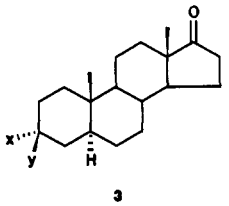
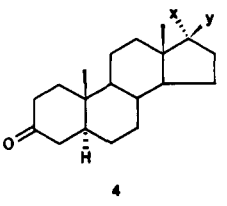


3



4

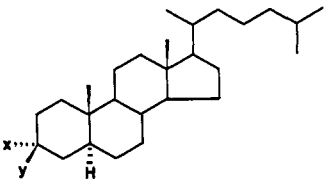
3a (3 α): x = OH, y = H

3b (3 β): x = H, y = OH

4a (17 α): x = OH, y = H

4b (17 β): x = H, y = OH

4c: x = H, y = CH_2=CH-CO_2-



5

5a (3 α): x = OH, y = H

5b (3 β): x = H, y = OH

5c: x = H, y = CH_2=CH-CO_2-

is in complete contrast to reduction in solution, which gives ca. 99% preference for reduction at the 3-position.[8] In contrast, when polymer beads imprinted with **5c** were used, essentially complete reduction of the 3-position was obtained, (entry 7, Table I). These latter beads were also used with their "true" substrate cholestan-3-one, **2**. The cholestanol obtained in this way was predominantly the less readily available 3α-OH isomer **5a** (3α-OH/3β-OH = 72/28, entry 4, Table I). Again this is in sharp contrast to the result from hydride reduction in homogeneous solution, which gives a ratio 3α-OH/3β-OH = 10/90.

In order to ascertain that nonspecific surface effects from the polymer are not the origin of these results, a hydroxylated polymer without molecular imprints was prepared by copolymerizing methyl acrylate and divinylbenzene. This polymer was activated in the same way as the imprinted polymers and then reacted with **1** and **2**. The results (entries 8 and 9, Table I) were essentially the same as those for reaction in homogeneous solution.

It is interesting to note that some stereocontrol is evident also in the reduction of the 17-keto group of **1** because the 17α-OH/17β-OH ratio is higher in the reduction with template polymer (30/70) than without (4/96). The result is, however, much less spectacular than that for the reduction of **2**, probably due to the interference from the 18-methyl group.

The polymer quality is important to the results, and early experiments with very swellable polymers, which are often advantageous because of fairly free diffusion of solvents and reactants, were less successful. Examples are entry 2, Table I, which shows about 15% reduction at the 3-position of **1**, and entry 5, which gave only 26% of the 3α-OH isomer **5a**. Also, bulk polymers, which have been frequently used in the earlier studies, are less satisfactory, and the result from one experiment with compound **2** (entry 6, Table I) shows only marginally better selectivity for the 3α-OH isomer than reduction in homogeneous solution. Although the studies described here are still at an early stage, they appear promising and very clearly show that selective functionalization is possible on the basis of molecular shape and stereochemical information transferred from the imprint molecules to the polymer matrix together with the attractive interactions between the partial charges present on the ketones and the reactive center.

Acknowledgment. We are grateful to NUTEK and Carl Tryggers Stiftelse för vetenskaplig forskning for financial support.

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Zirconacyclobutanes from Thermal Rearrangement of Permethylzirconocene Bis(allyl) and Related Complexes. An Unprecedented Synthesis of β-Substituted Metallacyclobutanes

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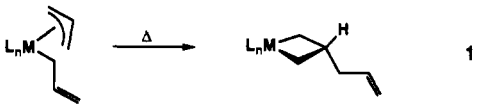
The investigation of metallacyclobutane complexes has been a compelling focus in organotransition metal chemistry for two decades.[2] Metallacyclobutanes are known throughout the transition series and have been prepared by numerous methods,[2] including cyclopropane oxidative addition,[3] cyclometalation,[4] coupling of alkenes with metal alkylidenes or alkylidene precursors,[2a] addition of 1,3-dimagnesiopropanes and related dianions,[5] the rearrangement of a σ-cyclopropyl hydride complex,[6] and nucleophilic addition to the central carbon of η^3-allyl complexes.[7] Here we report an unprecedented entry into the metallacyclobutane structural class via an unusual thermal rearrangement of zirconium bis(allyl) and related complexes (eq 1).



