A novel photorearrangement of 1,3-diketonatoborinate: a photoinduced intramolecular alkylation on a conjugated carbonyl system

Jun-ichi Ishiyama and Yuan L. Chow

Abstract: Irradiation of borinates derived from 9-borabicyclo[3,3,1]nonane and 1,3-diketones at their π - π * transition band caused a rearrangement from their triplet excited state to give boronate intermediates that could be hydrolyzed to the corresponding aldols. The primary photolysis involves the scission of one of the B—C bonds followed by a 1,3- or 1,5-migration and the formation of a more stable B—O bond by radical pathways. The triplet state reaction was established by quenching and heavy atom effect experiments. The overall reaction pattern is an irreversible 1,2- or 1,4addition of an alkyl-boron group to an α , β -conjugated ketone system by radical processes. Evidence showed that the non-isolated boronates also underwent secondary photoreactions followed by hydrolysis to afford enones corresponding to dehydration products of aldols; mechanisms are suggested for these secondary steps. The photoreaction was more facile in nonpolar solvents than in polar solvents; different solvents also gave different product compositions. In the presence of dilute acetic acid, the photolysis gave a high yield of aldols, suggesting a rapid acetolysis of the B—C bond in boronates to acetylborates. Under oxygen, the photolysis was complicated by radical oxidation to give totally different products.

Key words: borinate photochemistry, charge transfer absorption, alkylborane addition, boronate intermediates, B—C bond homolytic scission.

Résumé : L'irradiation de borinates dérivés du 9-borabicyclo[3.3.1]nonane et des 1,3-dicétones au niveau de leur bande de transition π - π^* provoque un réarrangement à partir de leur état excité triplet pour conduire à des boronates intermédiaires que l'on peut hydrolyser en aldols correspondants. La photolyse primaire implique la scission de l'une des liaisons B—C, suivie d'une migration 1,3 ou 1,5 et la formation d'une liaison B—O plus stable par le biais de voies radicalaires. On a établi l'implication d'une réaction de l'état triplet à l'aide d'expériences de désactivation et d'effets isotopiques. Le schéma de la réaction globale est une addition, 1,2 ou 1,4 irréversible, d'un groupe alkyl-bore sur un système cétonique α , β -insaturé par des processus radicalaires. Les données montrent que les boronates qui n'ont pas été isolés subissent aussi des photoréactions secondaires qui, suivies d'une hydrolyse, fournissent les énones qui correspondent aux produits de déshydratation des aldols; on suggère des mécanismes pour ces étapes secondaires. La photoréaction est plus facile dans les solvants non polaires; les divers solvants donnent aussi des compositions de produits différentes. En présence d'acide acétique dilué, la photolyse fournit un rendement élevé d'aldols; ceci suggère que, dans les boronates, il se produit une acétolyse rapide de la liaison B—C pour donner des acétylboronates. En présence d'oxygène, la photolyse est compliquée par une oxydation radicalaire qui conduit à des produits totalement différents.

Mots clés : photochimie du borinate, absorption du transfert de charge, addition d'alkylborane, intermédiaires boronates, scission homolytique de la liaison B—C.

[Traduit par la Rédaction]

Introduction

We observed some 10 years ago that dialkylborinates derived from simple 1,3-diketones (such as 5-7 in Scheme 1, see below) underwent photolysis to give rearranged products. The work has been left dormant since we noted that

two short communications on the photoreaction of allied borinates (where the bicyclononane ring in 5-7 is replaced by di-*n*-butyl or dicyclohexyl groups) had already been published in 1986 (1). These works were a study based on suggestions derived from an earlier communication by another group (2). While an additional related communication was

Received February 17, 1999.

J. Ishiyama¹ and Y.L. Chow.² Department of Chemistry, Simon Fraser University, Burnaby, BC V5A 1S6, Canada.

¹Visiting Professor from Fukushima National College of Technology, Taira, Fukushima, Japan; Overseas Research Fellow (1997) supported by the Ministry of Education, Science, Sports and Culture, Government of Japan. ²Author to whom correspondence may be addressed. Telephone: (604) 291-3352. Fax: (604) 291-3765. e-mail: ychow@sfu.ca

Scheme 1.



published later (3), the detailed photochemical reaction of allied borinates has not, to our knowledge, been described. In the meantime, the photochemistry and photophysics of boron compounds continue to attract investigations, and interesting results have been published in relation to photoinduced electron transfer (4), photo-cycloadditions (5), exciplex formations (5), and unusual emission patterns (6, 7). We were attracted by the abnormally deep-colored appearance of these borinates, and were puzzled by what appeared to be an unusually strong CT band in their UV-visible spectra. More recently, we undertook an in-depth investigation of borinates 5-7, and discovered that our results were not in total agreement with the earlier communications (1). The chemical and physical behavior of these borinates is interesting and promises to stimulate new studies of allied boron compounds, particularly in relation to their excited states and radical reactions. We wish to describe the results from our group.

Results

The reaction of 9-borabicyclo[3,3,1]nonane (BBN, 1) with a 1,3-diketone (2–4) in THF readily gave the corresponding

B-diketonato-9-borabicyclo[3,3,1]nonane, **5**–**7**, in high yields (8); these borinates were abbreviated as AABBN (for B-acetylacetonato-, 6) (8b), BABBN (for B-benzoylacetonato-, 7) and DBMBBN (for B-dibenzoylmethanato-, 5). They were prepared equally easily from 9-methoxy-BBN $(1, H = OCH_3)$ and 9-(2-aminoethanolato)-BBN (1, H =NH₂CH₂CH₂O) in comparable yields. These colored (from yellow to orange) crystalline dialkylborinates 5-7 prominently showed strong UV absorption that is slightly blueshifted from that of the parent diketone (6); this UV band was red-shifted in more polar solvents and must arise from a π - π^* transition. They also showed a broad and weaker but well-defined band that was assigned as a CT transition (Fig. 1). Since the intensity of these absorption bands obeyed the Beer-Lambert law in cyclohexane and methylene chloride, it was concluded that these borinates existed as monomers up to 0.1 M. The borinates showed a strong IR absorption band for the B-O bond at 1376-1378 cm⁻¹ and a ¹³C NMR signal for the C-B carbon at about 23 ppm, which was slightly broadened owing to the boron quadrupole couplings. It should be noted that whereas the chemical shift of olefinic hydrogen moved downfield in the order 6-7-5, the ¹³C chemical shift of the corresponding

Fig. 1. The absorption spectra of (a) 6 at 1.05×10^{-4} M, (b) 7 at 3.69×10^{-5} M, and (c) 5 at 3.48×10^{-5} M in cyclohexane.



Table 1. Relative peak % of the photolysis of 6 from GC analysis.

