

Table I

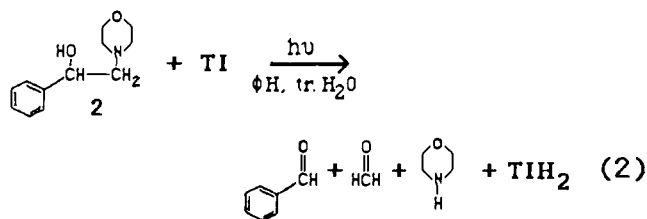
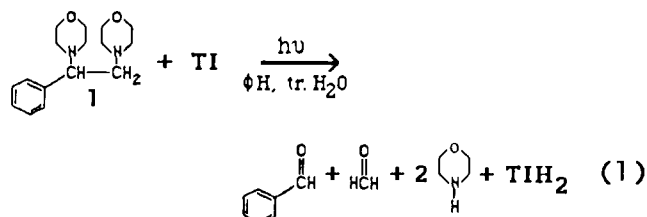
	rates of bleaching in benzene ^a				rates of thioindigo bleaching ^c		
	TI	L	DCA	TCA	benzene ^d	CH ₂ Cl ₂	CH ₃ CN
rel rates	0.56	0.66	6.09	33.08	0.22	0.44	3.49
1/2			14.65 ^b				
	ϕ_b^e		k_q^h		peak ⁱ potential		
	TI ^f	L ^g	TI	DCA			
1	2.7×10^{-3}	0.22	3.3×10^9	9.8×10^9	0.975 V		
2	1.2×10^{-2}	0.29	1.8×10^9	4.6×10^9	1.050 V		
1/2	0.23	0.73	1.86	2.15			

^aIrradiation of vacuum degassed solutions, UV-vis monitored, equal concentrations of **1** and **2**. ^bTrace H₂O. ^cUV-vis monitored, bleaching being the decrease in the 544 nm TI absorption as it is consumed during the photoreaction. TI concentration = 5×10^{-5} M. ^dConcentrations of **1** and **2** corrected for differential quenching. ^eQuantum yield of bleaching of UV-vis absorption. ^fConcentrations of **1** and **2** corrected for differential quenching. Secondary actinometer used: known reaction of TI/TEA. ^gEqual concentrations of **1** and **2**, ferrioxalate actinometry; room temperature. ^hQuenching constant, Ar degassed samples, acceptor concentration = 2×10^{-5} M. ⁱPeak potential measured against a Ag wire reference electrode which is corrected by using an internal standard of ferrocene, CH₃CN, electrolyte = 0.2 g/4 mL of TBA PF₆.

report here studies of the photooxidative fragmentation of 1,2-ditertiary amines, a reaction which is probably also quite general and which shows both similarities and yet remarkable contrasts to the aminoalcohol cleavage.

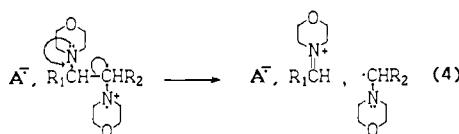
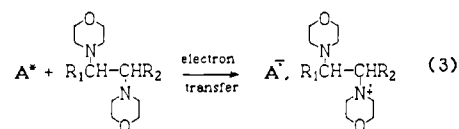
Diamine **1** was synthesized by palladium-promoted diamination of styrene with morpholine in tetrahydrofuran.^{18,19} The similarly substituted aminoalcohol **2** was prepared by reaction of morpholine with styrene epoxide.²⁰ The acceptors, thioindigo (TI), 9,10-dicyanoanthracene (DCA), 2,6,9,10-tetracyanoanthracene (TCA), and β -lapachone (L)²¹ were prepared and purified as reported elsewhere.^{16,22,23} Photolyses were performed with either a 200 or 450 W mercury lamp equipped with appropriate filters to selectively excite only the acceptor. Solutions (benzene, methylene chloride, or acetonitrile) containing the diamine or aminoalcohol and acceptor were vacuum degassed through several freeze-pump-thaw cycles; photoreactions were monitored either by changes in the UV-vis absorption spectra of the acceptors with use of a Hewlett-Packard 8451 diode array spectrophotometer or by product analysis with use of NMR spectroscopy (benzene-*d*₆) on a GE-NMR-QE-300 spectrometer.

