Control of Organic Photoreactions by Molecular Design. The Photochemistry of Ortho-Ortho Phenyl-Bridged 4,4-Diphenyl-2-cyclohexen-1-ones†

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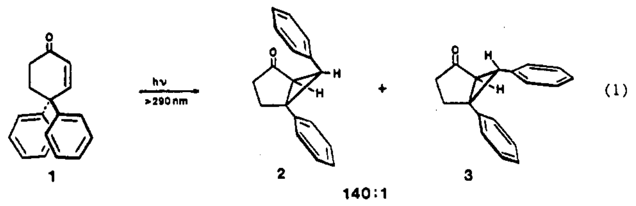
Spiro[2-cyclohexene-1,9′-fluoren]-4-one (**6**) and 6′,7′-dihydrospiro[2-cyclohexene-1,12′(5′*H*)-dibenzo[*a*,*d*]-cycloocten]-4-one (**9**) have been synthesized and their photochemistry has been studied. The irradiation products are compared to those of the previously reported 4,4-diphenyl-2-cyclohexen-1-one (**1**). The zero-carbon ortho–ortho phenyl linkage in **6** results in a major diversion from the normal reaction course due to geometrical constraint while rearrangement of three-carbon-bridged **9** parallels the reaction observed for **1**. Mechanisms to account for the products formed are presented and discussed.

Introduction

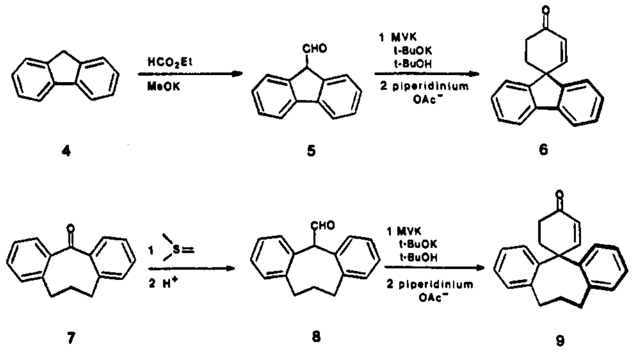
In 1964, it was reported[1] that the photolysis of 4,4-diphenyl-2-cyclohexen-1-one (**1**) at 300–340 nm (n → π* band) results predominantly in the formation of the *trans*- and *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-ones, **2** and **3**, in a ratio of 140:1, respectively (see eq 1). Following electronic excitation and intersystem crossing to the triplet, phenyl migration, electron demotion, and three-ring closure afford the bicyclic ketones. The preferential production of the trans stereoisomer has been attributed[2] to a concerted mechanism governed by orbital overlap; the minor cis product is thought to arise from a small stepwise component in the overall process or from secondary photochemistry of the trans product.



The ability to exercise greater control in organic photoreactions is an important goal for organic chemists since this would increase their utility in synthetic applications. To this end, the current study was initiated to explore the possibility of altering the stereochemical outcome of the well-characterized 4,4-diphenyl-2-cyclohexen-2-one rearrangement by bridging the ortho positions of the two phenyl groups that normally migrate apart during the reaction course. Then, by varying the length of the connecting chain, we hoped to establish the limits of this control.

The initial synthetic targets were spiro[2-cyclohexene-1,9′-fluoren]-4-one (**6**) and 6′,7′-dihydrospiro[2-cyclohexene-1,12′(5′*H*)-dibenzo[*a*,*d*]cycloocten]-4-one (**9**) which correspond, respectively, to substrates having ortho–ortho phenyl bridges of zero and three carbons. A priori, it was expected that **6** would be prevented from giving the normally favored trans diphenyl product due to strain imposed by the zero-carbon linkage as the phenyls move apart. On the other hand, molecular models suggested that the three-carbon bridge in **9** would be sufficient to permit the formation of a trans diphenyl product. This bridged trans diphenyl bicyclic product, though strained, should still predominate if a concerted mechanism is operating and would serve as additional evidence supporting an orbital overlap controlled process.

