ization coefficient[4] (~2 × 10^{-3}) and the magnitude of the heat of vaporization[3,4] (30 kcal mol^{-1}, compared with ~50–60 kcal mol^{-1} for the S–N bond strength) both suggest that the vapor species does not have the open-chain structure of the solid polymer but involves an exothermic rearrangement such as ring formation.[4] A comprehensive molecular orbital treatment[11] of the $(SN)_4$ tetramer has described several possible cyclic isomers. Some of these, such as the "chair" form, should have a dipole moment but again might be rendered nonpolar by low frequency vibrations or pseudorotation. There are also two cyclic isomers that lack a dipole moment (and are distinct from S_4N_4); both of these are predicted to have a triplet ground state. Future experiments can test the role of vibrations by cooling the vapor in a supersonic expansion and can look for triplet character by use of magnetic deflection analysis.

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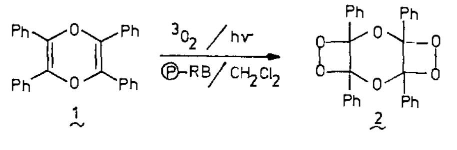
A Stable Bisdioxetane[1]

Sir:

Singlet oxygenation of tetraphenyl-*p*-dioxin (**1**) affords the bisdioxetane **2** (eq 1). This unusual "high energy" substance (a) represents the first authentic and stable bisdioxetane that has been prepared, isolated, and characterized; (b) is unusually stable, melting with decomposition at 103–104 °C, $t_{1/2}$ = 36 min at 80 °C, and E_a = 26 ± 1 kcal/mol; (c) affords quantitatively benzoic anhydride on thermal decomposition; (d) produces triplet excited benzoic anhydride in 22 ± 1%, as determined by the triplet-selective benzonorbornadiene titrimetric method;[2] and (e) results in a triplet–singlet excited states ratio $\phi^T/\phi^S \sim 2000$, using the DPA/DBA method.[3] To the best of our knowledge, this novel hyperenergetic molecule is the most efficient chemical source[4] for triplet excited anhydrides.

(eq 1)



Irradiation of a 0.1 M CH_2Cl_2 (freshly distilled from EDTA disodium salt) solution of *p*-dioxin **1**, prepared by *p*-toluenesulfonic acid catalyzed cyclization of benzoin,[5] with a General Electric 150-W sodium street lamp at −78 °C for 2 h in the presence of polymer-bound Rose Bengal[6] under a continuous stream of dry oxygen gas, afforded the crude bisdioxetane **2** quantitatively after rotoevaporation (0 °C at 10 Torr) of the CH_2Cl_2, positive peroxide test (KI/HOAc). Low temperature (−50 °C) silica gel chromatography, eluting with CH_2Cl_2, afforded analytically pure bisdioxetane **2** (Atlantic Analytical Laboratories, Atlanta, Ga.), mp 103–104 °C (decomposition with light emission), in 70% yield. The structural assignment is based on the following spectral data: ^1H NMR ($CDCl_3$, Me_4Si) δ 7.05 (12 H, meta and para aromatic protons, m), 7.40 ppm (8 H, ortho aromatic protons, m);[7] IR ($CHCl_3$) 3020, 1600, 1470, 1450, 1380, 1175, 910, 690, 640 cm^{-1}. Furthermore, on thermolysis at 80 °C in C_6H_6 benzoic anhydride is formed quantitatively with light emission, as confirmed by comparison of ^1H NMR and IR spectra and TLC (silica gel, CH_2Cl_2 eluant) retention times with those of the authentic material. The above data clearly establish the bisdioxetane structure; however, the stereochemistry of the phenyl substituents, i.e. all syn or syn-anti, is unknown.