1

Permethylzirconocene bis(allyl) complex **2** was obtained from the addition of allylmagnesium chloride to dichloride **1**[8] (Scheme

(1) Department of Chemistry, Indiana University, Bloomington, IN.

(2) Reviews: (a) Feldman, J.; Schrock, R. R. *Prog. Inorg. Chem.* **1991**, *39*, 1. (b) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science: Mill Valley, CA, 1987; Chapters 9 and 16. (c) Lindner, E. *Adv. Heterocycl. Chem.* **1986**, *39*, 237. (d) Dragutan, V.; Balaban, A. T.; Dimonie, M. *Olefin Metathesis and Ring Opening Polymerization of Cycloolefins*; Wiley: New York, 1986. (e) Grubbs, R. H. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 8, p 499. (f) Chappell, S. D.; Cole-Hamilton, D. J. *Polyhedron* **1982**, *1*, 739. (g) Puddephatt, R. J. *Coord. Chem. Rev.* **1980**, *33*, 149.

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(6) Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1984**, *106*, 7272.

(7) (a) Ephritikhine, M.; Green, M. L. H.; MacKenzie, R. E. *J. Chem. Soc., Chem. Commun.* **1976**, 619. Ephritikhine, M.; Francis, B. R.; Green, M. L. H.; MacKenzie, R. E.; Smith, M. J. *J. Chem. Soc., Dalton Trans.* **1977**, 1131. Adam, G. J. A.; Davies, S. G.; Ephritikhine, M.; Todd, P. F.; Green, M. L. H. *J. Mol. Catal.* **1980**, *8*, 15. (b) Hegedus, L. S.; Darlington, W. H.; Russell, C. E. *J. Org. Chem.* **1980**, *45*, 5193. Carfagna, C.; Galarini, R.; Musco, A.; Santi, R. *Organometallics* **1991**, *10*, 3956 and references therein. Hoffmann, H. M. R.; Otte, A. R.; Wilde, A. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 234. (c) See ref 6 and the following: McGhee, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 3388. (d) Tjaden, E. B.; Stryker, J. M. *J. Am. Chem. Soc.* **1990**, *112*, 6420. Wakefield, J. B.; Stryker, J. M. *J. Am. Chem. Soc.* **1991**, *113*, 7057. Tjaden, E. B.; Stryker, J. M. *Organometallics* **1992**, *11*, 16.

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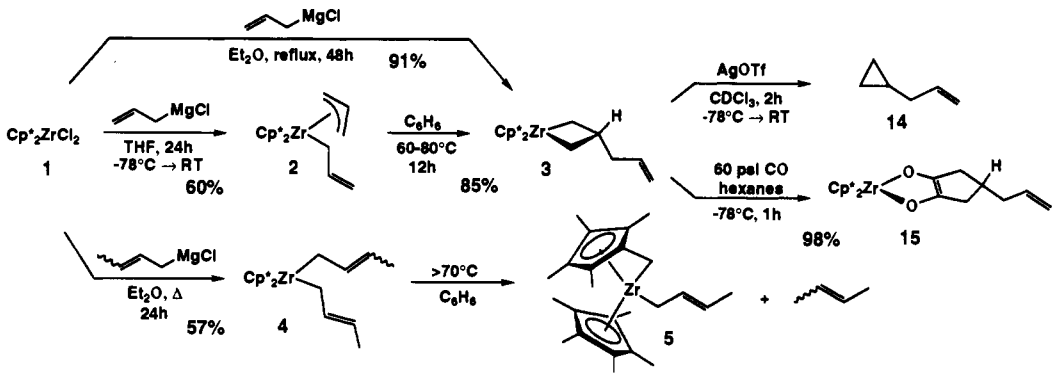
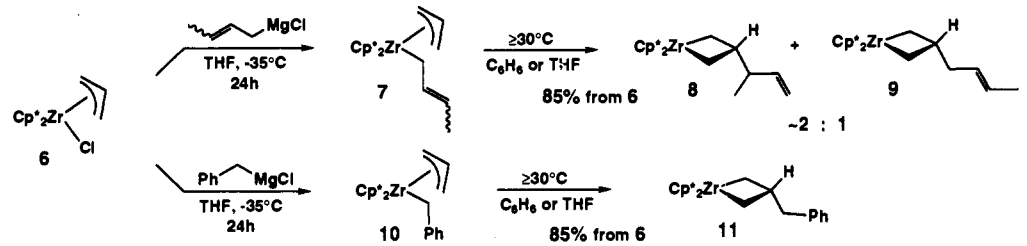
Scheme I