	$R_{\rm T}({\rm min})^a$											
	1.23	1.82	3.89	4.25	4.87	5.23	6.09	8.73	13.44			
300 nm	1.9	13.0	1.8	3.3	1.4	5.8	41.0	24.0	4.3			
254 nm ^e	7.7	11.0	0.6	14.0	1.8	1.7	31.0	25.0	3.8			
Products	b	15	14a	13	С	14	12	6	d			

"There are more peaks in the vicinity of solvent that were identified as acetylacetone, cyclooctane, and bicyclo[3,3,0]octane by the coinjection of an authentic sample or by its mass spectral pattern.

^bCyclooctanone by coinjection.

^c1,1'-Bicyclooctyl by the MS pattern.

^dUnknown.

"There are more peaks of small areas over the whole range in this than in the photolysis with the 300 nm source.

olefinic carbon moved upfield in the same order. The reversed order of chemical shifts could be related to the ring current generated by resonance involving the borinate ring.

DBMBBN **5** gave a broad (380–500 nm) fluorescence band with λ_{max} 415 nm in methylene chloride on excitation at the π - π^* transition at 330 nm, but no emission on excitation at the CT band. AABBN **6** in cyclohexane (and methylene chloride) showed a narrow fluorescence peak at 280 nm on excitation at 259 nm, and at 393 on excitation of the CT band at 353 nm. In both spectra weak emission humps at longer wavelengths (e.g., those at 320 and 370 nm in the former and at 432 and 507 nm in the latter) were assumed to arise from decomposed intermediates. While these fluorescence spectra were stable in cyclohexane, those in acetonitrile showed complex shapes and changed with time lapses. Their study remains to be continued later.

Irradiation of DBMBBN **5** in methylene chloride at 350 nm gave unconjugated enone **9** and a mixture of isomeric enones **10** in addition to a smaller amount of aldol **8**; the amount of all enones increased at the expense of **8** during isolation. Injection of this sample into GC showed that **9** and **10** were present in 14 and 30%, respectively, but **8** was thermally decomposed to give a new peak showing $M^+ = 217$ by a CI mode. By the EI mode, this GC peak showed the major m/e fragment at 216 (M^+), 133 ($C_6H_5COCH_2CH_2$), 105 (C_6H_5CO , 100%), and 77 (C_6H_5); this MS pattern is compatible with the structure of **11**,which could be easily

formed from the retro-aldol reaction of **8** on injection into GC. Similar photolysis of **5** in a solution containing 0.2% of acetic acid (by volume) afforded aldol **8**, in a 41% isolated yield, but no enones **9** and **10**; the yields of the latter two were small as shown by GC analysis. However, in the presence of methanol (<1%) or acetic anhydride, analogous photolysis caused marginal effects. On the other hand, similar photolysis of **5** in a mixture of methylene chloride and acetonitrile (1:4) gave only enones **9** and **10** in 38 and 36% yield, respectively. While enone **9** could be isolated by chromatography, enone **10** decomposed during the operation.

In the initial stage, AABBN 6 was photolyzed in a mixture of cyclohexane and methylene chloride (9:1) under a blanket of dry nitrogen with 300 nm light in order to obtain a higher yield of aldol 12 at a reasonable rate. Irradiation with 254 nm light was faster by a factor of two than that with 300 nm light, but irradiation with 350 nm light (i.e., excitation of the CT band), on the contrary, caused no significant decomposition in 24 h. Photolysates were chromatographed to give aldol 12 and enones 13 and 14 in yields of 54, 7 and 1%, respectively, by 254 nm irradiation, and 54, <1, and 14%, respectively, by 300 nm irradiation. The GC spectrum of the crude product showed these and other product peaks, including those of acetylcyclooctane (15) and the geometric isomer 14a; both of them were too small to be isolated (see Table 1). As is typical of a radical reaction, there were also several small by-product peaks that

Table 2. Relative product % from photolysis ^a of 6.

	$R_{\rm T}$ (min)								
	3.66 ^b	6.43	6.97	8.20	9.38				
Product	15	14a	13	14	12				
Tube	2	2	3	4	2				
Tube 2 ^c	9	2	3	4	28				
Tube 3^d	4	12	57	22	5				
Tube 4^d	2	11	37	24	3				
Tube 7 ^e	2	9	22	20	5				
Tube 8 ^e	2	8	38	18	6				
Tube 9 ^e	2	10	51	13	8				

^{*a*}See text for details of the solutions; the irradiation time was 4 h for tubes 1–4 and 2.5 h for tubes 7 and 8; the corresponding factor for products to the internal standard (hexadecane) was arbitrarily set at 10:1.

^bThis peak is derived from **12** upon injection of photolysates.

"Tube 3 contains 0.167 M acetic acid.

^dTubes 3 and 4 contain phenyl bromide, 0.0082 and 0.0041 M, respectively.

⁶Tubes 7–9 contain 1,2-dibromoethane, 0.02, 0.04, and 0.08 M, respectively.

were more visible in the 254 nm irradiation. GC-MS and (or) the coinjection of authentic samples identified these minor GC peaks as those of cyclooctane, cyclooctene, 1,1'bicyclooctyl, and cyclooctanone. In the presence of <1% acetic acid, a similar 300 nm photolysis of AABBN 6 gave predominantly aldol 12 and only trace amounts of enones 13-14, though the rate of AABBN conversion was scarcely affected (Table 2); indeed 12 was prepared in good yield by this procedure. Aldol 12 was partially decomposed on GC injection to give the peaks of itself and 15 in a 6:4 ratio; GC-MS by the CI mode showed two peaks to have M⁺ at 213 and 155. The latter GC peak exhibited the m/e at 154 (M⁺), 139, 111, 69 (100%), and 43, which supported the structure of 15. Aldol 12 also slowly decomposed to 15 either in solution or neat; decomposition was more rapid on heating, during which enones 13 and 14 were also formed in small amounts as shown by GC and NMR monitors. In dilute acidic (HCl) methanol, 12 decomposed slowly to 14 and 15 at room temperature, but rapidly and mainly to enone 13 on refluxing. The enone distribution suggested that unconjugated enone 13 is thermally more stable than the conjugated 14, probably because of steric crowding.

