing. By comparing the emission from slowly dissolving *suspensions* of I to the emission of *solutions* of II, however, we estimate the ratio to be 0.25; the additional light available from V increases this ratio to 0.37. Under ideal conditions this ratio would certainly be closer to unity.

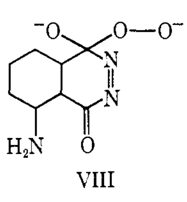
Diazaquinone VI has frequently been considered a critical intermediate in the chemiluminescence of luminol, but its lability has precluded a rigorous test of its role. Diazaquinone VI has been proposed to be: (1) the light emitter,[7] (2) a nonchemiluminescent by-product,[8] (3) the source of an intermediate diacyl



VI



VII



VIII

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[1] (a) T. J. Kealy, *J. Am. Chem. Soc.*, **84**, 966 (1962); (b) R. A. Clement, *J. Org. Chem.*, **25**, 1724 (1960); (c) E. Fahr and H. Lind, *Angew. Chem. Intern. Ed. Engl.*, **5**, 372 (1966).

[2] (a) E. H. White in "Light and Life," W. D. McElroy and B. Glass, Ed., Johns Hopkins Press, Baltimore, Md., 1961, p 183; (b) E. H. White, O. C. Zafiriou, H. M. Kägi, and J. H. M. Hill, *J. Am. Chem. Soc.*, **86**, 940 (1964); (c) E. H. White and M. M. Bursey, *ibid.*, **86**, 941 (1964); (d) F. McCapra, *Quart. Rev.* (London), **26**, 485 (1966).

[3] H. D. K. Drew and R. F. Garwood, *J. Chem. Soc.*, 836 (1939).

[4] The method of Kealy[1a] was unsatisfactory in this application.

[5] R. Gatt and M. L. Kremer, *Trans. Faraday Soc.*, **64**, 721 (1968).

[6] Emission spectra of I and II were measured by scanning spectrographic plates with a microdensitometer; spectra of II and IV were measured with an Aminco-Bowman spectrophotofluorimeter. At high concentrations, I also yields a green emission similar to the fluorescence of II (sodium salt).

[7] A. Bernanose, T. Bremer, and P. Goldfinger, *Bull. Soc. Chim. Belges*, **56**, 269 (1947); *Chem. Abstr.*, **42**, 4855 (1948).

[8] F. H. Stross and G. E. Branch, *J. Org. Chem.*, **3**, 385 (1938).

diradical generated by spontaneous loss of nitrogen,[9] (4) the source, *via* hydrolysis, of diimide which reacts with VI to yield excited VII,[10] and (5) a species which reacts with hydroperoxide ion, eventually yielding light.[2b,11]

Our experiments with pure I render proposals 1–4, as applied to hydrazide II, untenable. Path 1 is incompatible with the ultraviolet spectrum and nonfluorescence of I, (2) predicts that I is nonchemiluminescent, (3) requires that the diazaquinone lose nitrogen very rapidly, and (4) predicts that I should chemiluminesce in the absence of hydroperoxide ion.[10b] We infer that luminol and other hydrazides which react under similar conditions to yield the excited state of the corresponding dicarboxylate ion[2] also do not chemiluminesce by pathways 1–4.

Since I yields chemiluminescence and since its cyclopentadiene adduct III can be isolated[11] from the chemiluminescent reaction of II with hydrogen peroxide and hemin (or hypochlorite ion), and also from the persulfate oxidation[12,13] of II, compound I must be responsible for some of the light emission from the hydrazide II. It seems probable that diazaquinones are intermediates in the major light-producing pathway of other cyclic hydrazides as well.[14] Kinetic studies[12] of the persulfate oxidation of VII support this hypothesis.

Species corresponding to VIII may originate from the reaction of diazaquinones with hydroperoxide ion, or alternatively from reaction of diazasemiquinones (generated *via* one-electron processes) with hydroperoxy radicals. Closure of VIII to an *endo*-peroxide might then yield the immediate precursor of the excited dicarboxylate ion, although evidence concerning these points is lacking.

Acknowledgment. This investigation was supported by Public Health Service Research Grant No. NB 07868 of the National Institute of Neurological Diseases and Blindness.

[9] J. R. Totter, W. Stevenson, and G. E. Philbrook, *J. Phys. Chem.*, **68**, 752 (1964).

