

The THF complex of 2,6-diboraadamantane, **10**, was prepared as follows. To a suspension of 5.4 g (28 mmol) of **9** in 40 mL of THF was added at 25 °C 1.0 mL (19 mmol) of H₃B-SMe₂ with stirring. After 2 h, the solvent was pumped off, and the resulting solid was recrystallized from a mixture of CH₂Cl₂ and pentane to obtain 5.9 g (76% yield) of the bis(THF) complex: mp 145–147 °C; ¹H NMR (CDCl₃), multiplet centered on δ 4.3 (8 H, α protons of THF), another multiplet at δ 2.1 (8 H, β protons of THF), unresolved peak at δ 1.83 (8 H, methylene groups), and a broad peak at δ 0.85 (4 H, methine protons); ¹¹B NMR, single resonance at δ 21.5.

This study clearly illustrates the novelty of cyclic hydroboration in the synthesis of boraheterocycles. It describes the preparation and characterization of the 2,6-diboraadamantane ring system for the first time. The synthesis involves only two steps, representing a truly simple and novel construction of a tricyclic molecule from a monocyclic precursor.

Known organoborane conversion reactions are being examined for this 2,6-diboraadamantane system as a possible route to other adamantane derivatives. However, the chemical properties of the 2,6-diboraadamantane are themselves highly interesting and deserve exploration.

References and Notes

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- Some of the SMe₂ is lost during the thermal treatment. Therefore, it is necessary to add additional SMe₂ while recrystallizing **1**.
- The redistribution reaction between β-methoxy-9-BBN and H₃B-SMe₂ gives 9-BBN dimer in quantitative yield. For details, see: Brown, H. C.; Kulkarni, S. U. *J. Organomet. Chem.*, **1979**, *168*, 281–293.
- Trialkylboranes (R₃B) in general do not form strong isolable complexes with Et₂O or THF, but the corresponding complexes of **6** have been prepared and characterized.⁵
- The ¹H and ¹¹B NMR chemical shifts are with reference to tetramethylsilane and BF₃·OEt₂ respectively; the positive sign represents downfield from the reference.
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Norrish Type I Reaction of Aliphatic Cyclic Imides. General Reaction Pattern, Competition with Type II Processes, and Some Synthetic Applications¹

Summary: Aliphatic cyclic imides generally undergo Norrish type I reaction (α-cleavage) to form ene formimides, which, if the formimide and the olefin are conjugated, may lead to azetidinediones.

Sir: Extensive studies of photoreactions of cyclic imides have been described,² mainly involving Norrish type II reaction² and Paterno-Büchi reaction.^{2,3} While these reactions are evidently analogous to those of simpler carbonyl compounds,² Norrish type I reaction (α-cleavage), one of representative photoreactions of the carbonyl system,⁴ has not been studied except a very few examples.^{2,5} We now wish to report that

aliphatic cyclic imides undergo Norrish type I reaction generally to form ene formimides, and that, when the formimide and the olefin are conjugated with each other in the product, namely with certain succinimides as starting substrates, secondary transformation follows to give azetidinediones.⁶

The occurrence of type I reaction has been observed for *N*-ethylcamphorimide with ene formimide and ene carboxamide as products.^{5d} Further, irradiation of **1a**, a succinimide

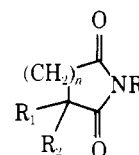


1a, *n* = 4; R = C₂H₅
b, *n* = 4; R = H
c, *n* = 4; R = CH₃
d, *n* = 2; R = C₂H₅
e, *n* = 2; R = H
f, *n* = 2; R = CH₃