BABBN 7 in methylene chloride was irradiated with 300 nm light to give low yields of four enones that could be derived from aldols 16 and 17; these aldols continued to decompose during separation. With difficulty, enones 20-21 were finally isolated only in semi-pure states by preparative TLC. The same solution containing 1% of acetic acid was irradiated under similar conditions to give aldol 16 (46%) and a small amount of a mixture containing the alternative aldol 17. Aldol 16 when injected into the GC gave only one peak, which showed the MS pattern corresponding to 11 both by EI and CI modes. The fact that both aldols 8 and 16 decomposed to give the common ketone 11 provided a rationale for the structural correlation among them. The GC injection of the impure fraction of 17 under the same conditions gave the major peak corresponding to 15 as shown by the $R_{\rm T}$ and MS pattern. A crude product obtained from terminating a 60% photoreaction of 7 at 300 nm irradiation was subjected to GC analysis conditions as above to record the ketone peaks of **11** and **15** in a 27%/15% ratio in the absence, and in a 56%/20% ratio in the presence, of acetic acid. Similar photoreaction at 350 nm irradiation either in the presence or absence of acetic acid recorded the ketone peaks in a ratio of 12:10 by GC analysis. As the ratio of **11:15** virtually represents the ratio of **16:17** in the crude product, the latter must be coalescing to the 1:1 ratio.

AABBN 6 was used as a model to study the excited state reaction of these borinates. Photolysis of 6 with 300 nm light in various solvents showed the decreasing efficiency order of cyclohexane >> THF ~ benzene > acetonitrile > methylene chloride in the ratio of 1.00:0.74:0.71:0.60:0.49. When the photolysis was carried out in the presence of a trace amount of water (i.e., using purging nitrogen directly from a cylinder without drying), it was noteworthy that this ratio was nearly leveled, although cyclohexane and benzene were still the better solvents. GC examinations showed that the major product was aldol 12 for the reaction in methylene chloride and enone 14 for those in cyclohexane and benzene. Sensitized photodecomposition of 6 with benzophenone by 350 nm irradiation was an ideal setup since the sensitizer absorbed strongly in the 350 nm region where 6 showed no photoreactivity; this irradiation caused much more efficient decomposition than that by direct irradiation at 300 nm, and resulted in enormously accelerated disappearance of 6 as well as the efficient formation of enones 13 and 14a in addition to a few unknown GC peaks. The reaction was complicated by the sensitizer itself being consumed, but the occurrence of triplet energy transfer was indicated by the absence of benzopinacol in the crude product; this implied that triplet excited benzophenone had been quenched (9). While the interpretation was not unambiguous, this observation, coupled with the efficient product yields, supported that efficient sensitization must have occurred. Under the oxygen blanket, the photolysis of 6 was not totally quenched but instead slightly accelerated, and gave oxidation products obviously due to the participation of O_2 in the product formation as is often observed in free radical reactions (10). While the result was inconclusive, in view of the smallness in the rate increase, oxygen quenching had probably occurred but was masked by the enhanced radical reactions.

The photoreaction of 6 was quenched efficiently by 1,3pentadiene at the 3.5 mM level, and also by vinyl ethyl ether and furan (at 5 mM). The former diene is a typical triplet quencher, but the latter ethers do quenching by some other mechanisms, most likely intercepting the singlet state by electron transfer (9). No new compound was formed from these quenching experiments. Further, the consumption of 6was accelerated by more than an order of magnitude in the presence of bromobenzene (4 mM) and 1,2-dibromoethane (5 mM). In both cases, both enones 13 and 14, particularly the former unconjugated one, were produced in significantly increased amounts with increasing bromide concentrations, while the yield of aldol 12 was affected little, as shown in Table 2. The fluorescence peak of AABBN 6 in cyclohexane at 280 nm by excitation at λ_{ex} 259 nm was quenched by the presence of increasing concentrations of 1,2-dibromoethane. The Stern–Volmer plot was a straight line with the slope (K_{sv}) of 20.0. This demonstrated that singlet excited **6** interacted with the bromide and mutated rapidly to the triplet state by heavy atom effects (11). Similar spectroscopic exScheme 2.



periments with bromobenzene and 1,3-pentadiene could not be carried out owing to the overlap of the absorption in the 260 nm region.

The structure of the products was primarily determined from NMR spectral evidence, in some cases with partially pure samples. The primary photoproducts were obviously aldols 8, 12, 16, and 17, which served as the source for the observed products, enones and acylcyclooctanes, derived from the secondary reactions as shown in Scheme 1. The isolated aldols showed, among other required signals, the following key NMR signals to define the structure unambiguously. Firstly, they showed a pair of AB quartets due to the diastereotopic proton of -CO-CH₂-, with the chemical shifts progressively moved downfield as a CH₃ group was replaced by a C_6H_5 group. Secondly, they had the carbonyl ¹³C signal at 211 ppm for the acetyl and at 202 ppm for the benzoyl group. Finally, the monosubstituted cyclooctyl group showed eight ¹³C signals indicating that the eight carbons are nonequivalent, that is, in each pair the corresponding -CH2- groups were diastereotopic to one another due to the vicinal chiral centers. The unconjugated enones 9, 13, and 20 showed (i) a two-proton singlet in the 3.0-4.0 ppm region and a carbonyl ¹³C signal at 199-208 ppm for the CH₂-CO, and (*ii*) eight ¹³C signals (including one olefinic at about 137 ppm) for the cyclooctylidene group. Among the conjugated enones, only 14, 14a, and 21 were isolated, the last two as mixtures. Both 14 and 21 were always formed as the major isomer and assigned to the configuration shown for steric reasons. Both enones 10 and 19 (and (or) their isomers) could be detected with GC-MS but could not be isolated because of decomposition during column chromatography. The isomeric enone pair 14 and 14a showed nearly identical spectral patterns not only in MS but also in the ¹³C and ¹H NMR spectra, which gave little evidence to assign the cis-trans isomerism. These two conjugated enones and

21 exhibited (*i*) an olefinic proton singlet at 6.05, 6.05, and 6.72 ppm, (*ii*) a set of pertinent ¹³C signals for an α , β -unsaturated carbonyl system, and (*iii*) five ¹³C signals for the cyclooctyl group due to its rapid rotation. In addition, the NMR spectra of these enones also showed the required signals with appropriate chemical shifts.

Discussion

The overall reaction resembles the well-known classic 1.2- or 1.4-addition of an alkylborane onto α , β -unsaturated carbonyl compounds (12), except that the present reaction is promoted by light and occurs intramolecularly through free radical mechanisms. Thus, electronic excitation provides an alternative pathway to promote this alkylborane addition. The failure for excitation in the CT band to promote the reaction must imply that this excited state is rapidly deactivated to the ground state, i.e., that is the only channel available. These borinates 5-7 undergo a deep-seated rearrangement upon excitation of the π - π * transition band in a wide range of solvents; the photolytic efficiency is better in nonpolar than in polar media and the product patterns vary widely depending on reaction conditions. The overall result indicates that the products are formed in consecutive multistep processes involving intermediates that are sensitive to the photolysis conditions. The overall reaction is approximated as the primary photoinduced rearrangement to give the precursors of aldols 8, 12, 16, and 17, followed by secondary decomposition of the precursors under the photolysis conditions.