Scheme I. Synthesis of the Photochemical Reactants



Results

Synthesis of the Photochemical Substrates. The syntheses of the compounds used in this study are summarized in Scheme I. Spiro[2-cyclohexene-1,9′-fluoren]-4-one (**6**) was prepared by the method of Plieninger and co-workers.[3] Starting from fluorene, formylation[4] followed by spiroannulation with methyl vinyl ketone afforded the spirofluorenyl ring system in 39% overall yield. The eight-ring spiro enone **9** was prepared starting from the known 5,6,7,12-tetrahydrodibenzo[*a*,*d*]cycloocten-12-one (**7**).[5] Epoxidation with dimethylsulfonium methylide[6] and subsequent acid-catalyzed rearrangement to the homologous aldehyde[7] was followed by condensative spirocyclization with methyl vinyl ketone to give **9** in 17% overall yield.

Exploratory Photochemistry and Structure Elucidation of the Photoproducts. The photochemical reactions were carried out by using conditions comparable to those reported for 4,4-diphenyl-2-cyclohexen-1-one.[1] Irradiation of a 10^{-2} M solution of **6** in degassed *tert*-butyl alcohol through a Pyrex filter led to the formation of two photoproducts. The spectra of the major photoproduct

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† This paper is dedicated to Professor Howard E. Zimmerman on the occasion of his 60th birthday.

(1) Zimmerman, H. E.; Wilson, J. W. *J. Am. Chem. Soc.* **1964**, *86*, 4036–4042.

(2) (a) Zimmerman, H. E.; Hancock, K. G. *J. Am. Chem. Soc.* **1968**, *90*, 3749–3760. (b) Zimmerman, H. E. *Tetrahedron* **1974**, *30*, 1617–1628.

(3) Plieninger, H.; Ege, G.; Ullah, M. I. *Chem. Ber.* **1963**, *96*, 1610–1617.

(4) Von, I.; Wagner, E. C. *J. Org. Chem.* **1944**, *9*, 155–169.

(5) Winthrop, S. O.; Davis, M. A.; Herr, F.; Stewart, J.; Gaudry, R. *J. Med. Chem.* **1963**, *6*, 130–132.

(6) Corey, E. J.; Chaykovsky, M. *J. Am. Chem. Soc.* **1965**, *87*, 1353–1364.

(7) Ackerman, K.; Chapuis, J.; Horning, D. E.; Lacasse, G.; Muchowski, J. M. *Can. J. Chem.* **1969**, *47*, 4327–4333.

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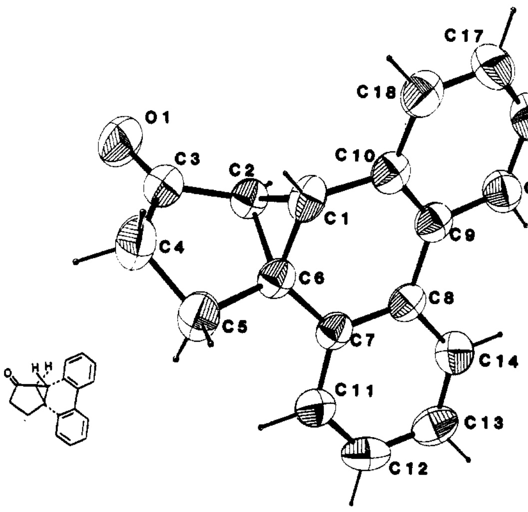
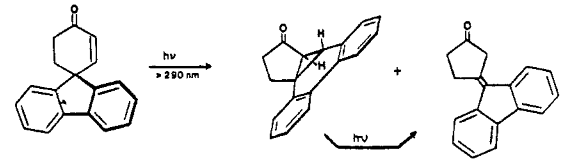


Figure 1. ORTEP drawing of photoproduct 10.

