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Supplementary Material Available: IR, ^1H NMR, MS, and microanalytical data on **3a**, **3b**, and **4** (2 pages). Ordering formation is given on any current masthead page.

Adiabatic Photochemistry of *o*,*o*'-Dibenzenes

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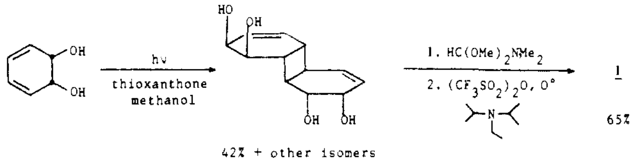
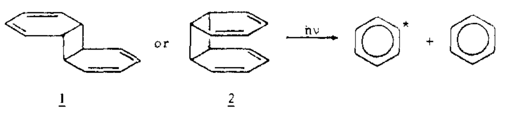
The 4n-subset of benzene dimers is a group of energy-rich compounds which are expected to exhibit interesting physical and chemical properties.[1-6] Among the *o*,*o*'-dimers the anti isomer **1** has been known for some time,[1-4] while the syn isomer **2** has been synthesized recently in our laboratory.[6] Although the preliminary studies on the properties of **1** have been reported by several groups,[1-4] detailed studies of its properties have been hindered by its limited supply. In this communication, we wish to report a new efficient synthesis of **1**, a more detailed study of its thermal and photochemical decomposition, and a comparison of the results from the two isomeric *o*,*o*'-dibenzenes. We have found that the photochemical decomposition of **1** and **2** is adiabatic, yielding excited benzene efficiently. Since the photolyses of **1** and **2** may be induced with light longer than 300 nm where benzene exhibits no detectable absorption, the result demonstrates that the high-energy content of **1** and **2** may be utilized to excite the reaction product, benzene, with light of lower energy than that normally needed for the direct irradiation.

Since **1** undergoes fairly rapid thermolysis at 40°,[1] the key step in our new synthesis is based on the efficient deoxygenation of 1,2-diols under mild conditions, a procedure developed in our laboratory.[7] The photosensitized dimerization[8] of the *cis*-3,5-cyclohexadienediol (Aldrich 30,152-3, **3**) yielded a mixture of dimers from which the desired tetraol **4** was isolated by recrystallization (42%). Tetraol **4** was then deoxygenated to **1** (65%) in 0.5-g lot.



(1)

Although it has been reported that both thermolysis and photolysis of **1** yield benzene as the product,[1] the kinetic parameters of thermolysis, other than an estimated value of $\Delta H^{\ddagger}$, have not been evaluated, and the nature of the electronic state of benzene formed in the photolysis is not known. Since there is a significant difference between the thermolytic behaviors of **1** and **2**, the kinetic parameters of thermolysis of **1** were analyzed in two different solvents, cyclohexane and acetone. Furthermore, in the conversion of photoexcited **1** or **2** to an excited benzene and a ground-state benzene (reaction 2), the orbital symmetry is conserved in this energetically favorable process.[9] Therefore, the photolyses of **1** and **2** to benzene are likely to be adiabatic ones following the current concept of adiabatic photochemical reactions.[9] The results are tabulated in Table I.



(2)

Table I

	anti-*o*,*o*'-dibenzene	*syn*-*o*,*o*'-dibenzene[a]
	Thermal Decomposition (in Cyclohexane)	
$\Delta H^{\ddagger}$	24.9 ± 1.4 kcal·mol^{-1} (23.6 ± 0.3 kcal·mol^{-1})[b]	22.5 ± 1.3 kcal·mol^{-1}
$\Delta S^{\ddagger}$	0.1 ± 2.4 eu (−3.4 ± 1.0 eu)[b]	−14.0 ± 2.2 eu
$\Delta G^{\ddagger}$ (298 K)	24.8 ± 1.7 kcal·mol^{-1} (24.6 ± 1.4 kcal·mol^{-1})[b]	26.7 ± 2.0 kcal·mol^{-1}
	Photochemical Decomposition[c]	
Φ-[compd]	1.04 ± 0.09[d]	1.01 ± 0.14[d]
$\Phi C_6H_6^*$	0.32 ± 0.03[e]	0.41 ± 0.03[f]