The experimental probes described provide good qualitative evidence that the primary photoreaction is derived from the triplet excited state of these borinates 5-7. Two of these probes are unambiguous; that is, efficient triplet quenching (9) by 1,3-pentadiene, and a heavy atom effect to enhance

Scheme 3.



the population of the triplet state induced by brominecontaining compounds (11). The other two, the benzophenone sensitization and oxygen quenching, are complicated by the participation of the reagents in the reactions; the former, which cannot be analyzed quantitatively owing to the change in the product pattern, also supports triplet state energy transfer on the basis of the detailed observations.

In the previous communications (1), the authors stated that the photoreaction of some similar dialkylborinates could not be quenched by either oxygen or 1,3-pentadiene, which led them to suggest a singlet state reaction. Though the present dialkylborinates **5–7** are not exactly the same as theirs, the corresponding results for these two quenchers are just the opposite to, and more complicated than, those stated in their reports. It is interesting to compare details of the two experimental descriptions.

The reaction mechanism is proposed in Scheme 2, in which the carbonyl triplet excited state 22, as represented by the diradical model (9), is the species initiating the radical pathway. The step 22 to 23 is analogous to the homolytic substitution of a borane by an alkoxy radical, the driving force of which is derived from a bond energy gain of about 30-40 kcal/mol in the conversion of a B-C bond to a B-O bond (13). Triplet excited state biacetyl has been shown to interact with borane either directly or through the acetyl radical (14). The intramolecular attack in 22-23 should be more facile than any intermolecular attacks. The subsequent recombination of the radical pair 23 can occur at the carbon of either O-C bond; the direction is controlled by the nature of the R groups to give boronate 24. The migration can be highly regiospecific if the R and R' groups possess a large electronic gradient (1). Thus, the primary photolysis is assumed to terminate on the formation of 24. Its simple hydrolysis should give aldols 25, the process of which appears to be relatively sluggish under the photolysis conditions; thus GC analysis at times shows poor reproducibility depending upon sampling times. As will be discussed below, the conversion of 24-25 can also involve an excitation step. However, the work-up does not require highly nucleophilic hydrogen peroxide anion (1) to hydrolyze borate esters. While the efficiency of the borinate photodecomposition does not correlate strictly with solvent polarity, its rate is generally faster in hydrocarbons than in polar solvents. It is noteworthy that water, even in a trace amount, can retard the efficiency; the retardation is more significant in cyclohexane. The mechanism may be related to the coordination process at the boron center and remains to be elucidated. Efforts to isolate boronate 24 for an intermediate identification under anhydrous conditions have not been successful in providing a workable sample.

The mechanistic studies have been encumbered by unpredictable variations of the product pattern on changing the photolysis conditions; their effects have been traced to the secondary reactions and the reactivity of accompanying intermediates. The probable concurrence of thermal as well as photolytic pathways for intermediates adds further complexity that poses a formidable problem in portraying the mechanism(s). Nevertheless, certain observations can be explained with obvious and straightforward rationales. First of all, about 1% acetic acid does not affect the rate of photolysis, as shown in Table 2, but may rapidly attack boronate 24 by a pre-rate-determining nucleophilic coordination (15, 16) to form acetyl-borate 26, which should be more easily hydrolyzed than 24 to afford 25. Unless absorbing excitation light, both 25 and 26 are not photolabile and can afford good yields of aldols such as is the case for 8 and 12, which are obtained clean even after prolonged irradiation under the given conditions. In contrast, the photolysis of borinate 7 generates borate 26 with $R = C_6H_5$ and $R' = CH_3$ (corresponding to aldol 17), which possesses the α -boratoxystyryl chromophore and must be labile to 300 nm irradiation, but not to 350 nm irradiation. Indeed, two observations support this argument; they are the formation of much less 17 than 16 (as measured by the GC peak of 15 and 11) under the former (300 nm) irradiation and that of as much 17 as 16 under the latter (350 nm) irradiation. The high yield of aldol 8 in the photolysis of 5 under 350 nm irradiation must have a similar cause. Likewise, if aldols 25 with $R = C_6H_5$ are formed by adventitious water, they will be sensitive to 300 nm light and may cause a further complication to product patterns. To avoid these uncertainties, photolysis should be carried out under dry conditions. Further, there is no doubt that ketones 11 and 15 are formed by thermal and (or) acid-catalyzed retro-reactions from the aldols, slowly during isolation and more rapidly on injection in the GC port; when the port is cleaned the decomposition of 12 is drastically reduced.

Explanations of other observations are less straightforward and must rely on indirect rationales. In view of the sluggish acid-catalyzed dehydration of **12** at a room temperature (16), enone formation through simple thermal reactions cannot make a substantial contribution to high yields of enones such as those shown in Table 1. On the basis of the following evidence, we propose, as the cause of the enone formation, that boronate **24** undergoes photo-rearrangement followed by hydrolysis (Scheme 3). Firstly, the photoreaction of borinates **5–7** affords lower yields of aldols in the absence of acetic acid than in the presence, suggesting that exposure of **24** to light causes photoreactions to give enones (e.g., see Table 2). The borinate photoreactions carried to a high conversion always furnish more enones. Secondly, the photolysis of 7 with 300 nm irradiation always gives much less 17 than 16, particularly in the absence of acetic acid. This is a good indication that the intermediate 24 $(R = C_6H_5, R' = CH_3)$, corresponding to 17, having an α boronatostyryl chromophore, can absorb more light energy from 300 nm irradiation and undergo photolysis more extensively. The corroborating evidence is the formation of nearly the same amount of 16 and 17 in 350 nm irradiation, in which both corresponding intermediates 24 are scarcely irradiated. Thirdly, the dominance of either 13 or 14, depending on the wavelength of excitation (see Table 1), supports the participation of an excited state of 24, which is the intermediate in the absence of acetic acid. Finally, in the presence of benzophenone as a sensitizer or a bromide as a triplet enhancer, enones 13 and 14 are disproportionately increased in comparison to aldol. We speculate that the excited state of either promoter interacts with intermediates, through exciplexes or otherwise, which may increase either conjugated 14 (e.g., in the presence of bromobenzene) or unconjugated enone 13 (e.g., in the presence of 1,2-dibromoethane) 12, as shown in Table 2.

While 24 is not available for study at this stage, the bond reorganization as shown in Scheme 3 is suggested to account for the photochemical transformations to give the enone precursors 27 and 28. The former, 27, can be arrived at by a retro-Diels–Alder reaction; the latter, 28, by a 1,3-hydrogen shift from 24. The alkyl B=O bond may be regarded as an analogue of an acyl carbonium ion, and is expected to react with water vigorously to give the observed enones. The proposed boronate intermediates in Scheme 3 involve much un-explored chemistry of their ground and excited states, which promises to open up a new area of investigation. In this regard, the origin of the broad CT absorption band must be related to the electronic structure of borinates 5–7 and will be studied.