indicated a complex structure isomeric with starting material. ^{13}C NMR data was consistent with a [3.1.0] bicyclic structure showing 5 aliphatic carbons and 11 signals corresponding to aromatic ring carbons but the ^{1}H NMR, IR, and UV data defied unequivocal interpretation. The compound was, therefore, subjected to single-crystal X-ray analysis which revealed the compound to be [8b*R*-(8bα,8cβ,11a*S**)]-8b,8c,10,11-tetrahydro-9*H*-cyclopenta[1,3]cyclopropa[1,2-*l*]phenanthren-9-one (**10**). The ORTEP drawing of photoproduct **10** is given in Figure 1. The identity of the minor photoproduct was elucidated from its spectral data to be 3-fluorenylidenecyclopentanone (**11**). The mass spectrum verified a structure isomeric with the starting material. Proton NMR showed three 2-H signals, one isolated (singlet, δ 3.90) and two adjacent methylenes (two triplets, δ 3.52 and 2.82) with no vinyl absorptions. The ^{13}C NMR spectrum indicated the presence of only three aliphatic carbons. Finally, IR and UV lent additional support for a structure incorporating a nonconjugated carbonyl.

Both photoproducts from **6** were observed to be primary photoproducts. Independent irradiation of each photoproduct through Pyrex showed that **10** rearranges slowly to **11**, which is photoinert. The photochemistry of compound **6** is summarized in eq 2.



6 10 11 (2)

Irradiation of **9**, under identical conditions, was also observed to afford two major photoproducts. Mass spectral data indicated that each was isomeric with the starting enone. The IR showed cyclopropyl-conjugated carbonyls and the weak UV absorptions suggested isolated carbonyl and aromatic chromophores. Analysis by ^{1}H NMR proved unfeasible due to the aliphatic envelope of the three-carbon connector. The two products were, thus, subjected to single-crystal X-ray structural analysis which permitted their assignments as **12** and **13**. The ORTEP drawings of these structures are given in Figures 2 and 3.

Compound **12**, the trans diphenyl product, appeared initially to be the only photoproduct but, upon extended irradiation, compound **13**, the cis diphenyl product, was formed at the expense of **12**. Since **13** could be observed only at 53% conversion, it is not possible to conclude whether it is truly a primary photoproduct. Control experiments, performed by using the same irradiation conditions, showed that **12** rearranges to **13** while the reverse reaction does not occur. The photochemistry of **9** is depicted in eq 3.

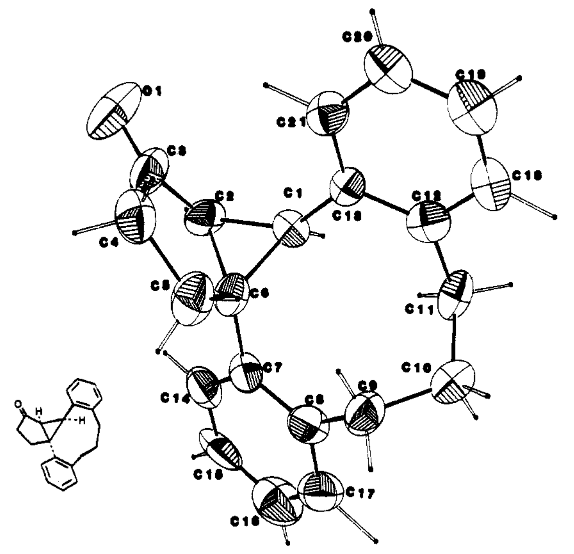


Figure 2. ORTEP drawing of photoproduct 12.

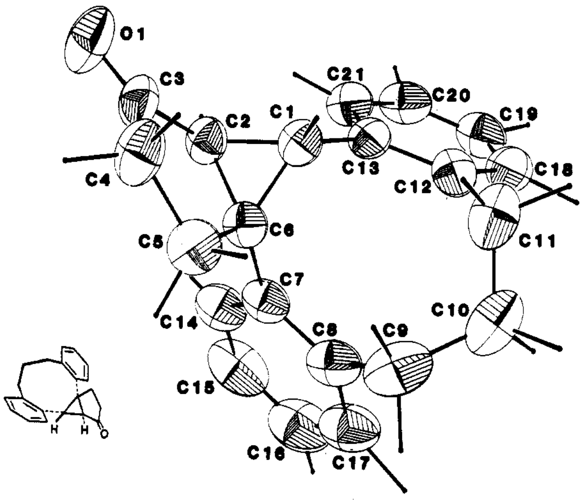
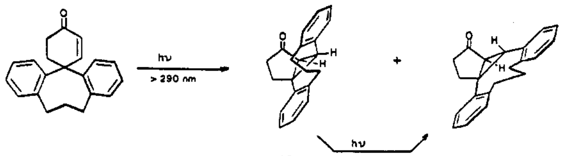


Figure 3. ORTEP drawing of photoproduct 13.