Scheme II



I).[9,10] As in the zirconocene series,[10,11] the allyl ligands in complex **2** are fluxional and in rapid equilibrium at room temperature by ^{1}H NMR spectroscopy, broadening but not reaching the slow-exchange limit even at −80 °C. Infrared spectroscopy, however, indicates a structure having one η^3-allyl and one η^1-allyl ligand.[10a,11c] On warming to ≥50 °C, bis(allyl) complex **2** converts slowly and quantitatively to β-allylzirconacyclobutane **3**, isolated in 85% yield after crystallization from pentane.[9,12] A higher overall yield of zirconacycle **3** is obtained directly from the dichloride on addition of allyl Grignard in ether at reflux for a prolonged period.[13] Kinetic analysis of this facile rearrangement reveals that the reaction is first order in substrate [k = 2.2(2) × 10^{-5} s^{-1} in C_6D_6 at 41 °C] to greater than 3 half-lives at each of three concentrations. The rate of the rearrangement is unaffected by ambient light and a small but significant solvent effect is observed: the reaction proceeds faster in cyclohexane-d_{12} [4.2(2) × 10^{-5} s^{-1} at 41 °C] than in either C_6D_6 or THF-d_8 [2.1(2) × 10^{-5} s^{-1} at 41 °C]. Activation parameters reveal little entropic contribution [$\Delta H^{\ddagger}$ = 25(1) kcal mol^{-1}, $\Delta S^{\ddagger}$ = −0.3(3) eu, calculated using five temperatures from 40 to 80 °C]. These data are inconsistent with a polar mechanism for the rearrangement (i.e., dissociation to ionic fragments), but consistent with either concerted or free radical pathways.

Further insight into mechanistic and synthetic aspects of the rearrangement was obtained via changes in the bis(allylic) framework. Addition of crotyl Grignard (mixture of *E* and *Z* isomers[14]) to dichloride **1** gave bis(crotyl) complexes **4** as a 1.5:1 mixture of *E,E* and *E,Z* isomers.[9] As observed for $(C_5H_5)_2Zr(crotyl)_2$,[10c] the isomeric complexes **4** equilibrate slowly at room temperature. In contrast to bis(allyl) **2**, however, both crotyl ligands in complex **4** are η^1-coordinated at the primary carbon. This structural difference is accompanied by a complete change in reactivity: no reaction is obtained at temperatures up to ca. 70 °C, at which point the complex undergoes σ-bond metathesis, giving "tuck-in" crotyl complex **5**[9] and 2-butene by NMR spectroscopy. The identity of complex **5** has been confirmed by independent synthesis.[15]

These results suggest that η^3-coordination, readily accessible to the allyl ligands in complex **2** but not the crotyl ligands in complex **4**, is required for facile rearrangement. This leads to two predictions: (1) the mixed allyl crotyl complex **7** *will* rearrange, and (2) it will do so by preferential migration of the η^1-crotyl ligand. To evaluate this hypothesis, allyl crotyl complex **7** was prepared by treatment of the allyl chloride complex **6**[16] with crotyl

(9) Complete spectroscopic and analytical data are included as supplementary material.

(10) $(C_5H_5)_2Zr(allyl)_2$ and analogous crotyl derivatives are known: (a) Martin, H. A.; Lemaire, P. J.; Jellinek, F. *J. Organomet. Chem.* **1968**, *14*, 149. (b) Yamamoto, Y.; Maruyama, K. *Tetrahedron Lett.* **1981**, *22*, 2895. (c) Mashima, K.; Yasuda, H.; Asami, K.; Nakamura, A. *Chem. Lett.* **1983**, 219.