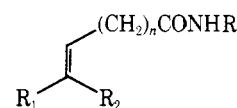
2a, *n* = 5; R = C₂H₅
b, *n* = 5; R = CH₃
c, *n* = 3; R = C₂H₅
d, *n* = 3; R = CH₃

with α,α'-disubstituents on the imide ring, gave the ring-expanded type II product in relatively poor yield,^{5d} the results suggesting concomitant occurrence of some competing reactions such as type I reaction. Irradiation⁷ of **1b** (cis) in 10 mM acetonitrile for 2 h gave 1-cyclohexanecarboxamide (40%), and the recovered **1b** (28%) turned out to be a mixture of cis and trans isomers (3:1) as determined by ¹H NMR,⁸ indicating that α-cleavage of the (O=C)-C bond occurred and the recombination resulted in scrambling of the ring juncture of **1b**. Interestingly a similar reaction of **1c** gave a spiro azetidinedione **2b** (27%; mp 92–93 °C) in place of an enamide, and a stereochemical mixture of **1c** (36%; cis/trans = 2:3).⁹ Careful reexamination of the photolysis of **1a** now gave, additionally, a homologous spiro azetidinedione **2a** (17%; mp 63–64 °C), and the recovered **1a** was a mixture (cis/trans = 1:1). Similar treatment of **1d** also afforded a spiro product **2c** (5%).

In order to see detailed structural requirements of the type I processes, photolysis of some unsymmetrically substituted imides **3** was examined. Irradiation of α-monosubstituted succinimides, **3a** and **3b**, afforded cis-trans mixtures of acrylamides **4a** (13%) and **4b** (10%), respectively. Similarly the