9 12 13 (3)

Several experimental findings suggest that considerable strain exists in the tricyclic photoproducts **10**, **12**, and **13**. While **10** derives strain from the enforced near-planarity of the two phenyl rings and the fusion of the [3.1.0] bicyclic system to a 9,10-dihydrophenanthrene, strain is evident in the three-carbon trans-bridged **12** as well. Comparison of the C1–C2–C3 angle (see Figures 2 and 3) in **12** with that in **13** shows that strain opens the angle from 114° to 121°. Additionally, lithium–liquid ammonia reduction of the tricyclic compounds cleaves only the external three-ring bond in contrast to the non-phenyl-bridged substrates.[8] This points to the fact that the bridging ortho–ortho

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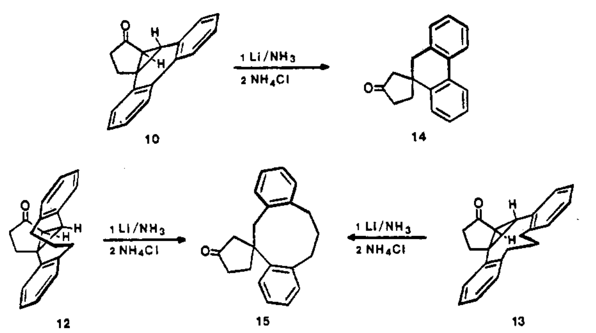
(8) Zimmerman, H. E.; Caufield, C. E.; King, R. K. *J. Am. Chem. Soc.* **1985**, *107*, 7732–7744, and references cited therein.

Scheme II. Li/NH_3 Reductions of 10, 12, and 13



connector is exerting much of its strain on the C1–C2 bond. Furthermore, the phenyl–phenyl linkage must lock the external three-ring bond into a conformation that aligns better with the π orbital of the carbonyl radical anion. Thus, the built-in control elements have the further effect of improving selectivity in these reductive three-ring openings. A summary of these results is provided in Scheme II.

Reaction Profiles and the Behavior of the Photoproducts. Figure 4 depicts the reaction profile for the irradiation of compound 6. From this, it can be seen that rapid buildup (nearly linear at low conversion) of the cis diphenyl product 10 is accompanied by the formation of 3-fluorenylidenecyclopentanone (11) at a considerably slower rate. A separate plot (Figure 5) of the formation of 11 from 10 reveals that this reaction occurs at a rate that is too slow to account for all of the 11 detected in low conversion photoreactions of 6. Thus, it appears likely that 11 arises from both primary and secondary photochemical processes.

The reaction profile for the eight-ring spiro enone 9 is illustrated in Figure 6. During the initial stages of the reaction, the trans diphenyl product 12 is observed to build up rapidly to ca. 85% of the mixture with only traces of the cis diphenyl product formed. As the reaction proceeds beyond this point, product 13 begins to build up slowly. Eventually, at 95% conversion, it becomes clear that the cis product is produced at the expense of the trans. This was confirmed by a control irradiation of 12 which showed nearly linear conversion to 13.

None of the cis photoproduct 13 was detected prior to 53% conversion (15-min irradiation) where 0.4% of 13 could be reproducibly detected. This corresponds to a ca. 115:1 ratio of trans/cis at this point—very close to the ratio observed for the unbridged analogue 1. The lack of measurable 13 at lower conversions of 9, however, prohibits conclusive assignment of 13 as a primary photoproduct.