(11) Other d^0 group IV allyl complexes: (a) Blenkers, J.; De Liefde Meijer, H. J.; Teuben, J. H. *J. Organomet. Chem.* **1981**, *218*, 383. (b) McDade, C.; Bercaw, J. E. *J. Organomet. Chem.* **1985**, *279*, 281. See also: Sanner, R. D. Ph.D. Dissertation, California Institute of Technology, 1977. Erwin, D. K. Ph.D. Dissertation, California Institute of Technology, 1979. Roddick, D. M. Ph.D. Dissertation, California Institute of Technology, 1984. (c) Erker, G.; Engel, K.; Dorf, U.; Atwood, J. L.; Hunter, W. E. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 914. Erker, G.; Berg, K.; Krüger, C.; Müller, G.; Angermund, K.; Benn, R.; Schroth, G. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 455. Erker, G.; Berg, K.; Angermund, K.; Krüger, C. *Organometallics* **1987**, *6*, 2620. (d) Highcock, W. J.; Mills, R. M.; Spencer, J. L.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1986**, 829. (e) Jordan, R. F.; LaPointe, R. E.; Bradley, P. K.; Baenziger, N. *Organometallics* **1989**, *8*, 2892. (f) Vance, P. J.; Prins, T. J.; Hauger, B. E.; Silver, M. E.; Wemple, M. E.; Pederson, L. M.; Kort, D. A.; Kannisto, M. R.; Geerligs, S. J.; Kelly, R. S.; McCandless, J. J.; Huffman, J. C.; Peters, D. G. *Organometallics* **1991**, *10*, 917 and references therein. (g) Wielstra, Y.; Duchateau, R.; Gambarotta, S.; Bensimon, C.; Gabe, E. *J. Organomet. Chem.* **1991**, *418*, 183. (h) Horton, A. D. *Organometallics* **1992**, *11*, 3271.

(12) IR and NMR spectroscopic data for the zirconacyclobutane complexes are fully consistent with known zirconacyclobutane complexes: See refs 2a and 5c and the following: Seetz, J. W. F. L.; Van de Heisteeg, B. J. J.; Schat, G.; Akkerman, O. S.; Bickelhaupt, F. *J. Mol. Catal.* **1985**, *28*, 71.

(13) The addition of allyl Grignard to $(C_5H_5)_2MoCl_2$ gives the analogous β-allylmolybdacyclobutane. No mechanistic information was reported, but the reaction is proposed to proceed via central carbon alkylation of the ionized mono(allyl) intermediate $[(C_5H_5)_2Mo(\eta^1\text{-allyl})]^+Cl^-$.[7a]

(14) Hutchison, D. A.; Beck, K. R.; Benkeser, R. A.; Grutzner, J. B. *J. Am. Chem. Soc.* **1973**, *95*, 7075.

(15) "Tuck-in" complex **5** is obtained in 86% yield on addition of crotyl Grignard in Et_2O to the "tuck-in" chloride complex $(\eta^5\text{-}C_5Me_5)(\eta^5{:}\eta^1\text{-}C_5Me_4CH_2)Zr(Cl)$, itself prepared by thermolysis (125 °C, toluene, 3 days, 80%) of $(C_5Me_5)_2Zr(CH_2{}^tBu)Cl$, as reported for analogous complexes: Bulls, A. R.; Schaefer, W. P.; Serfas, M.; Bercaw, J. E. *Organometallics* **1987**, *6*, 1219. Carney, M. J.; Walsh, P. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1990**, *112*, 6426. See also: Shock, L. E.; Brock, C. P.; Marks, T. J. *Organometallics* **1987**, *6*, 232. Addition of allyl Grignard under the same conditions gives the corresponding allyl "tuck in" **13**.

(16) Complex **6**[9] is prepared in 40–50% yield by treatment of dichloride **1** with allyl Grignard (1.2 equiv, THF, 0 °C), followed by a period at reflux to convert the accompanying bis(allyl) complex **2** to the more soluble zirconacyclobutane **3** (ca. 30%), from which allyl chloride **6** and residual dichloride **1** are readily separated by fractional crystallization from cold pentane. Treatment of the crude mixture with a second aliquot of allyl Grignard followed by heating converts the remaining dichloride to **6** and a small amount of zirconacycle **3**, from which pure allyl chloride **6** is obtained by recrystallization. Higher yielding procedures will be described in a full account.