On thermal decomposition of 0.0001 M C_6H_6 (freshly distilled from EDTA disodium salt) solutions of **2**, direct chemiluminescence can be visibly observed in a dark room. The direct chemiluminescence emission intensity, monitored on a Mitchell-Hastings photometer,[8] decays via first-order kinetics, affording a rate constant $k_1 = (3.83 \pm 0.10) \times 10^{-4}\ s^{-1}$ at 80 °C ($t_{1/2}$ = 36 min) and an activation energy $E_a = 26 \pm 1$ kcal/mol. Thus, the stability of this novel bisdioxetane is comparable with that of the monodioxetanes such as tetramethyl-1,2-dioxetane.[9]

The direct chemiluminescence efficiency was calculated[9] to be $\phi^{DC} = 7.70 \times 10^{-7}$ einstein/mol from the total initial intensity $I_0 = 4.16 \times 10^{-14}$ einstein/L s, initial bisdioxetane concentration $[\mathbf{2}]_0 = 1.41 \times 10^{-4}$ M, and the first-order rate constant $k_1 = 3.83 \times 10^{-4}\ s^{-1}$ at 80 °C in C_6H_6. Unfortunately, no photophysical data appears to be published on the fluorescence or phosphorescence of benzoic anhydride to permit estimating the excitation yield from the above ϕ^{DC} data.

For this reason we decided to determine the triplet yield of benzoic anhydride by means of the recently established[2] triplet-selective titrimetric method, in which benzonorbornadiene (**3a**) is converted into its tricyclic isomer **3b** (eq 2) under triplet sensitization. After heating solutions of **2** ([**2**] = 0.0273 M) and **3** ([**3a**] = 0.211–0.529 M) in C_6H_6 at 80 °C in sealed tubes for 4 h to assure complete decomposition of the bisdioxetane **2**, the ratios of [**3b**] to [**3a**] as a function of [**3a**] were determined by GLC.[10] A double reciprocal plot of the chemical yield of **3b** vs. [**3a**] afforded an intercept value of 9.0 ± 0.3 on triplicate analysis. Using the literature value[11] of 0.50 for the photoisomerization yield of **3b** from **3a**, the triplet benzoic anhydride yield from **2** was determined to be 22 ± 1%.

(eq 2)

We then proceeded to determine the triplet/singlet ratio, i.e., ϕ^T/ϕ^S, employing the well-established DPA vs. DBA enhanced chemiluminescence technique.[3] Using C_6H_6 solutions which contained [**2**] = 1.45 × 10^{-5} M and [DPA] = [DBA] = (1.0–10.0) × 10^{-3} M, the enhanced chemiluminescence yields (ϕ^{EC}) for DPA and DBA were separately de-

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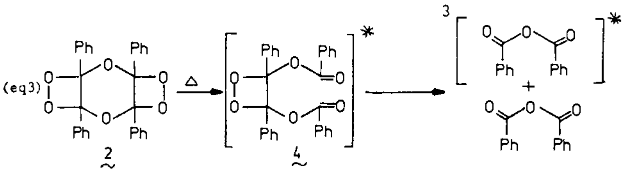
termined at 80 °C on the Mitchell-Hastings photometer, as described previously.[12] The respective ϕ^{EC} values at infinite concentration of the fluorescer, extrapolated from double reciprocal plots, were 3.48×10^{-5} einstein/mol for DPA and 1.70×10^{-3} einstein/mol for DBA. Using the fluorescence yields of DPA as 100% and DBA as 10% and a triplet-singlet energy-transfer efficiency $\phi^{ET} \sim 25\%$,[13] we estimated the triplet/singlet ratio as $\phi^T/\phi^S \sim 2000$. Thus, like the monodioxetanes,[9] the bisdioxetane **2** is also inefficient in chemienergizing a singlet excited product. In this context it is important to point out that no CIEEL[14] involvement could be observed for the bisdioxetane **2** with rubrene.