Studies of the photolysis of benzene solutions of TI with **1** and **2** show that both donors undergo oxidative fragmentation according to eq 1 and 2, formally analogous to the reactions previously observed with a variety of aminoalcohols.^{11-13,16} Comparable reaction of **1** can be mediated by irradiating solutions containing a variety of light-absorbing acceptors such as DCA, TCA, and L in a number of different organic solvents. Thus when reaction is monitored by the appearance of benzaldehyde in the NMR (C₆D₆, with a trace of D₂O),²⁴ reaction is observed to proceed faster for **2** than **1**. Correspondingly, the bleaching of the TI absorption at 544 nm is found to proceed faster for **2** than **1** by a factor of 1.78:1 in benzene.²⁵ The peak oxidation potential

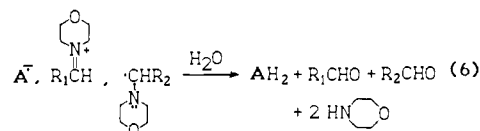
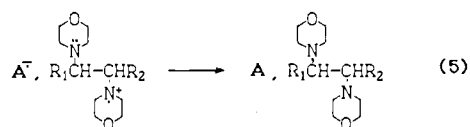


of **1** is slightly higher (Table I) than that of **2** which is reflected in higher fluorescence quenching constants (k_q) for TI and DCA by the diamine **1**; quantum yields corrected for differential quenching show that **2** is 4.4 times more reactive than **1** in the cleavage with TI/benzene.

A general mechanism for the oxidative photofragmentation of ditertiary amines, analogous to that proposed for amino alcohols, is given by eq 3-6. While a number of paths leading from the

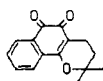


initial fragmentation products to the final products (eq 6) can be proposed, the major factor limiting the overall efficiency of reaction should be the competition between fragmentation (eq 4) and reverse electron transfer (eq 5). Cation radicals of both ami-



noalcohols and 1,2-diamines have been calculated and found to have very low bond energies for the C-C bond between the two heteroatom centers.^{26,27} In benzene, reaction should involve formation of anion radical and reaction from a tightly associated geminate ion pair; under these conditions the anion-mediated reaction should be facilitated and it is therefore not surprising that for a strongly basic anion radical (TI), reaction of **2** is faster than **1**. In contrast to the wide variation of reactivity of the aminoalcohol with solvent polarity and acceptor differences, reaction of diamine **1** shows relatively little change with either; this is reflected in pronounced changes in the relative efficiencies for reaction (1/2). The efficiency of the photoreaction of **1** with TI (toluene) exhibits a strong increase with temperature; if it is assumed that the only temperature-dependent step is the fragmentation (eq 4), the

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 (24) The fragmentation reaction (eq 3, 4, and 6) appears to be the only observed pathway from the relatively clean NMR spectrum.
 (25) Equal concentrations of **1** and **2** (3.2×10^{-4} M).

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Arrhenius plot²⁸ gives an activation energy of 3.9 kcal/mol for the cleavage.

The subtle mechanistic differences between electron-transfer photofragmentation of aminoalcohols and diamines are underlined by comparing the reactivity of **1** and **2** under various conditions. The independence of reactivity on acceptor anion radical basicity is manifested by a pronounced sensitivity of the relative reactivity to acceptor. Thus, **1** is far more reactive than **2** with cyanoaromatics whose anion radicals are relatively poor bases (Table I) and correspondingly less reactive than **2** with quinones such as TI or L where the oxygen-localized radical anion should be quite basic. The relative reactivity **1/2** with the same acceptor (TI, Table I) also shows a strong increase with solvent polarity resulting in an order reversal in the case of CH₃CN. The increase in reactivity reflects a nearly constant reaction efficiency of **1/TI** for the three solvents, contrasted to a sharp decrease in reactivity for **2/TI** as solvent polarity increases; due to the requirements for direct involvement of the anion radical in the fragmentation of the aminoalcohol.

We expect photooxidative fragmentation of 1,2-diamines to be a general process; the reactions of dissecondary, diprimary, or mixed amines should be particularly interesting. These compounds should have the possibility of both deprotonation-assisted and unassisted fragmentation reactions within the geminate radical ion pair. This should result in an increase of the relative reactivity of the diamine with acceptors with basic radical anions and in nonpolar media but still permit reactivity to persist when aminoalcohols are unreactive. In summary, these studies demonstrate that chemically clean oxidative photofragmentation of 1,2-diamines can occur by a mechanism similar to the cleavage of aminoalcohols but in a process which may be much more versatile.