Grignard (0.98 equiv), leading to isolation of complex **7** as a 2:1 mixture of *E* and *Z* isomers (Scheme II).[17] Consistent with previous spectroscopic observations, the allyl ligand in this complex is rapidly fluxional at ambient temperature, while the crotyl ligand is η^1-bonded exclusively at the primary carbon, but equilibrating slowly at room temperature between *E* and *Z* isomers.[18] The rearrangement of complex **7** proceeds even at room temperature and, as anticipated, occurs *exclusively by migration of the crotyl ligand*. Isomeric zirconacyclobutane complexes **8**[9] and **9**[9] are obtained in a ratio of 2:1; the major product **8** derives from crotyl migration with allylic transposition. Analytically pure zirconacycle **8** is obtained by fractional crystallization from cold pentane; solutions enriched in the minor isomer **9** have been characterized spectroscopically.[19]

Allylic transposition, however, is not a requirement for facile rearrangement. Allyl benzyl complex **10**[17] (Scheme II), prepared by the addition of benzyl Grignard to chloride complex **6**, rearranges under conditions similar to those for complex **7**, affording β-benzylzirconacyclobutane **11**[9] in high yield. Some "activation" of the migrating group is also necessary: $(C_5Me_5)_2Zr(allyl)Me$, **12**,[9] prepared from complex **6** and MeMgI, fails to rearrange, finally decomposing at 110 °C to yield a complex mixture of products including methane and "tuck-in" allyl complex (η^5-C_5Me_5)(η^5:η^1-$C_5Me_4CH_2$)Zr(allyl), **13**,[9] the latter confirmed by independent synthesis.[15] While this result suggests that radical-stabilizing substituents are required to observe facile migration, neither the precise nature of this stabilization nor the involvement of metal–carbon bond homolysis in the rearrangement mechanism has as yet been unambiguously determined.

The zirconacyclobutane complexes are versatile templates for conversion to organic ring systems. Oxidation of β-allylzirconacycle **3** with AgOTf induces reductive elimination,[20] giving allylcyclopropane **14** quantitatively (Scheme I), identified by comparison to an authentic sample.[21] Quantitative conversion to the carbocyclic enediolate **15**[9] is obtained on treatment with CO, a well-precedented transformation for metallocene dialkyl complexes.[22] The carbonylation procedure thus completes a zirconium-mediated net transformation of 2 equiv each of allyl Grignard and CO to a highly functionalized cyclopentanoid ring system, indicative of the potential utility of zirconacyclobutanes in synthetic transformations.

In summary, the thermal rearrangement of zirconocene bis(allyl) and related complexes to zirconacyclobutanes has been demonstrated, proceeding via an unprecedented reactivity pattern involving hydrocarbyl ligand migration to the β-carbon of an η^3-allyl moiety.[23] Although a concerted mechanism cannot be excluded, the product distribution obtained from the rearrangement of complex **7** is suggestive of a radical-mediated process. The concerted pathway, best visualized as the insertion of a tethered olefin into the zirconium–carbon bond of the migrating ligand, demands that the migration proceeds exclusively to the internal olefin carbon, leading to the observed Zr(IV) metallacycle, rather than the geometrically more accessible terminal carbon, leading to the formally Zr(II) olefin complex. It should be noted that thermal migratory insertion of olefins into *neutral* zirconocene alkyl complexes is unknown. Perhaps significantly, however, the photochemical, *free radical-mediated* insertion of ethylene into the metal–methyl bond of $(C_5H_5)_2ZrMe_2$ has been described.[24] Further definition of the scope and mechanistic details of this novel isomerization process are under investigation.

Acknowledgment. We thank Professors R. F. Jordan and J. E. Bercaw for insightful discussions, suggestions, and access to unpublished results. We also acknowledge the expertise of D. Mahlow and A. Dunn of the University of Alberta Microanalytical Laboratory for elemental analyses of many very difficult compounds. Financial support from the National Science Foundation (U.S.) and an American Cyanamid Faculty Award is gratefully acknowledged.

Supplementary Material Available: Spectroscopic and analytical data for compounds **2–13** and **15** (7 pages). Ordering information is given on any current masthead page.