Experimental section

Materials and instrumentation

Commercial 1,3-diketones (Aldrich) were recrystallized or distilled, but 9-borabicyclo[3.3.1]nonane (9-BBN, 0.5 M solution in THF) was used as received. For preparative photolysis, reagent grade solvents were distilled with proper dehydrating agents. Solvents of spectroscopic grade (BDH) were used for optical spectra. Benzophenone, 1,3pentadiene, bromobenzene, and 1,2-dibromoethane were purified as described in earlier publications (5, 10, 11). The sample of 1,3-pentadiene was a mixture of *trans/cis* 55:45 by GC.

Melting points were determined on a Fisher–Johns block and not corrected. Infrared spectra were recorded with a Perkin–Elmer model FT1605 spectrometer, ultraviolet and visible spectra with a Varian–Cary 210 spectrophotometer, fluorescence spectra with either a PTI LS-1 or Perkin–Elmer MPF-44B, and GC–MS with a Hewlett–Packard 5985B. NMR spectra were taken with Bruker AMX-400 or AMX-600 using TMS as the internal standard. Gas chromatography was carried out at the injection port temperature of 150– 250° C with a Hewlett–Packard 5790 equipped with a 15 m \times 0.2 mm BB-1 or OV-1 capillary column and HP 3390A integrator.

Irradiation was carried out in a Rayonet Photochemical Reactor in quartz (for 254 and 300 nm irradiation) or Pyrex (for 350 nm irradiation) test tubes (12×100 nm) placed in a "merry-go-round." A bottom fan circulated the air to maintain a constant temperature of $30-34^{\circ}$ C. For analytical and sensitized photolysis, solutions were added with a known concentration of hexadecane or eicosane as the internal standard before irradiation. The corresponding factor of AABBN to hexadecane was determined for each column to calculate percent conversions.

Preparation of borinates 5–7

To a solution of a 1,3-diketone in THF, a calculated amount of 9-BBN was added by syringe under a nitrogen blanket at room temperature while the solution was stirred magnetically. The precipitate in nearly a quantitative yield was filtered and recrystallized under nitrogen purging. 9-Methoxy-9-borabicyclo[3,3,1]nonane (1.0 M solution in hexane) or 9-(2-aminoethyleneoxy)-9-BBN was also used to give nearly quantitative yields.

DBMBBN (5)

The precipitate was recrystallized in CH₂Cl₂ and hexane (2:1) or THF and hexane (2:1) and cooled to -20° C to give deep red crystals, mp 266–267°C; IR (Nujol): B–O stretching at 1376.5 cm⁻¹; ¹H NMR (CDCl₃) & 1.00 (2H, br s), 1.55–1.65 (2H, m), 1.70–1.80 (4H, m), 1.90–2.10 (6H, m), 6.90 (1H, s), 7.50 (4H, t), 7.60 (2H, t), 8.10 (4H, d); ¹³C NMR (CDCl₃) & 23.0 (br), 24.91, 31.41, 92.67, 128.24, 128.86, 133.73, 134.14, 183.11; MS (EI) *m/e* (relative intensity): 344 (16, M⁺), 287 (18), 261 (28), 248 (43), 235 (17), 105 (100). Anal. calcd. for C₂₃H₂₅BO₂: C 80.23, H 7.27; found: C 80.32, H 7.35. This compound is soluble in THF and methylene chloride but much less soluble in benzene and acetonitrile.

BABBN (7)

The precipitate was recrystallized in THF and diethyl ether (1:1) by cooling to -20° C to give brilliant red crystals, mp 196–197°C; IR (Nujol): B–O stretching at 1377.7 cm⁻¹; ¹H NMR (CDCl₃) & 0.90 (2H, br s), 1.50–1.60 (2H, m), 1.60–1.70 (4H, m), 1.80–2.00 (6H, m), 2.25 (3H, s), 6.30 (1H, s), 7.45 (2H, t), 7.60 (1H, t), 7.95 (2H, d); ¹³C NMR (CDCl₃) & 23.0 (br), 24.79, 24.83, 24.98, 31.14, 31.36, 96.42, 128.15, 128.78, 133.53, 133.63, 181.79, 191.84; MS (EI) *m/e* (relative intensity): 282 (22, M⁺), 239 (13), 225 (35), 199 (55), 186 (100), 173 (40). Anal. calcd. for C₁₈H₂₃BO₂: C 76.61, H 8.21; found: C 76.75, H 8.45.

AABBN (6)

The precipitate was recrystallized in degassed hexane to give bright yellow crystals, mp 121–122° C; IR(Nujol): B–O stretching at 1376.6 cm⁻¹; ¹H NMR (CDCl₃) & 0.80 (2H, br s), 1.40–1.50 (2H, m), 1.58–1.66 (4H, m), 1.70–1.90 (6H, m), 2.10 (6H, s), 5.55 (1H, s); ¹³C NMR (CDCl₃) & 23.0 (br), 24.29, 24.73, 31.07, 100.63, 190.44; MS (EI) *m/e* (relative intensity): 220 (25, M⁺), 177 (12), 163 (50), 137 (80), 124 (100), 111 (31). Anal. calcd. for C₁₃H₂₁BO₂: C 70.91, H 9.55; found: C 70.68, H 9.45. **6** is soluble in cyclo-

hexane and benzene but less soluble in methylene chloride and acetonitrile.

Preparative photolysis of borinates

DBMBBN

A solution of **5** (0.10 g, 0.29 mmol) in anhydrous THF (50 mL) was distributed in 12 Pyrex tubes, sealed with septa, and purged with dry nitrogen for 5 min. The tubes were rotated in a merry-go-round under irradiation with RPR 3500 A lamps (24 W × 16) for 24 h. The photolysate gave two major GC peaks, at R_T 3.60 and 4.20. The crude product was chromatographed on a short column of silica gel 60 (20 cm³) to afford an impure fraction of the former peak that was rechromatographed to give **9**; ¹H NMR (CDCl₃) δ : 1.50–1.80 (10H, m), 2.11 (2H, br t), 2.30 (2H, br t), 4.10 (2H, s), 7.20–7.60 (8H, m), 7.81 (2H, m); MS (EI) *m/e*: 318 (5, M⁺), 213 (11), 105 (100), 91 (15), 77 (25); MS (CI) *m/e*: 319 (100, M⁺+1). Anal. calcd. for C₂₃H₂₆O: C 86.75, H 8.23; found: C 86.95, H 8.64.