[10] (a) H. O. Albrecht, *Z. Physik. Chem.*, **A136**, 321 (1928); (b) H. Kautsky and K. H. Kaiser, *Z. Naturforsch.*, **5b**, 353 (1950); (c) W. S. Metcalf and T. J. Quickenden, *Nature*, **206**, 507 (1965).

[11] The trapping of an adduct from luminol has recently been claimed: Y. Omote, T. Miyake, and N. Sugiyama, *Bull. Chem. Soc. Jap.*, 40, 2446 (1967).

[12] M. M. Rauhut, A. M. Semsel, and B. G. Roberts, *J. Org. Chem.*, **31**, 2431 (1966).

[13] The initial oxidation of luminol by persulfate ion does not require hydrogen peroxide.[12]

[14] Our previous report[2b] that phthalazine-1,4-dione is essentially nonchemiluminescent is correct (phthalate ion is *non*fluorescent). The corresponding hydrazide does chemiluminesce weakly, however, but the reaction pathway is different from that found for the other hydrazides (work in progress).

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Received July 8, 1968

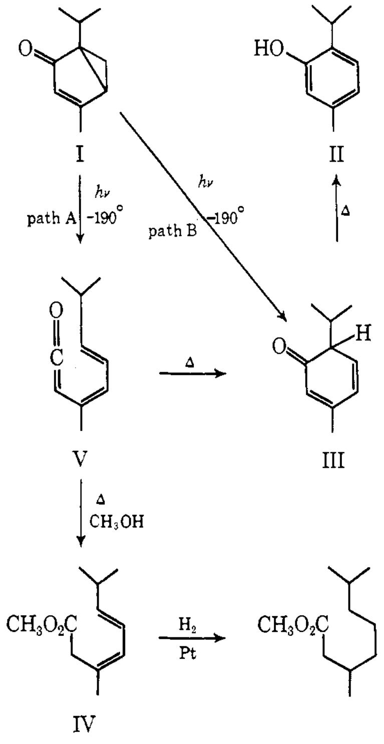
Low-Temperature Photochemistry of Umbellulone and Lumisantonin[1]

Sir:

Wheeler and Eastman reported in 1959 that irradiation of neat umbellulone (I) at room temperature gave quantitatively thymol (II).[2] We have studied the photochemistry of umbellulone (I) at −190°. Our results define two mechanistic paths leading from I to II under these conditions.

Irradiation (Pyrex filter) of neat umbellulone in a liquid nitrogen cooled infrared cell leads to formation of two primary photoproducts, a ketene derivative ($\nu_{C=O}$ 2113 cm^{-1}) and a product with absorption at 1670 and 1630 cm^{-1}. Thymol is not a primary photoproduct under these conditions. During warm-up, the product with absorption bands at 1670 and 1630 cm^{-1} goes rapidly to thymol at about −90° and the ketene goes to thymol[3] above −70°. The absorption bands at 1670 and 1630 cm^{-1} and the conversion to thymol permit tentative identification of this product as the dienone (III) (Scheme I).

Scheme I



Irradiation of umbellulone in methanol at room temperature gives only thymol, but the ketene derivative can be trapped by irradiating unbellulone in an ether–methanol (4:1) glass at −190°, then warming. The structure of the methyl ester (IV) thus obtained follows from its empirical formula, spectral properties,[4] and hydrogenation to methyl 3,7-dimethyloctanoate (identified by comparison with an authentic sample). The structure of the ketene then is V. The 3,4 double bond

[1] Photochemical Transformations. XXVII.

[2] J. W. Wheeler and R. H. Eastman, *J. Amer. Chem. Soc.*, **81**, 236 (1959).

[3] The glass is warmed until the 1670- and 1630-cm^{-1} bands have disappeared (∼−80°) and then cooled to −190°. During the warming, the disappearance of the 1670- and 1630-cm^{-1} bands and the appearance of thymol bands can be followed. The spectrum of the glass after the initial warm-up and recooling to −190° shows the absorption bands of thymol and shows no change in the intensity of the ketene band. A second warm-up is then carried out. The ketene band is monitored and ketene begins to disappear above −70°. The disappearance of the ketene absorption correlates with an increase in the intensity of the thymol absorption bands.

[4] Molecular weight 182 (mass spectrum); $\nu_{\max}^{\text{film}}$ 1739 cm^{-1}; 3 olefinic H (δ 4.9–6.3, m), OCH_3 (δ 3.63, s), CH_2 (δ 3.08, s), isopropyl methine H (δ 2.2–3.0, m), olefinic methyl H (δ 1.87), isopropyl methyl H (δ 1.0, d, J = 6.5 Hz).