Our present results illustrate that stable bisdioxetanes can be prepared without difficulty. Their thermal behavior is quite analogous to that of the monodioxetanes,[9] affording high yields of triplet excitation. In the particular case of the bisdioxetane **2**, triplet-excited anhydride can be generated chemically. Although the details of the mechanism of chemienergization of triplet-excited anhydride product are obscure at this time, the thermal activation of 26 kcal/mol is just enough to dissociate one of the dioxetane rings in the bisdioxetane **2**. Presumably, first a triplet-excited intermediary monodioxetane **4** is formed (eq 3). The lifetime of triplet-excited **4** is expected to be short, probably of the order of a vibrational period, and the triplet excitation is utilized internally to dissociate the second dioxetane ring in **4** to afford triplet-excited benzoic anhydride. We are in the process of preparing the dioxetane **4** to test these mechanistic speculations.



Recently chemienergized benzoic anhydride has been claimed[4] in the low-temperature ozonolysis of diphenylacetylene, but our bisdioxetane **2** presents a more convenient and efficient chemical source for triplet-excited anhydrides. We are actively pursuing the utility of bisdioxetanes in our chemienergization work.

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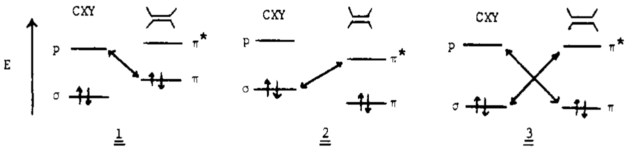
Unification of the Carbenic Selectivity Spectrum. The Ambiphilicity of Methoxychlorocarbene

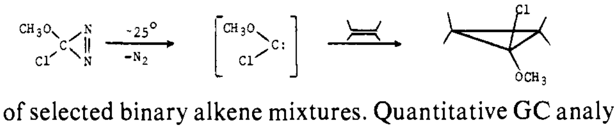
Sir:

In frontier molecular orbital (FMO) terms, the addition of a singlet carbene to an alkene involves simultaneous interactions of the vacant carbenic p orbital (LUMO) with the filled alkene π orbital (HOMO), and of the filled carbenic σ orbital (HOMO) with the vacant alkene π^* orbital (LUMO).[1] This formulation easily accommodates both the familiar "electrophilic" carbenes (CCl_2, CF_2)[2] and the less common "nucleophilic" carbenes (e.g., $(CH_3O)_2C$),[3] while simultaneously suggesting the existence of ambiphilic[4] carbenes.

For example, the FMO situations for CCl_2 and CF_2 in additions to common alkenes are such that the most proximate, dominant orbital interaction is LUMO carbene/HOMO alkene[5,6] (**1**) leading to electrophilic addition. Here, net electron density is transferred from alkene to carbene in the transition state;[7] addition is facilitated by increasing the number of alkyl groups on the alkene's sp^2 carbons. Alternatively, when the HOMO-carbene/LUMO-alkene interaction is dominant (**2**) nucleophilic carbenic additions are observed,[3] in which net electron density is transferred from carbene to alkene in the transition state;[7] addition is facilitated by placing electron-attracting groups on the alkenic carbons.[3,6] Finally, if the HOMO's and LUMO's of a carbene and a simple alkene (e.g., propene) are such as to lead to comparable energy gaps for both sets of orbital interactions (**3**), then ambiphilic carbene reactivity should be demonstrable; substitution of strongly electron-donating or -withdrawing substituents on the alkene should convert situation **3** into **1** or **2**, respectively. The FMO formulation thus naturally suggests a *continuum* of carbenic behavior ranging from electrophilicity, through ambiphilicity, to nucleophilicity.



In this communication, we present the first unequivocal, experimental demonstration of an ambiphilic carbene,[4] thereby unifying the spectrum of carbenic reactivities. Methoxychlorocarbene[8] was generated by the ambient temperature thermolysis of methoxychlorodiazirine[9] (eq 1), in large excesses of selected binary alkene mixtures. Quantitative GC analysis (calibrated tc detector) of the known[8] product cyclopropanes, coupled with standard competition reaction analysis,[2] gave the primary relative reactivites summarized in Table I. These data are normalized to a *trans*-butene standard in Table II. Satisfactory cross-check experiments[2] linked the relative reactivites of the triads $Me_2C{=}CMe_2$, $Me_2C{=}CH_2$, and *t*-Me-



(1)