When the photolysis was carried out in a mixture of methylene chloride and acetonitrile (1:1), the GC spectra showed both peaks in 38 and 36% yields. The fraction of $R_{\rm T}$ 4.20 (10) decreased rapidly on chromatography; one of its impure fractions showed ¹H NMR (CDCl₃) δ : 0.90 (2H, m), 1.50– 2.00 (12H, m), 2.72 (1H, m), 6.60 (1H, s), 7.11 (2H, m), 7.22 (3H, m), 7.30 (2H, m), 7.70 (2H, m), 8.01 (H, m); MS (EI) *m/e* (relative intensity): 318 (60, M⁺), 207 (5), 192 (5), 105 (100), 91 (11), 77 (31); MS (CI) *m/e*: 319 (100, M⁺+1).

In a separate photolysis, DBMBBN (0.17 g) in methylene chloride (50 mL) containing acetic acid (0.5 mL) was irradiated in a similar way to afford a 65% conversion. Repeated chromatography on a long silica gel column (40 cm³) gave 8as colorless crystals; ¹H NMR (CDCl₃) δ: 1.20–1.80 (14H, m), 1.96 (1H, q), 3.25 and 3.95 (AB quartet, diastereotopic -CH₂-, J = 16.3 Hz), 4.88 (1H, br s), 7.12 (1H, t), 7.23 (2H, t), 7.40 (2H, d), 7.43 (2H, t), 7.55 (1H, t), 7.84 (2H, d); ¹³C NMR (CDCl₃) δ: 26.31, 26.40, 26.70, 26.93, 27.08, 27.76, 28.03, 44.13, 47.49, 79.43, 125.75, 126.34, 127.79, 127.98, 128.59, 133.49, 137.35, 146.19, 202.56. Anal. calcd. for C₂₃H₂₈O₂: C 82.10, H 8.39; found: C 82.45, H8.12. This compound on injection to GC-MS gave a single peak for 11, at an early $R_{\rm T}$ of 1.77 min, which showed $M^++1 = 217$ by the CI mode, and m/e: 216 (M^+ , 10%), 133 (12), 120 (12), 105 (100), and 77 (35) by the EI mode.

BABBN

A solution of **7** in methylene chloride was irradiated for 24 h with RPR 3000A lamps, and the crude product was chromatographed to give four fractions, each containing a major component, that showed the $R_{\rm T}$ of the major component at 7.6, 8.5, 8.8, and 9.7 min and M⁺+1 = 257 of the major peak by the CI mode. Fraction one contained mostly **20** ($R_{\rm T}$ 8.8); ¹H NMR (CDCl₃) & 1.50–1.68 (10H, m), 1.69 (3H, s), 2.20 (2H, br t), 2.31 (2H, br t), 3.75 (2H, s), 7.40 (2H, m), 7.51 (1H, t), 7.95 (2H, m); ¹³C NMR (CDCl₃) & 19.30, 16.19, 26.22, 26.67, 26.99, 27.56, 31.41, 32.11, 44.38, 121.92, 128.09, 128.52, 132.70, 132.76, 137.63, 198.96; MS (EI) *m*/*e*: 256 (15, M⁺), 241 (3), 105 (100), 95 (21), 77 (31); MS (CI) *m*/*e*: 257 (M⁺+1). Fraction two con-

tained 21 (R_T 9.7) as the major component; ¹H NMR (CDCl₃) δ: 1.50–1.80 (14H, m), 2.18 (3H, s), 2.35 (1H, tt), 6.71 (1H, br s), 7.45 (2H, m), 7.51 (1H, m), 7.90 (2H, m); ¹³C NMR (CDCl₃) δ : 18.09, 26.08, 26.43, 26.70, 31.78, 41.19, 118.73, 123.38, 128.14, 139.09, 139.76, 166.44, 192.22; MS (EI) *m/e*: 256 (5, M⁺), 241 (6), 171 (12), 145 (71), 105 (100), 77 (41); MS (CI) *m/e*: 257 (M⁺+1). Fraction three contained **18** (R_T 7.6); ¹H NMR (CDCl₃) δ : 1.50–1.70 (10H, m), 2.05 (3H, s), 2.10 (2H, br t), 2.35 (2H, br t), 3.45 (2H, s), 7.05 (2H, m), 7.20 (3H, m); MS (EI) m/e: 256 (60, M⁺), 241 (100), 238 (26), 213 (45), 198 (25), 143 (51), 131 (80), 117 (75), 91 (90); MS (CI) *m/e*: 257 (100, M⁺+1), 239 (25), 199 (81). Fraction four contained **19** ($R_{\rm T}$ 8.5); ¹H NMR (CDCl₃) δ: 1.40–1.60 (10H, m), 1.61 (2H, m), 1.70 (3H, s), 1.81 (2H, m), 2.60 (1H, m), 6.05 (1H, s), 7.10 (2H, m), 7.30 (3H, m); MS (EI) *m/e*: 256 (15, M⁺), 241 (3), 105 (100), 95 (22), 77 (32); MS (CI) m/e: 257 (M⁺+1).

In a similar experiment, 7 (0.142 g, 0.51 mmol) in a solution of methylene chloride (50 mL) and acetic acid (0.5 mL) was irradiated for 23 h, and the photolysate was neutralized with K_2CO_3 . The crude product was chromatographed twice on a silica gel column to give a small fraction containing 17 and a fraction of 16 (0.026 g). ¹H NMR (CDCl₃) δ : 1.20– 1.90 (15H, m), 1.98 (3H, s), 2.87 and 3.22 (AB quartet, diastereotopic -CH₂-, J = 16.3 Hz), 4.45 (1H, br), 7.19 (1H, m), 7.28 (2H, m), 7.36 (2H, m); ¹³C NMR (CDCl₃) δ 26.20, 26.35, 26.72, 26.85, 27.04, 27.20, 27.46, 27.79, 32.22, 46.99, 49.88, 79.06, 125.61, 126.43, 127.65, 145.94, 211.72. The injection of 16 to GC gave a single peak at $R_{\rm T}$ 1.77 min, and the fragmentation pattern of **11**. The former fraction containing 17 was contaminated by benzoylacetone, and showed, on GC-MS determination, a peak at $R_{\rm T}$ 1.45 and the fragmentation pattern of 15 (vide infra).

A solution of **7** (0.023 g, 0.081 mmol) and eicosane (0.02 g, 0.071 mmol) in methylene chloride (10 mL) was divided in two quartz tubes; acetic acid (10) was added to the second one. These tubes, sealed with septa and purged with dry nitrogen, were irradiated with RPR 3000A for 19 h to give 70% conversions. The GC analysis of the photolysates (injection temperature 250°C) gave two peaks at 1.40 min (for **15**) and 1.59 min (for **11**) with a yield of 27%/15% for the first and 56%/20% for the second tube (with acetic acid).