[a] The values of activation parameters are from ref 6. [b] The values are from acetone solution. [c] Concentration of dibenzenes, 1.5–2.0 × 10^{-5} M in cyclohexane, $\lambda_{\text{excitation}}$, 300 nm. [d] The average of six separate determinations. [e] The average of three separate determinations. [f] The average of two separate determinations.

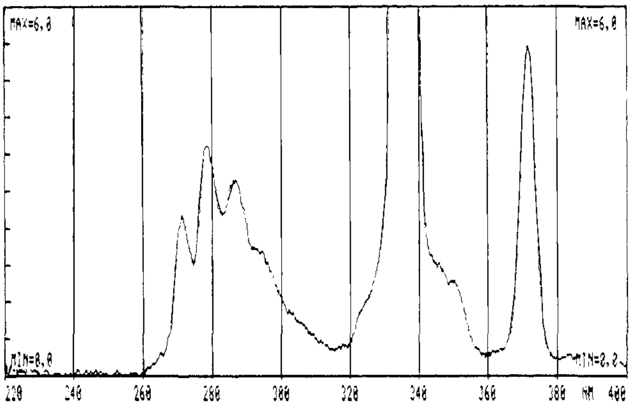


Figure 1. Formation of excited benzene as monitored by its fluorescence from the photolysis of **1**, $\lambda_{\text{excitation}}$ 335 nm, the peak at 374 nm is the Raman band of cyclohexane solvent.

We have found that the thermolysis of **1** proceeds with little or no activation entropy. This is not surprising for such a highly exoergic process, but it is very different from that of **2** which proceeds with an appreciably negative activation entropy.[6] Therefore, this observation is in agreement with our suggestion that the thermolyses of **1** and **2** are likely to proceed via very different reaction pathways.[6]

The efficiency of photolysis of **1** and **2** is determined with the aid of the ferrioxalate actinometry[10] and the formation of excited benzene from **1** and **2** monitored with a Perkin-Elmer MPF-66 spectrofluorimeter. Interestingly, the photolyses of both **1** and **2** proceed with unit quantum efficiency and yield excited benzene

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in fairly high efficiencies (Table I). Excited benzene is formed even when **1** is excited at the red-edge of its absorption (335 nm) where benzene exhibits no detectable absorption (Figure 1). The fluorescence excitation spectra of **1** and **2** monitored at the red-edge of benzene emission are the same as their absorption spectra indicating that excited benzene is derived from the excited dimers. It is not certain at this moment whether the higher efficiency of excited benzene formation from **2** is related to its higher energy content or the higher symmetry in the cycloreversion process.

Since the energy content of excited benzene is 110 kcal/mol[11] while that of the exciting light at 335 nm is only 85.3 kcal/mol, the result clearly demonstrates that a part of the chemical energy liberated from the photochemical dissociation of **1** or **2** is available for the excitation of benzene during the adiabatic conversion. Adiabatic photochemical reactions generally occur with light more energetic than that needed for the excitation of the product.[9] Previous contributions by Turro and his co-workers demonstrated the "red light-to-blue light uphill conversions" in the generation of n,π^* excited states of acetone from the direct or sensitized photolysis of tetramethyldioxetane,[12] but such upconversions have a propensity to occur in the triplet manifold. Therefore, our finding on the photon up-conversion in the singlet manifold of such an efficiency is unprecedented.

