

PHOTOCHEMICAL REACTIONS OF DIALKYLBOROYL TROPOLONATE COMPLEXES

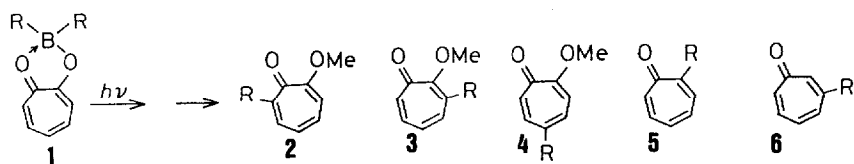
Keiji Okada,* Haruki Inokawa, and Masaji Oda*

Department of Chemistry, Faculty of Science, Osaka University,
Toyonaka, Osaka 560, Japan

Summary: Irradiation of a benzene solution of dialkylboroyltropolonates produced alkyl migrated tropolone and tropone derivatives. The product distribution and the mechanism of this rearrangement were investigated.

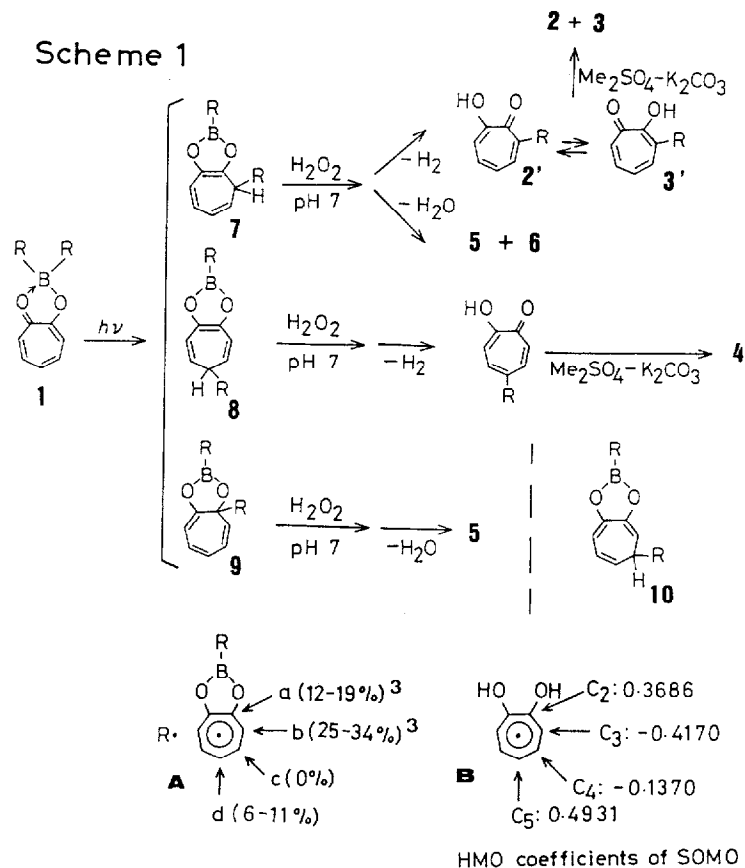
Reactions of organoboranes in their excited states have received growing interest in organic photochemistry. We have recently reported a novel photochemical rearrangement of dialkylboroylacetylacetonate complexes in which one alkyl group migrates from the boron to the carbonyl carbon.¹ A radical pair mechanism was proposed. This type of rearrangement may be a general reaction for the four coordinated alkylboroyl chelate complexes. In order to know the generality of this reaction and to obtain further insight into the mechanism, we have studied photochemical reactions of dialkylboroyltropolonate complexes (**1**), which have multiple reactive carbon centers and therefore would be suitable for a test of the radical pair mechanism.