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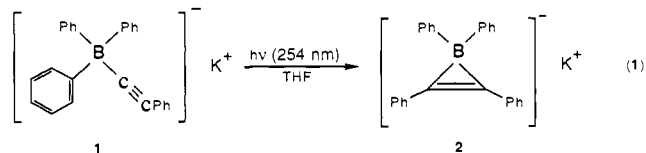
(28) Temperatures studied (-62, -42, -23, 0, +27, and +56 °C). Correlation coefficient for plot = 0.992.

1,1,2,3-Tetraphenylboratirene: First Isolation and Characterization of a Boratirene

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We report herein the preparation and characterization of the first example of a new class of highly strained boron-containing compounds. Irradiation (254 nm) of potassium triphenyl(phenylethynyl)borate (**1**) in THF solution gives 1,1,2,3-tetraphenylboratirene (**2**) as the predominant product, eq 1. Potassium tetraphenylboratirene is a stable, air- and water-sensitive, bright yellow crystalline solid.



Replacement of carbon by a tetravalent, anionic borate group forms a new family of compounds having the same bonding pattern and number of electrons as the hydrocarbon but differing in the number of nuclear protons. The effect of this atomic mutation on chemical and physical properties has been the object of long-standing and increasing theoretical¹ and experimental² in-

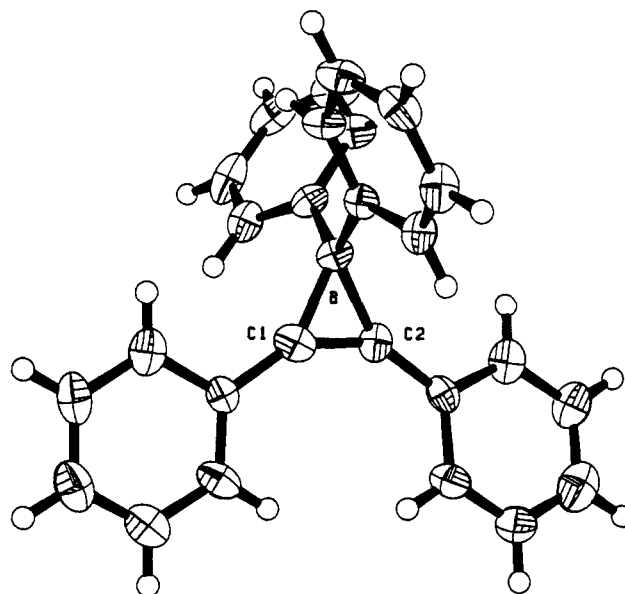


Figure 1. X-ray crystal structure for boratirene **2**. The potassium counter ion and a coordinated THF are not shown.

terest. For example, we recently reported that tetraphenylboratirane,³ a cyclopropane analogue, has an exceedingly low oxidation potential (-0.8 V, irreversible vs Ag/AgNO₃) when compared with the hydrocarbon. Similarly, we discovered that tetraphenylboratanorcaradiene⁴ is an intensely colored, red compound in contradistinction to its colorless hydrocarbon analogue. On the basis of ab initio molecular orbital calculations, these changes were attributed to an increase in occupied-orbital energies due to the net reduction of nuclear charge that occurs when borate replaces carbon. The synthesis and examination of the chemical and physical properties of boratirene **2** provide additional insight into this effect.

On the basis of our experience with the irradiation of [(Ph)₄B]⁻⁵ [(Ph)₃(PhPh)B]⁻⁴ and [(Ph)₃(PhCH=CH)B]⁻³ and Eisch's⁶ report that photolysis of [(Ph)₃(PhC≡C)B]⁻ followed by acid hydrolysis gives a 6:1 mixture of *cis*-stilbene and biphenyl, we supposed that irradiation of borate **1** would initiate a di- π -borate rearrangement⁷ and give boratirene **2**. Borate **1** is conveniently prepared from triphenylborane and lithium phenylacetylide. Its potassium salt is an air-stable, white crystalline solid that shows

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