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Tellurapyrylium Dyes as Photochemotherapeutic Agents. Surprising Tellurium Atom Effects for the Generation of and Rates of Reaction with Singlet Oxygen

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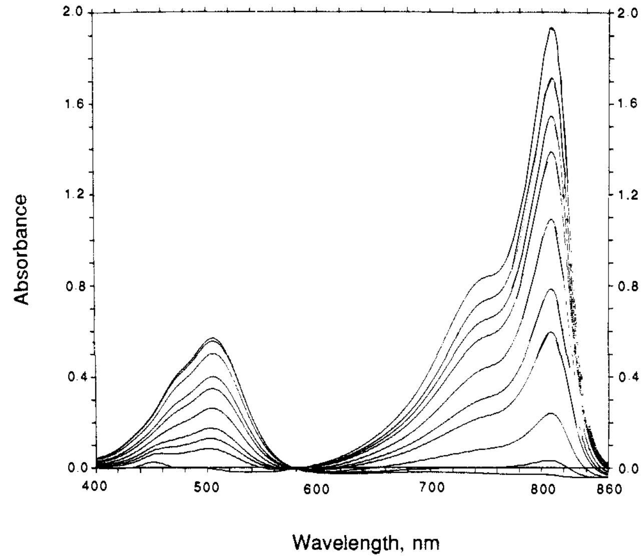
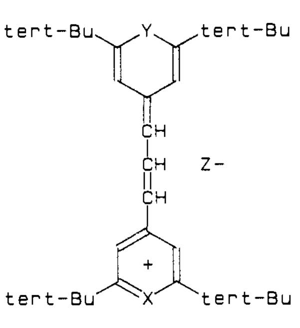
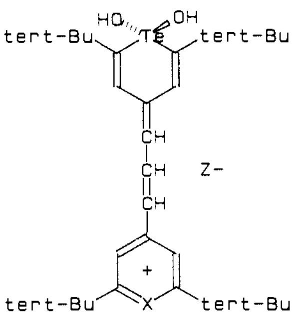


Figure 1. Isosbestic behavior for the conversion of **1** (5×10^{-5} M) to **6** in water. Total irradiation time was 3 min in a 1-cm square-quartz cell held 15 cm from a GE Sunlamp. Sampling was every 5 s for the first three points, every 20 s for the next three, and every 35 s for the final three.

Photochemotherapy (PCT) is a relatively new treatment of localized neoplasia which depends upon the light-activation of a tumor-specific photosensitizer.[1] At the present time, the limiting factor on the successful application of PCT has been the lack of a photosensitizer that absorbs light with a high degree of penetrance in tissue (wavelength range of 700-1200 nm for maximum penetration).[2] Near-infrared-absorbing tellurapyrylium dyes, including **1** and **2**, have been identified as potential photochemotherapeutic agents from in vitro studies.[3] Related non-tellurium-containing dyes do not show the phototoxic effect. We report our preliminary findings on the photochemistry of tellurapyrylium dyes **1-3** in air-saturated aqueous solution. Photoproducts derived from formal oxidative addition of hydrogen peroxide across one tellurium atom were isolated from photooxidation of **1** and **2**. From an analysis of the kinetics of photooxidation, the oxidizing species is not hydrogen peroxide but is singlet oxygen generated in a dye-sensitized process. The photooxidation products are not observed for **4** and **5**, non-tellurium-containing chalcogenapyrylium dyes.



1, X=Y=Te, Z=BF_4^-
2, X=Te, Y=Se, Z=ClO_4^-
3, X=Te, Y=O, Z=ClO_4^-
4, X=Se, Y=O, Z=ClO_4^-
5, X=Y=O, Z=ClO_4^-



6, X=Te, Z=BF_4^-
7, X=Se, Z=ClO_4^-

As shown in Figure 1, irradiation of an air-saturated, aqueous solution of **1** (5×10^{-5} M), with an unfiltered, tungsten bulb, gave rapid disappearance of the dye chromophore and clean formation of a new product, **6**, with an isosbestic point at 580 nm.[4] Similar behavior was observed upon irradiation of an aqueous solution of **2** (5×10^{-5} M, isosbestic point at 560 nm) to give a new product, **7**.[4] In carefully degassed aqueous solutions, no loss of chromo-

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