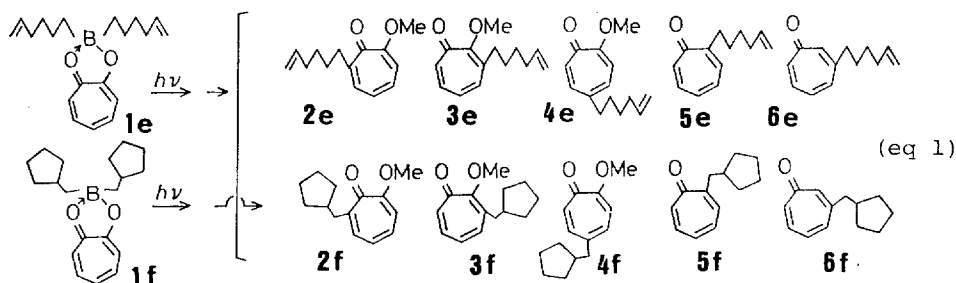
When a benzene solution of the borane chelate **1a** was irradiated with a 500-W Xenon lamp under nitrogen through a glass filter (>350 nm), the yellow color due to **1a** gradually disappeared. The products **2a**, **3a**, **4a**, **5a**, and **6a** were best separated and isolated by preparative TLC on silica gel after 1) oxidative hydrolysis with a solution of pH 7 phosphate buffer, THF, and aqueous 30% H₂O₂ (2.5:10:1(v/v)), and 2) O-methylation with dimethyl sulfate-K₂CO₃ in dry acetone. Similar products were formed from the tropolonate chelates having various alkyl groups in the yields shown in Table 1.² These products **2-6** are considered to be derived from the initial products **7-9**. Formal reaction pathways are shown in Scheme 1. The isomers of methyl tropolonate **2** and **3** must be derived from the tautomeric tropolones (**2'** ↔ **3'**), which would be formed through dehydrogenation under the conditions of oxidative hydrolysis, whereas the tropone derivatives **5** and **6** can be formed via dehydration under these conditions. Two precursors **7** and **9** can be formally considered for the formation **5**. However, the distinctly high ratio of **5e** : **5f** compared with **2(3,6)e** : **2(3,6)f** in the photolysis of **1e**, which is shown later, suggests that the precursor of **5** is **9** rather than **7**.³ The structural discrimination of **2** and **3** were achieved by ¹H NMR NOE experiment: difference NOE spectrum of **2** shows a clear NOE between the methoxy protons and tropolone ring proton (H₃).

Table 1. Quantum and Chemical Yields of Photoreactions of **1**

R	Quantum yield ^a	2 (%)	3 (%)	4 (%)	5 (%)	6 (%)
a: n-C ₄ H ₉	0.041 (0.040) ^b	22	6	6	12	6
b: c-C ₆ H ₁₁	0.0039 (0.0039) ^c	24	4	8	16	4
c: allyl	0.40 (0.40) ^c	20	5	11	18	- ^d
d: benzyl	0.18 (0.18) ^b	18	7	9	19	- ^d

a: Quantum yield of disappearance of **1** at 366 nm excitation in benzene under argon. **b:** Under aerated conditions. **c:** In the presence of piperylene (2 M) under argon. **d:** Less than 2%.