Separately, two tubes of methylene chloride solution containing 7 (0.0078 M) and eicosane (0.0071 M), one with the presence (10 μ L) and the other with the absence of acetic acid, were irradiated under similar conditions except for using RPR 3500A lamps for 24 h to cause a 40% conversion. The GC analysis gave a yield for **15/11** of 12%/10%, within experimental error, for both photolysates.

AABBN

A solution of AABBN **6** (0.048 g, 0.22 mmol) in a mixture of cyclohexane and methylene chloride (9:1, 20 mL) was distributed in four quartz tubes and sealed under nitrogen. The solution was irradiated with RPR 2540A lamps for 8 h to cause about 80% conversion. A separate solution prepared from 0.04 g of **6** was irradiated with RPR 3000A lamps under the same conditions for 18 h to cause a 75% conversion. Both solutions were examined by GC–MS analysis to afford the major peaks shown in Table 1. A similar experiment was carried out with RPR 3500A lamps for 24 h to give a 15% conversion of 6. The crude product from 254 nm irradiation was chromatographed on silica gel columns with n-hexane elution to give unreacted 6. With increasing amounts of methylene chloride in *n*-hexane, 13 (7.8 mg), 14 (trace amount), and 12 (18 mg, 54%) were isolated. The physical data of 12: IR (Nujol): 3488 (O-H stretching), 1699.7 (C=O stretching), 1171.8 (tert-C-O stretching) cm⁻¹. ¹H NMR (CDCl₃) δ: 1.12 (3H, s), 1.15– 1.25 (2H, m), 1.35-1.83 (13H, m), 2.19 (3H, s), 2.55 and 2.66 (diastereotopic -CH₂-, J = 16.3 Hz); ¹³C NMR (CDCl₃) δ 23.36, 26.40, 26.53, 26.98, 27.14, 27.75, 29.01, 32.10, 46.60, 50.04, 75.09, 211.52. Anal. calcd. for C13H24O2: C 73.54, H 11.39; found: C 73.82, H 11.48. The injection of 12 into GC at 250°C gave two peaks at $R_{\rm T}$ 1.85 and 6.04 min in the ratio of 6:4. The former peak arising from 15 showed M⁺+1 at 155 by theCI mode, and m/e at 154 (1), 139 (1), 111 (10), 97 (14), 69 (100%), 43 (60) by the EI mode. The latter peak was due to 12 itself and showed m/e by the CI mode at 213 (M^++1 , 2), 195 (31), 155 (100) and by the EI mode at 197 (1), 111 (10), 101 (100), 69 (21), 43 (61). The physical data of 13: ¹H NMR (CDCl₃) δ : 1.40–1.55 (6H, m), 1.15–1.72 (4H, m), 1.68 (3H, s), 2.10 (3H, s), 2.14–2.20 (2H, m), 2.20–2.26 (2H, m), 3.13 (2H, s); ¹³C NMR (CDCl₃) δ: 19.18, 26.07, 26.22, 26.70, 26.90, 27.59, 29.15, 31.29, 32.02, 49.80, 121.58, 138.15, 207.56; MS (EI) *m/e*: 194 (15, M⁺), 179 (16), 151 (10), 136 (12), 109 (26), 95 (100), 81 (35), 69 (42). Anal. calcd. for C₁₃H₂₂O: C 80.35, H 11.41; found: C 80.11, H 11.58.

The crude product from 300 nm photolysis was worked up similarly to give **13** (trace amount), **14** (4.3 mg), and **12** (14.3 mg, 54%). **14** showed the following physical constants: ¹H NMR (CDCl₃) δ : 1.40–1.78 (14H, m), 2.09 (3H, d, J = 1.5 Hz), 2.16 (1H, br s), 2.18 (3H, s), 6.05 (1H, q, J = 1.5 Hz); ¹³C NMR (CDCl₃) δ : 17.47, 26.02, 26.39, 26.59, 31.65, 48.84, 121.60, 166.11, 199.32; MS (EI) *m/e*: 194 (10, M⁺), 179 (41), 151 (10), 136 (15), 111 (41), 109 (55), 98 (30), 95 (81), 81 (45), 69 (75), 43 (100). Anal. calcd. for C₁₃H₂₂O: C 80.35, H 11.41; found: C 80.28, H 11.21.

Sensitized photolysis of AABBN 6

AABBN (0.101 g, 0.46 mmol), hexadecane (0.05 mmol), and benzophenone (0.042 g, 0.23 mmol) in a mixture of cyclohexane and methylene chloride (9:1, 50 mL) were irradiated with RPR 3000A as above for 6 h to cause a 76% conversion of 6. GC analysis of the photolysate showed the peak % of 15, 14a, 13, 14, and 12 to be 4.3, 11, 16, 3.1, and 4.2%. Separately, a cyclohexane solution of 6 (0.0052 M), hexadecane (0.00033 M), and benzophenone (0.0032 M) was irradiated with RPR 3500A for 2.6 h to give a 60% conversion; the control experiment without benzophenone gave a <2% conversion. The GC analysis gave the peak % for 15, 14a, 13, 14, and 12 of 0.5, 3.5, 6.1, 3.2, and 0.5%. In both GC analyses the benzophenone peak decreased and several minor peaks were observed in $R_T > 10$ min. Examination of the crude products with HPLC gave no benzopinacol peak by coinjection.

The former solution was worked up in the usual way to give **13** (5.4 mg, 8%), **14** (10.0 mg, 15%), **12** (30.3 mg, 42%), and a mixture of **14a** and benzophenone. This mixture showed ¹H NMR (CDCl₃) δ : 1.40–1.80 (14H, m), 2.08 (3H, d, J = 1.2 Hz), 2.15 (3H, s), 6.05 (1H, br s); ¹³C NMR δ :

17.42, 26.34, 26.54, 25.97, 31.60, 31.82, 48.80, 121.56, 165.09, 199.31. This sample showed a GC peak at R_T 3.7 in contrast to that of 5.4 for **14**; the GC–MS of the former peak showed MS (EI) *m/e*: 194 (40, M⁺), 179 (42), 151 (10), 136 (12), 123 (25), 109 (71), 95 (100), 81 (50), 69 (40), 43 (98).

Quantitative analysis of the photoreaction of AABBN 6

A solution of **6** (7.2 mg, 0.0364 mmol) in cyclohexane (25 mL) was divided between five test tubes (5 mL each); tubes 3 and 4 also contained acetic acid (2 μ L). Tubes 1–4 were sealed under dry nitrogen and kept in a dark place. Tube 5 was sealed under dry oxygen. After 5 days, GC analysis showed a peak at R_T 1.23 min, in trace amounts, for tubes 1 and 5, and 2% for tube 3; after 8 days the intensity was 2–3% for all tubes.

