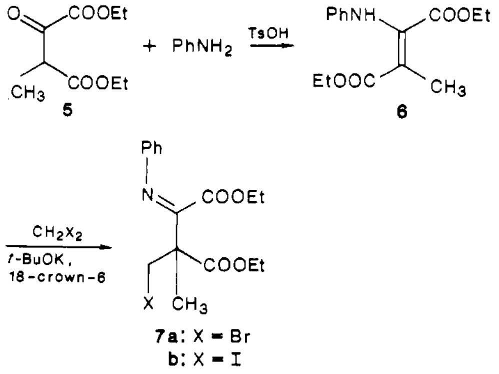
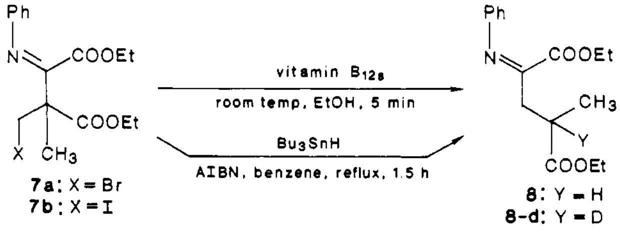
**Scheme I**



than a benzyl group,[10] we developed a synthesis of the phenyl substituted Schiff base.

Treatment of oxalylpropionate **5** with aniline in refluxing benzene for 48 h in the presence of *p*-toluenesulfonic acid yielded enamine **6**[11,12] (87%) (Scheme I). When **6** was treated with dibromomethane (or diiodomethane) in the presence of potassium *tert*-butoxide and 18-crown-6 in benzene at room temperature for 24 h, Schiff base **7a** (or **7b**) was produced (77% yield).[12] The imine double bond in **3** and in **7a** and **7b** was established to have the *Z* configuration by nuclear Overhauser experiments.

Methylaspartate Schiff base derivatives **7a** and **7b** rearrange to glutamate Schiff base **8** upon treatment with vitamin $B_{12s}$ in ethanol at room temperature in the dark for 5 min (56% yield)[12] or upon refluxing for 90 min in benzene with tri-*n*-butyltin hydride in the presence of AIBN. The position of the methyl group in rearrangement product **8** was established by direct comparison with an authentic sample of diethyl 4-methyl-2-ketoglutarate following hydrolysis of product **8**. The location of the methyl shows that the glycyl Schiff base fragment is the migrating group.[13] When the vitamin $B_{12s}$ rearrangement is conducted in EtOD, deuterium is incorporated at the position adjacent to the methyl group in product **8-d**.[12] Although this indicates that the reaction is terminated as a carbanion, it is quite possible that the rearrangement occurs by way of a radical intermediate and that is followed by electron transfer from coenzyme $B_{12}$ and then by protonation. The same product (**8-d**) is obtained when iodide **7b** is treated with tri-*n*-butyltin deuteride.



The rearrangement of **7a** and **7b** to **8** under the influence of vitamin $B_{12s}$ constitutes a new model for the glutamate–methylaspartate rearrangement.

Diphenylamine and hydroquinone were not effective inhibitors of the reactions of **7** with either vitamin $B_{12s}$ or tri-*n*-butyltin hydride. *m*-Dinitrobenzene, on the other hand, inhibited the tri-*n*-butyltin hydride rearrangement but had no effect on the vitamin $B_{12s}$ promoted rearrangement. This finding suggests that the mechanisms of the rearrangements carried out under the two sets of conditions may be different. Caution is required in reaching such a conclusion because one is not certain which step of the chain is intercepted by *m*-dinitrobenzene.[14]

In a comparison between the vitamin $B_{12s}$ dependent and the tri-*n*-butyltin hydride[9k] promoted methylmalonate rearrangement models, there is no contest; the $B_{12}$ model is more efficient (by an order of magnitude) in yielding rearrangement product, and the conditions for the $B_{12}$ reaction are far more suitable for a biological model reaction.[9g-j] In the present experiments the choice between the two sets of reaction conditions is more difficult, since both are quite efficient in terms of yield. Even so, the vitamin $B_{12}$ reaction may again be more biorelevant in terms of rate, mildness of reaction conditions, and compatibility of the hydroxylic medium.