Comparison of the reaction profiles for 6 and 9 show that the rate of reaction for 6 is only slightly slower than that for 9. Despite the fact that the zero-carbon chain alters the mechanism of the rearrangement, it does not qualitatively appear to have much effect on the reaction rate. Thus, while the concerted mechanism is the generally preferred pathway for most substrates, the stepwise component, which is observed to a minor extent in the unbridged analogue 1, becomes a favorable competitive process in cases where the concerted mechanism is precluded.

Mechanistic and Interpretative Discussion. The novel products formed in the irradiation of 6 can be attributed to the strain imposed by the ortho–ortho phenyl linkage. Since the zero-carbon connector is too short to span the distance separating adjoined positions in a trans diphenyl product, geometric constraint prohibits a concerted phenyl migration required for stereoselective formation of the trans product. A stepwise mechanism proceeding from a half-migrated species or simply a direct phenyl migration (bond a migration in 16) would relieve strain in the spiro framework and afford intermediate 17 (see Scheme III). The trigonal-planar geometry at C-4 of this intermediate then permits three-ring closure with cis-oriented phenyls.

The ring contraction required to form 11 involves migration of bond b in species 16. This process has been previously described in the photochemistry of 4,4-dimethyl-2-cyclohexen-1-one.[9] Alternatively, photoproduct

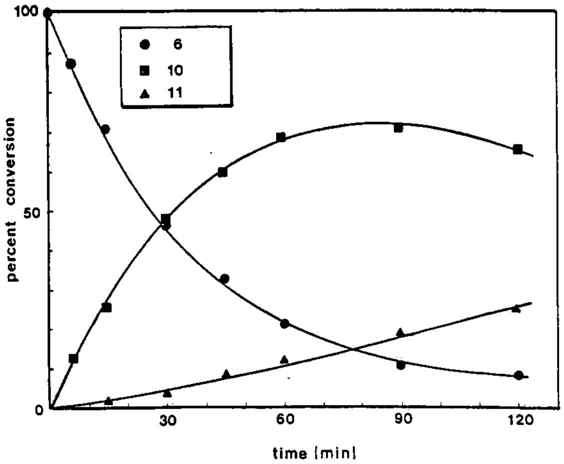


Figure 4. Reaction profile for irradiation of 6 through Pyrex.

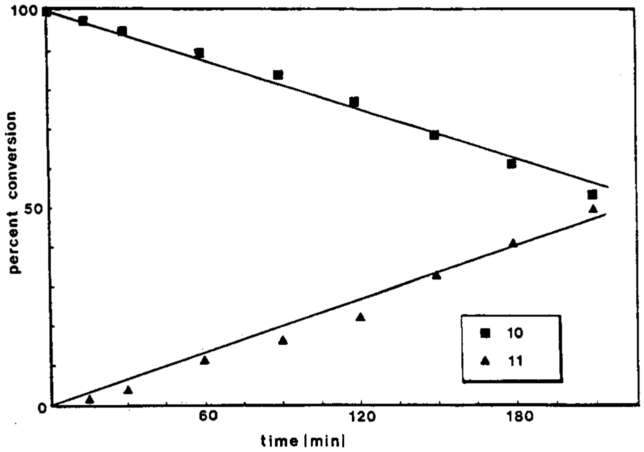


Figure 5. Reaction profile for conversion of 10 to 11.

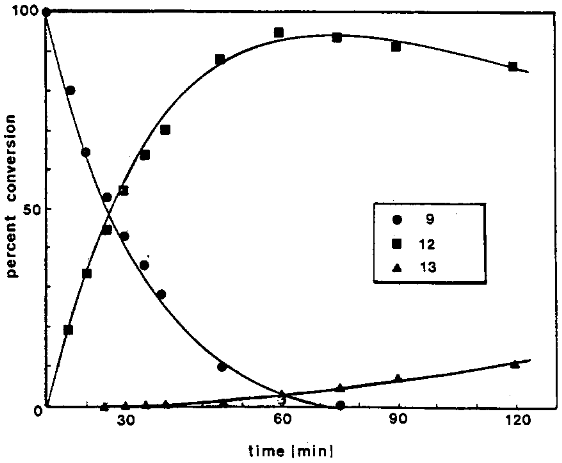


Figure 6. Reaction profile for irradiation of 9 through Pyrex.

