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CHEMISTRY OF 3,4-BIS-BIPHENYLENE-1,2-DIOXETANE

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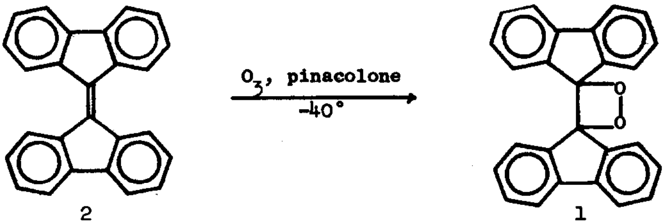
The thermal decomposition of 1,2-dioxetane may generate electronically excited carbonyl compounds.[1-6] The fluorescence of excited carbonyl compounds thus generated has been observed.[1,6] Wynberg recently reported that admantylideneadmantane peroxide exhibits a remarkable thermal stability (mp 162-3°) and its decomposition is chemiluminescent.[6] Chemiluminescent reactions usually involve the decomposition of a metastable energy rich intermediate.[7] The report by Wynberg implies that the thermal decomposition of a dioxetane at elevated temperatures may be a controllable unimolecular chemiluminescent reaction. In view of the low fluorescence efficiency of aliphatic carbonyl compounds ($\O_f = 1.0\text{-}4.4\times10^{-3}$),[8] the thermal decomposition of aliphatic 1,2-dioxetanes is not expected to be an efficient chemiluminescent process. Fluorenone fluoresces with an appreciable quantum efficiency even at room temperature ($\O_f = 0.043$ in DMF at 300°K,[9] $\O_f = 0.12$ in ethanol at 77°K[10]), and the decomposition of 3,4-bis-biphenylene-1,2-dioxetane (1) may be a more efficient chemiluminescent process than the decomposition of aliphatic dioxetanes. Although the compound has been suggested as an intermediate in the photooxygenation of bis-fluorenylidene (2), it has not been isolated and characterized.[11] In this communication we wish to report the synthesis and chemistry of this compound.



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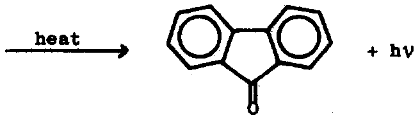

Compound 1 was synthesized from 2 by the elegant method developed by Story and coworkers.[12] A solution of 2 (984 mg) in pinacolone (50 ml) was treated with ozone at -40 to -45° until no more ozone was absorbed. The solvent was removed at 0.1 torr below 0°. The product (308 mg) separated as a white solid when the yellow viscous residue was treated with cold trichlorofluoromethane, mp 135° (dec), and it was recrystallized by dissolving in methanol and cooling the solution to -40°. Pure 1 was isolated as off-white prisms (210 mg), mp 150° (dec); ir (KBr) 1031, 1017 and 1010 cm^{-1}; uv max (ethanol) 305 (ϵ 5100) and 291 nm (ϵ 7800); nmr (CD_2Cl_2) δ 6.48-7.80 ppm (m, ArH); anal. (found) C, 86.79 and H, 4.50. The product is not appreciably contaminated with fluorenone as indicated by the lack of absorbance beyond 360 nm [fluorenone, λ_{max}(MeOH-EtOH) 380 nm (ϵ 250)[10]].

When a solution of 1 in benzene was refluxed for 4 hr, it was converted to fluorenone which was identified by its mp, ir spectrum, tlc (one spot), and 2,4-DNP derivative. A bluish-green luminescence was observed during the reflux of the benzene solution, and it was more intense in refluxing chlorobenzene (130°). The chemiluminescence observed was qualitatively similar to the fluorescence of fluorenone. The emission may be intensified by the addition of 9,10-diphenylethynylanthracene (DPEA). An intense yellowish-green emission remained observable for approximately 25 min from a reluxing solution of 1 and DPEA (5 mg each) in chlorobenzene (10 ml). The luminescence efficiency of these systems and the photoluminescence of 1 are being investigated.

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