**Acknowledgment.** This research was generously supported by the Institute for General Medical Sciences of the National Institutes of Health under grant GM 19906. We thank Professor Richard L. Schowen for his helpful comments.

---

[10] This line of argument would not be appropriate for a radical process since the corresponding carbonyl compound rearranges readily.[6b] See also: Dowd, P.; Choi, S.-C. *J. Am. Chem. Soc.* **1987**, *109*, 3493.

[11] The configuration about the double bond of **6** has been established to be *Z* by NOE experiments.

[12] All yields cited are those of isolated, pure products. All new substances showed satisfactory spectral data.

[13] See ref 9g regarding a similar experiment and conclusion.

[14] It has been suggested that the tri-*n*-butyltin radical is trapped either by electron transfer or by direct attachment to the nitro group of the dinitrobenzene. Cf. Tanner, D. D.; Blackburn, E. V.; Diaz, G. E. *J. Am. Chem. Soc.* **1981**, *103*, 1557. Ono, N.; Kamimura, A.; Kaji, A. *J. Org. Chem.* **1987**, *52*, 5111.

---

## Electron-Transfer Photofragmentation Reactions: Analogies and Divergences of the Reactivity of Ditertiary Amines As Compared with Aminoalcohols

Matthew A. Kellett and David G. Whitten*

*Department of Chemistry, University of Rochester*
*Rochester, New York, 14627*

*Received November 21, 1988*

The electron-transfer quenching of excited acceptors by amines and subsequent chemical reactions have been topics of extensive study.[1-10] Among the various reactions of the photogenerated radical ion pairs, fragmentation via C–C bond cleavage has been shown to be prominent and often a chemically clean path for aminoalcohols, aminoketones, and other systems;[11-15] recent experiments have shown that the dehydrofragmentation of aminoalcohols is strongly acceptor-dependent and consistent with a mechanism in which the acceptor anion radical acts as a base to promote cleavage of the donor cation radical in a reaction closely analogous to the two-electron "Grob" fragmentation.[16,17] We

---

[1] Davidson, R. S.; Lambeth, P. F.; Santhanam, M. *J. Chem. Soc., Perkin Trans. 2* **1972**, 2351.

[2] Bartholomew, R. F.; Brimage, D. R. G.; Davidson, R. S. *J. Chem. Soc. C* **1971**, 3482.

[3] Bartholomew, R. F.; Davidson, R. S. *J. Chem. Soc. C* **1971**, 2804.

[4] Pienta, N. J.; McKimmey, J. E. *J. Am. Chem. Soc.* **1982**, *104*, 5501.

[5] Davidson, R. S.; Santhanam, M. *J. Chem. Soc., Perkin Trans 2* **1972**, 2355.

[6] Garrera, H. A.; Gsponer, H. E.; Garcia, N. A.; Cosa, J. J. *J. Photochem.* **1986**, *33*, 257.

[7] Cohen, S. G.; Parola, A.; Parsons, G. H. *Chem. Rev.* **1973**, *73*, 141.

[8] Lewis, F. D. *Acc. Chem. Res.* **1986**, *19*, 401.

[9] Lewis, F. D.; Zebrowski, B. E.; Correa, P. E. *J. Am. Chem. Soc.* **1984**, *106*, 187.

[10] Beecroft, R. A.; Davidson, R. S.; Goodwin, D.; Pratt, J. E. *Pure Appl. Chem.* **1982**, *54*, 1605.

[11] Lee, L. Y. C.; Ci, X.; Gianotti, C.; Whitten, D. G. *J. Am. Chem. Soc.* **1986**, *108*, 175.

[12] Ci, X.; Lee, L. Y. C.; Whitten, D. G. *J. Am. Chem. Soc.* **1987**, *109*, 2536.

[13] Ci, X.; Whitten, D. G. *J. Am. Chem. Soc.* **1987**, *109*, 7215.