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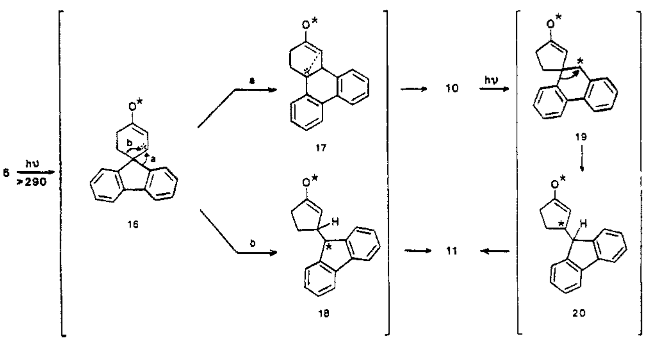
(9) Chapman, O. L.; Rettig, T. A.; Griswold, A. A.; Dutton, A. I.; Fitton, P. *Tetrahedron Lett.* **1963**, *2049*–2055.

Scheme III. Mechanistic Summary of the Photochemical Rearrangement of 6[a]

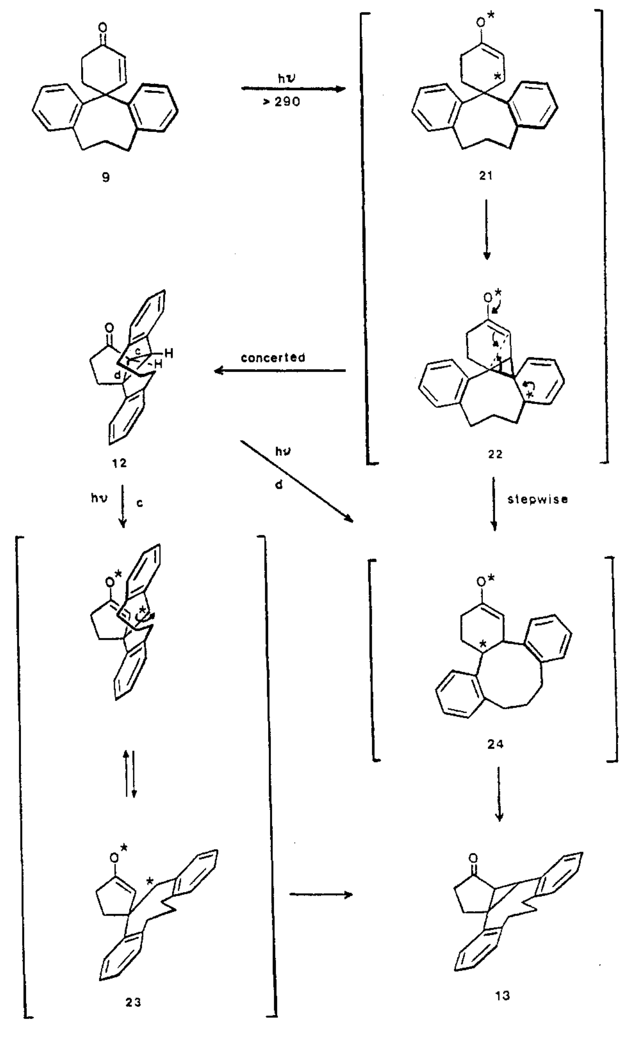


[a] * = ·/· or +/−

11 can arise from 10 by fission of the external, three-ring bond. This process has ample precedent in earlier studies of the unbridged analogue.[2,10] The exclusive formation of the nonconjugated enone product must derive from a combination of effects including conjugation to the fluorenyl system and relative stability of exo vs. endo π bonds in five rings. It has also been noted that photochemical conditions often deconjugate 3-alkyl 2-enones,[11,12] though literature precedent is unavailable in the cyclopentenone series. The total absence of any conjugated material, however, would seem to indicate that 11 does not derive from the conjugated enone.