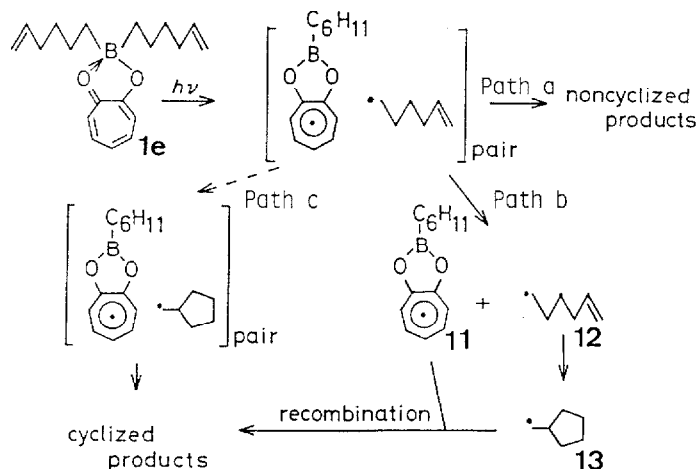




The reactions proceed with a wide range of quantum yields (Table 1) and cannot be quenched by dissolved oxygen (2×10^{-3} M) or piperylene (2 M), suggesting the singlet state to be a reactive excited state. The relatively high quantum yields for the allyl and benzyl substituted complexes may be due to easier homolytic boron-carbon bond cleavage giving stabilized allyl and benzyl radicals. The product distributions summarized in Table 1 may be rationalized by assuming the radical pair **A** as a primary intermediate in this photoreaction. The fact that no product is formed from attack **c** (via **10** in Scheme 1) in the radical pair **A** is in accordance with HMO calculation of 1,2-dihydroxytropyli radical: the SOMO coefficient at ring carbon C_4 (C_6) of this compound is considerably small compared to those at C_2 (C_1), C_3 (C_7), and C_5 (**B**). In addition, the participation of the radical species is supported by the formation of a small amount of 1,2-diphenylethane (8%) in the photolysis of **1d** which is a typical product from benzyl radical.

Further piece of evidence for radical mechanism in the main product formation is obtained by using the technique of radical clock.⁴ Thus, similar irradiation of a benzene solution of **1e**, which is readily available from tri(5-hexenyl)borane and tropolone, produced five fractions after aforementioned procedure (**2e+2f**; 9%, **3e+3f**; 3%, **4e+4f**; 8%, **5e+5f**; 18%, and **6e+6f**; 19%). Each fraction was found to be a mixture of the noncyclized and cyclized products (¹H NMR and GC; **2e:2f** = 57:43, **3e:3f** = 63:37, **4e:4f** = 68:32, **5e:5f** = 89:11, and **6e:6f** = 64:36) (eq 1). The cyclized products were identified and characterized by comparison with those derived from the photolysis of **1f** (**2f**; 12%, **3f**; 6%, **4f**; 8%, **5f**; 10%, and **6f**; 12%). The formation of considerable amount of the cyclized products is best rationalized by radical pair mechanism (Scheme 2).⁵ The singlet excited state of the borane complexes **1** gives the singlet radical pair which partly recombines to give the non-cyclized products (path a) and partly dissociates into free radicals via intersystem crossing of the radical pair (path b). The free 5-hexenyl radical (**12**) cyclizes to cyclopentylmethyl radical (**13**) which may recombine with the tropyli

Scheme 2



radical (11) to produce the cyclized products. The cyclization of 5-hexenyl radical in the singlet radical pair (path c) seems to be unlikely because of its relatively slow rate of the cyclization ($k = 2 \times 10^5 \text{ s}^{-1}$ at 25°C)⁶ compared to the rate of recombination (usually 10^7 - 10^{10} s^{-1})⁷ or intersystem crossing (10^8 - 10^9 s^{-1}).⁷ The relatively high yield of the cyclized products may be due to the resonance stabilization of the tropyli radical, the stabilization retarding the coupling in the radical pair to give higher chance of intersystem crossing.

Acknowledgment: This work was supported by the Grant-in-Aid for Scientific Research No 63540397 from Ministry of Education, Science and Culture, Japan.

References and Notes

1. K. Okada, Y. Hosoda, and M. Oda, *J. Am. Chem. Soc.*, **108**, 321(1986).
2. All the products were characterized by spectral data (NMR, IR, and Mass); the details will be reported elsewhere.
3. The minor contribution of 7 for the formation 5 can not be excluded. The values in parentheses in A are based on the assumption that the precursor of 5 is only 9.
4. D. Griller and K. U. Ingold, *Acc. Chem. Res.*, **13**, 317(1980).
5. The values of quantum yields (less than unity) and their insensibility to dissolved oxygen in this system as well as the previous results for dialkylborylacetylacetonate complexes suggest that the reactions do not involve radical chain processes which have been postulated in thermal rearrangement of 2-aryl-methoxytropones; H. Takeshita, H. Mametsuka, A. Chisaka, and N. Matsuo, *Chem. Lett.*, **1981**, 73.
6. C. Chatgililoglu, K. U. Ingold, and J. C. Scaiano, *J. Am. Chem. Soc.*, **103**, 7739(1981); D. P. Curran, *Synthesis*, **1988**, 417.
7. R. Kaptein; in "Chemically Induced Magnetic Polarization", ed by L. T. Muus, P. W. Atkins, K. A. McLauchlan, and J. B. Pedersen; D. Reidel; Dordrecht-Holland, 1977; pp 1-16.

(Received in Japan 27 April 1989)