[14] Davidson, R. S.; Orton, S. P. *J. Chem. Soc., Chem. Commun.* **1974**, 209.

[15] Okamoto, A.; Snow, M. S.; Arnold, D. R. *Tetrahedron* **1986**, *42*, 6175.

[16] Ci, X.; da Silvei, R. S.; Nicodem, D.; Whitten, D. G., in press.

**Table I**

| | rates of bleaching in benzene[a] | | | | rates of thioindigo bleaching[c] | | |
|---|---|---|---|---|---|---|---|
| | TI | L | DCA | TCA | benzene[d] | $CH_2Cl_2$ | $CH_3CN$ |
| rel rates | 0.56 | 0.66 | 6.09 | 33.08 | 0.22 | 0.44 | 3.49 |
| **1/2** | | | 14.65[b] | | | | |

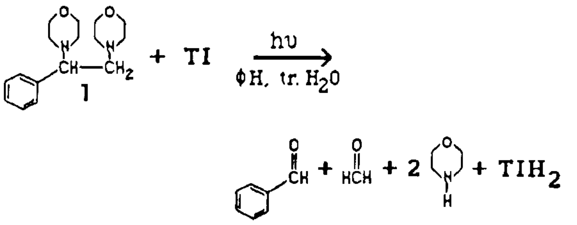
| | $\phi_b$[e] | | $k_q$[h] | | peak[i] potential |
|---|---|---|---|---|---|
| | TI[f] | L[g] | TI | DCA | |
| **1** | $2.7 \times 10^{-3}$ | 0.22 | $3.3 \times 10^9$ | $9.8 \times 10^9$ | 0.975 V |
| **2** | $1.2 \times 10^{-2}$ | 0.29 | $1.8 \times 10^9$ | $4.6 \times 10^9$ | 1.050 V |
| **1/2** | 0.23 | 0.73 | 1.86 | 2.15 | |

[a] Irradiation of vacuum degassed solutions, UV–vis monitored, equal concentrations of **1** and **2**. [b] Trace $H_2O$. [c] UV–vis monitored, bleaching being the decrease in the 544 nm TI absorption as it is consumed during the photoreaction. TI concentration = $5 \times 10^{-5}$ M. [d] Concentrations of **1** and **2** corrected for differential quanching. [e] Quantum yield of bleaching of UV–vis absorption. [f] Concentrations of **1** and **2** corrected for differential quenching. Secondary actinometer used: known reaction of TI/TEA. [g] Equal concentrations of **1** and **2**, ferrioxalate actinometery: room temperature. [h] Quenching constant, Ar degassed samples, acceptor concentration = $2 \times 10^{-5}$ M. [i] Peak potential measured against a Ag wire reference electrode which is corrected by using an internal standard of ferrocene, $CH_3CN$, electrolyte = 0.2 g/4 mL of TBA $PF_6$.

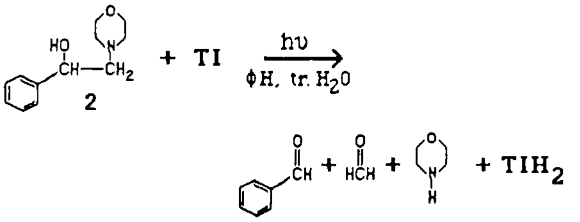
report here studies of the photooxidative fragmentation of 1,2-ditertiary amines, a reaction which is probably also quite general and which shows both similarities and yet remarkable contrasts to the aminoalcohol cleavage.

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 differenc organic solvents. Thus when reaction is monitored by the appearance of benzaldehyde in the NMR ($C_6D_6$, with a trace of $D_2O$),[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.