Solutions of **6** (0.054–0.056 M) in cyclohexane, benzene, THF, methylene chloride, and acetonitrile were prepared to contain fixed concentrations of hexadecane (0.0131–0.0121 M). These solutions, placed in quartz tubes and sealed under nitrogen dried over solid CaCl₂ and NaOH pellets, were irradiated with RPR 3000A lamps for 21 h. The photolysates were analyzed by GC, and the % conversion of **6** was determined to give >96, 71, 74, 52, and 61% with respect to the internal standard. A set of similar experiments purged with nitrogen directly from a tank without drying gave the % conversion of 60, 64, no data, 41, and 56%.

Four tubes of a solution of **6** (0.007 M) in cyclohexane containing hexadecane as the internal standard and 1,3-pentadiene (45:55 mixture of *cis/trans*) at 0.014, 0.007, 0.0035, and 0.0 M were prepared and sealed under nitrogen. A solution containing the same substrate concentrations in a mixture of cyclohexane and methylene chloride was also prepared and distributed in four tubes to make the second set. They were irradiated for 5 h, and analyzed by GC for the % conversion of **6** to give 21, 22, 23, and 60% for the first set in cyclohexane, and 16, 19, 20, and 64% for the second set in the mixture. No new reaction product with the dienes was detected.

Five tubes of solution in a mixture of cyclohexane and methylene chloride (9:1) containing 6 (0.0082 M) and hexadecane (0.0046 M) were prepared. Tube 1 served as the control run. Acetic acid (0.167 M) was added to tube 2, and phenyl bromide (0.0082 and 0.0041 M) to tubes 3 and 4, respectively. These tubes were sealed under dry nitrogen except for tube 5, which was bubbled with a slow stream of dry oxygen while all of them were irradiated with RPR 3000 lamps. GC analysis of the photolysates showed the remaining % of 6 in each tube to be 100, 100, 85, 88, and 90%, respectively, at 1 h irradiation, and 88, 84, 44, 46, and 52%, respectively, at 4 h irradiation. The details of GC analysis of photolysates 1-4 after 4 h irradiation are given in Table 2. The photolysate of 6 under oxygen contained completely different products of highly oxidized materials with $R_{\rm T}$ 2-5 min; column chromatography failed to give pure products.

Four tubes of similar solutions containing **6** (0.0088 M) and hexadecane (0.0034 M) were prepared as tubes 6-9, to which were added 1,2-dibromoethane at 0.0, 0.02, 0.04, and 0.081 M, respectively. These tubes were irradiated as above. GC analysis of the photolysates gave % of remaining **6** to be 100, 67, 63, and 52%, respectively, after 1 h irradiation, and 98, 47, 46, 29%, respectively, after 2.5 h irradiation. The de-

tailed product analyses of the 2.5 h photolysate by GC for tubes 7–9 are given in Table 2, but those for the control run (tube 6) were too small and are assumed to be similar to that shown for tube 1.

Acknowledgments

The authors wish to thank the Natural Sciences and Engineering Research Council of Canada for generous support of this project. J.I. gratefully acknowledges the award of an Overseas Research Fellowship from the Japanese Government through the Ministry of Education, Science, Sports, and Culture.

References

- (a) K. Okada, Y. Hosoda, and M. Oda. J. Am. Chem. Soc. 108, 321 (1986); (b) Tetrahedron Lett. 27, 6213 (1986).
- K. Utimoto, T. Tanaka, and H. Nozaki. Tetrahedron Lett. 1167 (1972).
- 3. K. Okada, H. Inokawa, and M. Oda. Tetrahedron Lett. **30**, 4395 (1989).
- (a) S. Chatterjee, P.D. Davis, P. Gottschalk, M.E. Kurz, B. Sauerwein, X. Yang, and G.B. Schuster. J. Am. Chem. Soc. 112, 6329 (1990); (b) J.D. Wilkey and G.B. Schuster. J. Am. Chem. Soc. 113, 2149 (1991).
- (a) Y.L. Chow and X.-E. Cheng. Can. J. Chem. 69, 1331 (1991); 69, 1575 (1991); (b) Y.L. Chow, S.S. Wang, C.I. Johansson, and Z.-L. Liu. J. Am. Chem. Soc. 118, 11725 (1996).

- (a) Y.L. Chow, Y.-H. Zhang, M.X. Zhang, and A. Rassat. Chem. Phys. Lett. 272, 471 (1997); (b) H.-D. Ilge, E. Birckner, D. Fassler, D. Kozmenko, M.D. Kuz'min, and H. Hartmann. J. Photochem. 32, 177 (1986).
- 7. J. Yoon and A.W. Czarnik. J. Am. Chem. Soc. **114**, 3874 (1992).
- (a) M.F. Hawthorne and M. Reintjes. J. Org. Chem. 30, 3851 (1965); (b) R. Koster and G.W. Rotermund. Liebigs Ann. Chem. 689, 40 (1965); (c) L.H. Toporcer, R.E.Dessy, and S.I.E. Green. Inorg. Chem. 4, 1649 (1965); (d) R. Boese, R. Koster, and M. Yalpani. Chem. Ber. 118, 670 (1985).
- (a) N.J. Turro. Modern molecular photochemistry. Benjamin– Cummings, Menlo Park, Calif. 1978; (b) J. Gersdorf, J. Mattay, and H. Gorner. J. Am. Chem. Soc. 109, 1203 (1987); (c) Y.L. Chow, M. Vanossi, and S.-S. Wang. J. Photochem. Photobiol. A: 88, 125 (1995).
- K.L. Pillay, K. Hanaya, and Y.L. Chow. Can. J. Chem. 53, 3022 (1975).
- 11. Y.L. Chow and X. Liu. Can. J. Chem. 69, 1261 (1991).
- (a) K. Negishi and H.C. Brown. J. Am. Chem. Soc. 95, 6757 (1973); (b) P. Jacob III. J. Organomet. Chem. 156, 101 (1978).
- 13. K.U. Ingold and B.P. Roberts. Free-radical substitution reactions. John Wiley & Sons, New York. 1971. pp. 46–62.
- (a) J. Grotewold and E.A. Lissi. Chem. Commun. 1367 (1968); (b) J. Chem. Soc. (B), 264 (1968).
- L.H. Toporcer, D.E. Dessy, and S.I.E. Green. J. Am. Chem. Soc. 87, 1236 (1965).
- (a) W. Gerrard, M.F. Lappert, and R. Shafferman. J. Chem. Soc. 3648 (1958); (b) E.W. Abel, W. Gerrard, and M.F. Lappert. J. Chem. Soc. 5051 (1957); 1451 (1958).