(17) Isomeric allyl crotyl complexes **7** and allyl benzyl complex **10** are too reactive in solution to be obtained in analytical purity; these complexes have been characterized spectroscopically.[9]

(18) This isomerization presumably occurs via intermediate η^3-crotyl and "internal" η^1-crotyl (3-butenyl) complexes, neither of which are detected spectroscopically.[10c]

(19) Trace quantities of a third product are observed by ^{13}C NMR spectroscopy of samples enriched in the minor isomer, consistent with a (*Z*)-butenyl-substituted zirconacyclobutane structure.

(20) Burk, M. J.; Tumas, W.; Ward, M. D.; Wheeler, D. R. *J. Am. Chem. Soc.* **1990**, *112*, 6133 and references therein.

(21) Srinivasan, R. *J. Am. Chem. Soc.* **1961**, *83*, 4923. Farneth, W. E.; Thomsen, M. W. *J. Am. Chem. Soc.* **1983**, *105*, 1843.

(22) Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 2716. Hofmann, P.; Frede, M.; Stauffert, P.; Lasser, W.; Thewalt, U. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 712. Erker, G.; Czisch, P.; Schlund, R.; Angermund, K.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 364. Petersen, J. L.; Egan, J. W., Jr. *Organometallics* **1987**, *6*, 2007.

(23) This rearrangement process bears at least superficial similarity to the proposed migration of a phenyl ligand to an η^3-oxaallyl intermediate in the formation of a β-phenyloxametallacyclobutane complex from $(Me_3P)_4Ru(OCMe{=}CH_2)(Ph)$; see: Hartwig, J. F.; Bergman, R. G.; Andersen, R. A. *Organometallics* **1991**, *10*, 3326.

(24) Van Leeuwen, P. W. N. M.; van der Heijden, H.; Roobek, C. F.; Frijns, J. H. G. *J. Organomet. Chem.* **1981**, *209*, 169.

Efficient Chiral Crystallization and Asymmetric Synthesis via Solid-State Di-π-methane-Type Photorearrangements

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The hitherto reported examples of so-called absolute asymmetric crystallization and synthesis[1,2] have established a simple, inexpensive, and nonclassical approach to the preparation of optically enriched compounds. In these cases, a molecularly achiral substrate adopts a chiral orientation—in the absence of "external" chiral inducing agents—during crystallization. The chirality of the molecule in the crystal can then be trapped through a solid-state (photo)reaction into product stereocenters.[2a] In a project aimed at a novel synthetic concept for access to mixed linearly and angularly fused polycyclic natural products, we came across photochemical solid-state di-π-methane-type rearrangements[3a,4]

(1) For an early reference to spontaneous asymmetric crystallization, see Havinga, E. *Chem. Weekbl.* **1941**, *38*, 642–649; *Biochim. Biophys. Acta* **1954**, *13*, 171–174.

(2) For some leading references on absolute asymmetric synthesis, see (a) Green, B. S.; Lahav, M.; Rabinovich, D. *Acc. Chem. Res.* **1979**, *12*, 191–197. (b) Scheffer, J. R.; Garcia-Garibay, M. In *Photochemistry on Solid Surfaces*; Anpo, M., Matsuura, T., Eds.; Elsevier: Amsterdam, 1989; pp 501–525. (c) Sekine, A.; Hori, K.; Ohashi, Y.; Yagi, M.; Toda, F. *J. Am. Chem. Soc.* **1989**, *111*, 697–699. (d) Vaida, M.; Popovitz-Biro, R.; Leiserowitz, L.; Lahav, M. In *Photochemistry in Organized and Constrained Media*; Ramamurthy, V., Ed.; Verlag Chemie: Weinheim, 1990; pp 247–302. (e) Chung, C.-M.; Hasegawa, M. *J. Am. Chem. Soc.* **1991**, *113*, 7311–7316. (f) Chen, J.; Scheffer, J. R.; Trotter, J. *Tetrahedron* **1992**, *48*, 3251–3274.

(3) (a) Roughton, A. L., Ph.D. Thesis, Max-Planck-Institut für Strahlenchemie, University of Essen, 1992. A more detailed account of these aspects is in preparation. (b) Solid-state irradiation afforded traces of intramolecular [2 + 2] photoproduct (ca. 2–5% of the isolated solution-phase products), which confirms some degree of ring rotation.

0002-7863/93/1515-2085$04.00/0