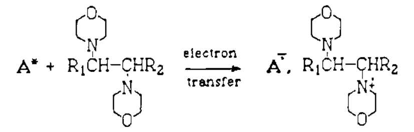


(1)

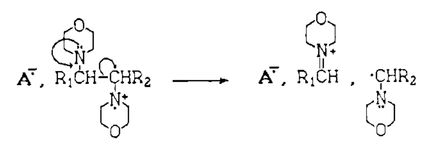


(2)

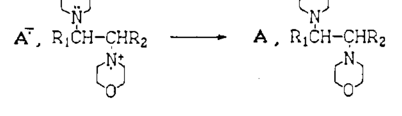
A general mechanism for the oxidative photofragmentation of ditertiary amines, analogous to that proposed for amino alcohols, is given by eq 3–6. While a number of paths leading from the initial fragmentation products to the final products (eq 6) can be proposed, the major factor limiting the overall efficiency of reaction should be the competition between fragmentation (eq 4) and reverse electron transfer (eq 5). Cation radicals of both aminoalcohols 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 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



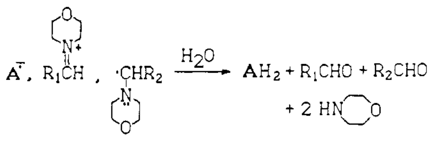
(3)



(4)



(5)



(6)

---

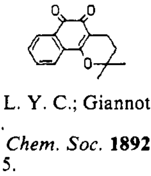
(17) Grob, G. A. *Angew. Chem., Int. Ed. Engl.* **1969**, 535.

(18) Kharasch, M. S.; Seyler, R. C.; Mayo, F. R. *J. Am. Chem. Soc.* **1938**, *60*, 882.

(19) Bäckvall, J. E. *Tetrahedron Lett.* **1978**, 163.

(20) Barker, N. G.; Cromwell, N. H. *J. Am. Chem. Soc.* **1951**, *73*, 1051.

(21) β-lapachone



(22) Schanze, K. S.; Lee, L. Y. C.; Giannotti, C.; Whitten, D. G. *J. Am. Chem. Soc.* **1986**, *108*, 2646.

(23) (a) Hooker, S. C. *J. Chem. Soc.* **1892**, *61*, 611. (b) Hooker, S. C. *J. Chem. Soc.* **1896**, *69*, 1355.

(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** ($3.2 \times 10^{-4}$ M).

(26) Wayner, D. D. M.; Dannenberg, J. J.; Griller, D. *Chem. Phys. Lett.* **1986**, *131*, 189.

(27) Dinnocenzo, J. P., unpublished results.

Arrhenius plot[28] 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 $CH_3CN$. 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 disecondary, 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.

**Acknowledgment.** We thank the Department of Energy (Grant No. DE-FG02-86ER13504) for support of this research. We also thank X. Ci for many helpful discussions and suggestions. M. A. Kellett is grateful for a Sherman Clarke Fellowship.

---

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

---

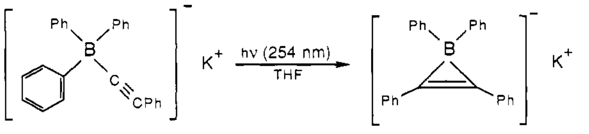
## 1,1,2,3-Tetraphenylboratirene: First Isolation and Characterization of a Boratirene

Michael A. Kropp and Gary B. Schuster*

*Department of Chemistry, University of Illinois*
*Roger Adams Laboratory*
*Urbana, Illinois 61801-3731*

*Received December 19, 1988*

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.



**1** **2** (1)

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 theoretical[1] and experimental[2] interest. For example, we recently reported that tetraphenylboratirane,[3] a cyclopropane analogue, has an exceedingly low oxidation potential (−0.8 V, irreversible vs $Ag/AgNO_3$) when compared with the hydrocarbon. Similarly, we discovered that tetraphenylboratanorcaradiene[4] 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.