Photoproduct 11 appears to be the result of an incomplete type A rearrangement. Previous work has suggested that the type A reaction, observed in 4,4-dialkyl-2-cyclohexenones, results predominantly from a $\pi \rightarrow \pi^*$ triplet excited state[13] while the concerted phenyl migration (type B reaction) typically observed in 4,4-diaryl-2-cyclohexenones occurs from an $n \rightarrow \pi^*$ triplet excited state.[2,10] It has also been noted that solvent polarity and hydrogen bonding has a marked effect on the relative energies of these two states,[14,15] nonpolar solvents favoring $n \rightarrow \pi^*$ triplet reactions and polar solvents favoring the $\pi \rightarrow \pi^*$ triplet reactions. The *tert*-butyl alcohol, utilized in the current study, was, therefore, considered as a possible explanation for the intervention of a type A mechanism in the photochemistry of 6. Though a solvent effect had not been reported for 4,4-diphenyl-2-cyclohexen-1-one,[1,2] a control irradiation of 6 was performed in benzene to test for a solvent dependence on the product ratio. Under nonpolar conditions, the production of 10 diminished while the rate of formation of 11 appeared to accelerate slightly over the reactions run in *tert*-butyl alcohol. This trend contradicts previous studies[14] where solvent has proven important. Hence, an alternative explanation would be that the strain which develops in the half-migrated type B intermediate suppresses phenyl migration and permits the less efficient type A process to compete without inversion of the states.

Scheme IV. Mechanistic Summary of the Photochemical Rearrangement of 9[a]



[a] * = ·/· or +/−

Considerable strain is relieved and more flexibility is introduced in the spirocyclic skeleton of 9 relative to 6. Analysis of molecular models indicates that the three-carbon phenyl–phenyl bridge in 9 would permit the formation of a trans diphenyl product (i.e., 12) though it would be expected to incorporate significantly more strain than its unbridged counterpart. This added strain is manifested in the facile and irreversible conversion of 12 to 13. This differs from the photoisomerization of 2 → 3 which is reversible and leads to a photostationary state of 43:57 in favor of the cis.[1] Thus, by linking the two phenyl rings, the less strained cis product 13 clearly becomes the more thermodynamically favored product in the present reaction. The stereochemical outcome of the photorearrangement of 9 would provide additional evidence for or against the concertedness of the reaction since a concerted mechanism would lead to a kinetic preference for the more strained trans product while a stepwise process would be expected to yield the thermodynamically preferred cis diphenyl product 13. The observation of a 115:1 trans/cis product ratio from 9 (compared with the 140:1 ratio reported from 1), therefore, constitutes compelling evidence for the concerted nature of the rearrangement.

It is known that photoisomerizations in the 5,6-diphenylbicyclo[3.1.0]hexan-2-one system proceed by preferential fission of the external three-ring bond (bond c, Scheme IV).[10] Opening of the external cyclopropane bond has extensive precedent[2,10,12,16] and derives from the nearly parallel alignment between the orbitals of this bond and

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[10] Zimmerman, H. E.; Hancock, K. G.; Licke, G. C. *J. Am. Chem. Soc.* **1968**, *90*, 4892–4911.

[11] Shiloff, J. D.; Hunter, N. R. *Can. J. Chem.* **1979**, *57*, 3301–3303.

[12] Dauben, W. G.; Shaffer, G. W.; Vietmeyer, N. D. *J. Org. Chem.* **1968**, *33*, 4060–4068.

[13] Bellus, D.; Kearns, D. R.; Schaffner, K. *Helv. Chim. Acta* **1969**, *52*, 971–1009.

[14] Dauben, W. G.; Spitzer, W. A.; Kellogg, M. S. *J. Am. Chem. Soc.* **1971**, *93*, 3674–3677.

[15] Brealey, G. J.; Kasha, M. *J. Am. Chem. Soc.* **1955**, *77*, 4462–4468.

[16] Dauben, W. G.; Schutte, L.; Shaffer, G. W.; Gagosian, R. B. *J. Am. Chem. Soc.* **1973**, *95*, 468–471.

the carbonyl π orbital containing the n $\rightarrow$ π^* promoted electron. Though cleavage of bonds corresponding to both c and d have been implicated in the photoconversion of **2** to **3**, any similar bond openings in **12** or **13** would invariably lead to the cis diphenyl product upon reclosure due to the stain imposed by the three-carbon phenyl–phenyl connector. The mechanisms operating in the photochemistry of **9** are given in Scheme IV.