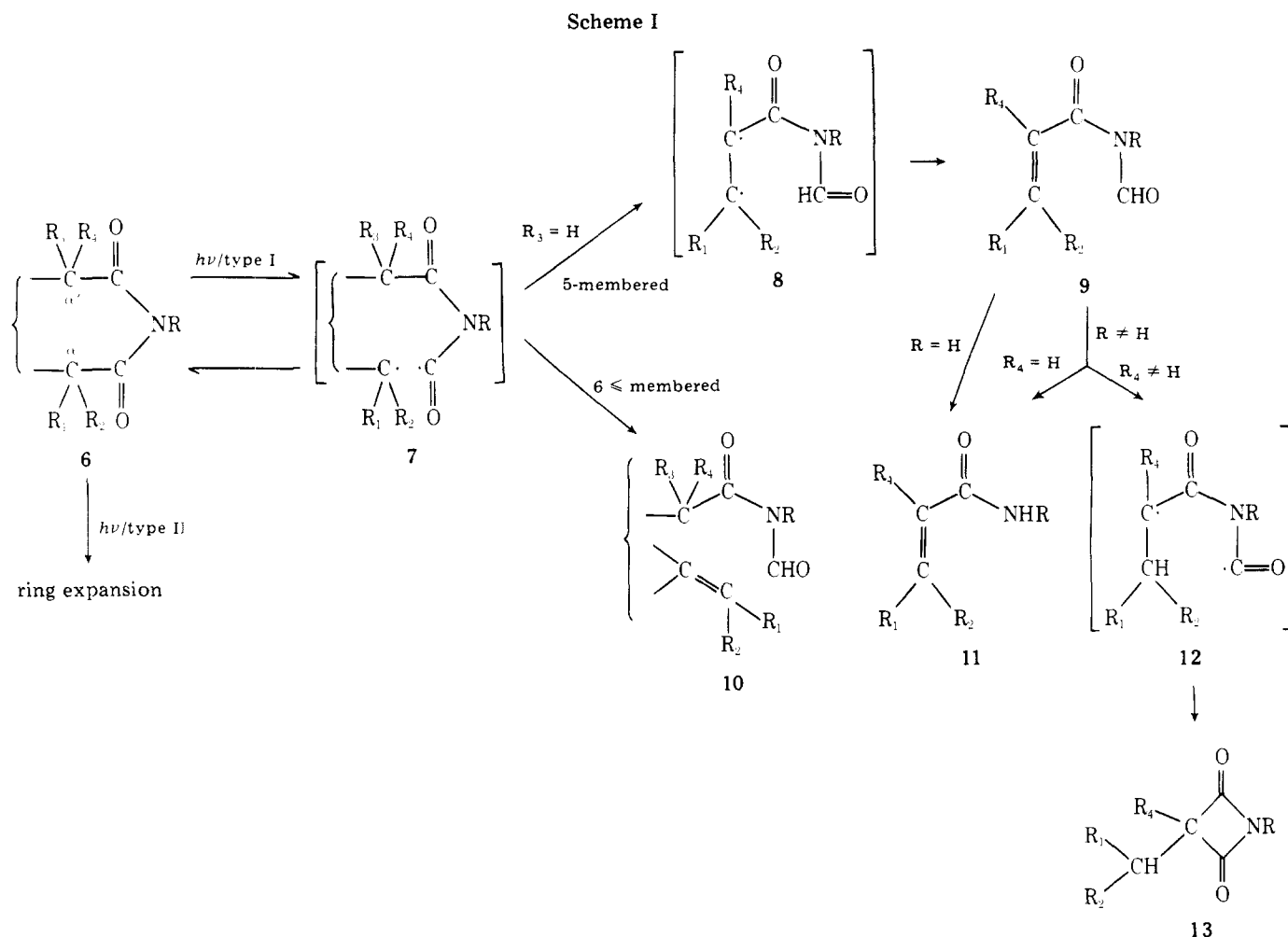


3a, *n* = 1; R₁ = CH₃; R₂ = R = H
b, *n* = 1; R₁ = R = CH₃; R₂ = H
c, *n* = 1; R₁ = R₂ = CH₃; R = H
d, *n* = 1; R₁ = R₂ = R = CH₃
e, *n* = 2; R₁ = R₂ = CH₃; R = H

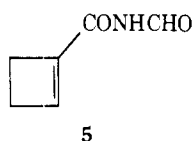


4a, *n* = 0; R₁ = CH₃; R₂ = R = H
b, *n* = 0; R₁ = R = CH₃; R₂ = H
c, *n* = 0; R₁ = R₂ = CH₃; R = H
d, *n* = 0; R₁ = R₂ = R = CH₃
e, *n* = 1; R₁ = R₂ = CH₃; R = CHO
f, *n* = 1; R₁ = R₂ = CH₃; R = H

α,α-dimethylsuccinimides, **3c** and **3d**, gave the corresponding acrylamides **4c** (55%; mp 106–107 °C) and **4d** (40%; mp 77–78 °C), respectively. By contrast, irradiation of α,α-dimethylglutarimide **3e** gave rise to ene formimide **4e** (22%; mp 88–89.5



°C) and ene amide **4f** (45%; mp 78–81 °C), in which the C=C bond and the amide (or imide) carbonyl are not conjugated. The above transformations suggest that the precursors of the amides would be the corresponding formimides. In fact, irradiation under similar conditions readily converted **4e** into **4f**, demonstrating that the primary photoproduct of α -cleavage (of the C–C bond) of the imide is the ene formimide, which, on further irradiation, subsequently undergoes the other type I reaction, namely, the cleavage of the (O=)–C–N bond¹⁰ of the *noncyclic* imide moiety. It is noteworthy that the absence of a substituent at the nitrogen excludes formation of an azetidinedione. To confirm the generality of this structural feature, photolysis of **1e** and **1f** was examined. As expected, **1f** gave a small-ring spiro system **2d** (mp 47–48 °C) in 31% yield,¹¹ while **1e** formed untractable polymeric products probably due to secondary reactions of initially formed unstable ene formimide **5**.

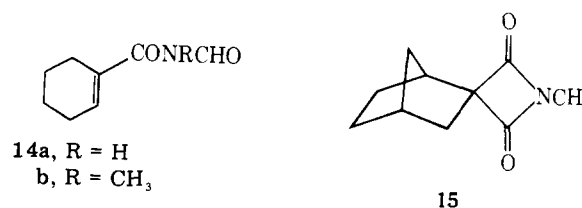


A general pattern of the type I processes of cyclic imides **6** which can accommodate all the observation is shown in Scheme I. Selectivity of the type I reaction can be interpreted in terms of cleavage of the weaker α bond or selective formation of the more stable alkyl radical determined by degree of substitution at the α (and α') carbon **7**. As postulated previously,^{5d} the imide radical **7** may intramolecularly abstract hydrogen to form either conjugated ene formimide **9** via **8** when the imide is five membered, or unconjugated ene