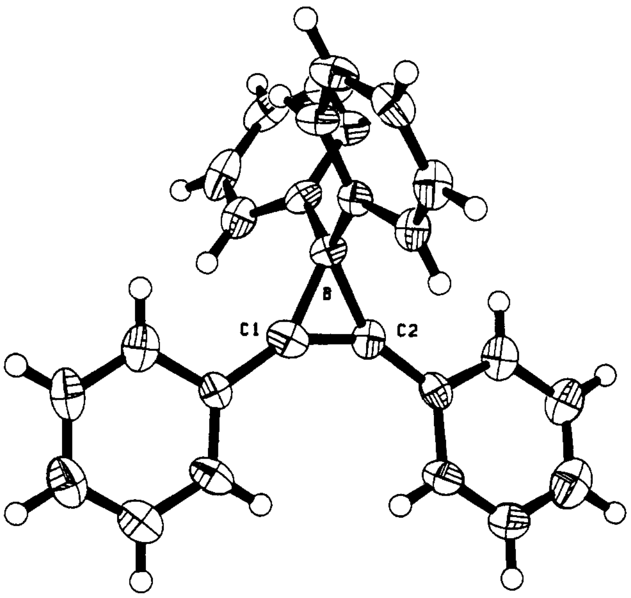


**Figure 1.** X-ray crystal structure for boratirene **2**. The potassium counter ion and a coordinated THF are not shown.

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's[6] report that photolysis of $[(Ph)_3(PhC{\equiv}C)B]^-$ 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 rearrangement[7] 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

---

(1) (a) Dewar, M. J. S. *Prog. Boron. Chem.* **1964**, *1*, 235. (b) Krogh-Jespersen, K.; Schleyer, P. v. R.; Pople, J. A.; Cremer, D. *J. Am. Chem. Soc.* **1978**, *100*, 4301. (c) Krogh-Jespersen, K.; Cremer, D.; Dill, J. D.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 2589. (d) Disch, R. L.; Sabio, M. L.; Schulman, J. M. *Tetrahedron Lett.* **1983**, *24*, 1863. (e) Frenking, G.; Schaefer III, H. F. *Chem. Phys. Lett.* **1984**, *109*, 521. (f) Pople, J. A.; Schleyer, P. v. R. *Chem. Phys. Lett.* **1986**, *129*, 279. (g) Drewello, T.; Kock, W.; Lebrilla, C. B.; Stahl, D.; Schwarz, H. *J. Am. Chem. Soc.* **1987**, *109*, 2922. (h) Sheldon, J. C.; Currie, G. J.; Bowie, J. H. *J. Am. Chem. Soc.* **1988**, *110*, 8266.

(2) (a) Letsinger, R. L.; Skoog, I. H. *J. Am. Chem. Soc.* **1955**, *77*, 5176. (b) van Tamelen, E. E.; Brieger, Gl.; Untch, K. G. *Tetrahedron Lett.* **1960**, 14. (c) Jutzi, P. *J. Organomet. Chem.* **1969**, *19*, P1. (d) Grisdale, P. J.; Williams, J. L. R. *J. Organomet. Chem.* **1970**, *22*, C19. (e) Eisch, J. J.; Galle, J. E. *J. Am. Chem. Soc.* **1975**, *97*, 4436. (f) Sobieralski, T. J.; Hancock, K. G. *J. Am. Chem. Soc.* **1982**, *104*, 7533. (g) Sobieralski, T. J.; Hancock, K. G. *J. Am. Chem. Soc.* **1982**, *104*, 7542. (h) Lee, D. Y.; Martin, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 5745. (i) Eisch, J. J.; Galle, J. E.; Kozima, S. *J. Am. Chem. Soc.* **1986**, *108*, 379. (j) Nakadaira, Y.; Sato, R.; Sakurai, H. *Chem. Lett.* **1987**, 1451. (k) Ashe III, A. J.; Drone, F. J. *J. Am. Chem. Soc.* **1987**, *109*, 1879.

(3) Kropp, M.; Bhamidapaty, K.; Schuster, G. B. *J. Am. Chem. Soc.* **1988**, *110*, 6252.

(4) Wilkey, J. K.; Schuster, G. B. *J. Am. Chem. Soc.* **1988**, *110*, 7569.

(5) Wilkey, J. K.; Schuster, G. B. *J. Org. Chem.* **1987**, *52*, 2117.

(6) Eisch, J. J.; Tamao, K.; Wilcsek, R. J. *J. Am. Chem. Soc.* **1975**, *97*, 895.

(7) Named by analogy to the well-known di-π-methane rearrangement. Zimmerman, H. E. *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, p 131.

0002-7863/89/1511-2316$01.50/0