formimide **10** when it is six (or more) membered. Further reaction pathways are open to photounstable **9**; i.e., when R = H, the other type I reaction (C–N cleavage) gives rise to ene amide **11**. When R \neq H, the reaction courses of **9** are dependent on the α' substituent R₄. When R₄ = H, the product is again **11**. In the cases where R₄ \neq H, formation of azetidinedione **13** is the major pathway presumably via **12**, a biradical intermediate as resulting from increased stabilization of the C α' radical.^{13,14}

We have now the guidelines to understanding whole photoreactions of aliphatic cyclic imides. Intermolecular reactions are concerned both with type II² and Paterno–Büchi reaction.³ Intramolecular reactions depend considerably upon structural features of the imides.¹⁵ While type II processes obviously require the presence of C γ –H^{2,12} mainly in the N substituents, increased α (and α') substitution in the ring favors type I reactions. Usually type II reactions predominate leading to ring-expansion products, whereas type I reactions become increasingly competing when the α and α' carbons hold two or more substituents.

Finally, the above photo-ring-contraction reaction closely related to the α cleavage may provide a new synthetic entry to various 3,3-disubstituted azetidinediones including spiro systems which are otherwise difficult to access. For example,



irradiation of *N*-methylbicyclo[2.2.1]heptane-2,5-dicarboximide afforded a complex spiro system **15** (bp₂ 128–130 °C, 36%) to illustrate possible synthetic utility of this method.

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- (6) When the manuscript was in preparation, Maruyama et al. independently reported α -cleavage of cyclic imides; Symposium on Photochemistry, Kyoto, Nov., 1978; Abstr. Papers, p 80.
- (7) Unless otherwise stated, irradiation was performed using a quartz immersion well in acetonitrile solution (10 mM) degassed with nitrogen with a 60-W low-pressure mercury lamp for 1–2 h (60–80% conversion). All new compounds gave satisfactory elemental analyses and reasonable spectral data (UV, IR, ¹H NMR, mass).
- (8) The *cis*–*trans* ratio of a mixture was determined by ¹H NMR observing the peaks of the C_α–H and C_{α'}–H.
- (9) The *trans* isomer **1c** (mp 119–120 °C), separated by preparative TLC, was readily transformed into *cis*-**1c** by treatment with alumina in dichloromethane.
- (10) α -Cleavage of a (O=C)–N bond is considered in the photoaddition of *N*-methylphthalimide with conjugated dienes: Mazzocchi, P. H.; Bowen, M. J.; Narain, N. K. *J. Am. Chem. Soc.* **1977**, *99*, 7063.
- (11) It is assumed, in analogy with the other photoreactions of aliphatic imides, that α -cleavage occurs via n, π^* state.^{2,3,12} Irradiation in the presence of oxygen significantly quenched the formation of **2d** from **1f**, suggestive of at least partial involvement of the triplet state.
- (12) Kanaoka, Y.; Hatanaka, Y. *J. Org. Chem.* **1976**, *41*, 400.
- (13) Intramolecular hydrogen abstraction by the β carbon in α,β -unsaturated carbonyl systems has been known: cf. Hasegawa, T.; Watabe, M.; Aoyama, H.; Omote, Y. *Tetrahedron*, **1977**, *33*, 485, papers cited therein.
- (14) In order to confirm the mechanism, ene imides **14** were prepared and irradiated. In fact, **14a** and **14b** gave 1-cyclohexenecarboxamide (87%) and **2b** (42%), respectively, in agreement with the postulate.
- (15) **Note Added in Proof:** Type I and II processes of noncyclic imides have been studied. Jameson, C. W.; Thesis, University of Maryland (1975). Mazzocchi, P. H.; Jameson, C. W.; unpublished results.

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