In summary, the present work demonstrates the feasibility of utilizing built-in control elements to direct photochemical reactions. It has been shown that alkyl chains connecting groups which normally migrate apart during the course of a reaction can significantly alter the mechanism of a photochemical reaction and even totally reverse stereochemistry in the final products. Future work will focus on ring size effects in these reactions and on the development of photochemically inert linkages that can be readily removed following reaction.

Experimental Section[17]

Spiro[2-cyclohexene-1,9′-fluoren]-4-one (6). This compound was prepared according to the procedure described by Plieninger and co-workers.[3] The physical and spectral properties matched those of this earlier report.

12-Formyl-5,6,7,12-tetrahydrodibenzo[*a*,*d*]cyclooctene (8). This compound was prepared according to the procedure of Muchowski and co-workers.[7] The physical and spectral data were identical with those reported.

6′,7′-Dihydrospiro[2-cyclohexene-1,12′(5′*H*)-dibenzo[*a*,*d*]cycloocten]-4-one (9). Starting from **8**, the general procedure of Plieninger and co-workers[3] for the preparation of **6** was used. The spiro compound was isolated as white crystals in 19.6% yield: mp 151–152 °C; IR ($CHCl_3$) 1685, 1618 cm^{-1}; ^{1}H NMR δ 7.52–6.98 (complex, 8 H), 6.90 (d, J = 10 Hz, 1 H), 6.22 (d, J = 10 Hz, 1 H), 2.99 (m, 2 H), 2.67 (m, 2 H), 2.47 (m, 1 H), 2.26 (m, 2 H), 1.97 (m, 1 H), 1.72 (m, 1 H), 1.53 (m, 1 H); ^{13}C NMR 199.7, 157.1, 145.3, 140.8, 139.0, 132.4, 131.4, 130.8, 128.1, 127.9, 127.3, 126.5, 126.3, 125.6, 52.2, 41.6, 34.3, 31.5, 31.0, 30.4 ppm; UV 306 nm (ϵ 1845), 264 (21 617); MS, *m/z* 288 (M^+).

Anal. Calcd for $C_{21}H_{20}O$: C, 87.50; H, 6.95. Found: C, 87.42; H, 6.92.

General Procedure for Exploratory Photochemical Runs. The procedure used paralleled that described by Zimmerman and co-workers[1,2] for the photolysis of 4,4-diphenyl-2-cyclohexen-1-one. In a typical run, 10 mmol of substrate dissolved in 1 L of degassed *tert*-butyl alcohol in a Kreil flask (Ace no. 6963) was irradiated through Pyrex by using a 450-W medium pressure Hanovia lamp in a quartz immersion well. Reactions of **6** were stopped at ca. 50% conversion as estimated by TLC or GC, the solvent was removed in vacuo, and the crude product was subjected to column chromatography on a 2.5 cm × 75 cm column of silica gel slurry packed in hexane and eluted with hexane containing increasing ether concentrations. Crude reaction mixtures from irradiation of **8** (50% conversion) were separated on 20 cm × 20 cm preparative thick layer chromatography plates. Typical mass balances in all exploratory runs ranged from 80% to 90%.

Column chromatography of the crude photolysate from irradiation of **6** yielded starting material (1.13 g, 4.53 mmol) followed, in sequence, by the following.

3-Fluorenylidenecyclopentanone (11): light yellow crystals from ether–hexane (0.17 g, 0.69 mmol); mp 170–171 °C; IR ($CHCl_3$) 1715 cm^{-1}; ^{1}H NMR δ 8.71 (m, 2 H), 8.05 (m, 1 H), 7.84 (m, 1 H), 7.65 (m, 4 H), 3.90 (s, 2 H), 3.52 (t, J = 7 Hz, 2 H), 2.82 (t, J = 7 Hz, 2 H), 2.82 (t, J = 7 Hz, 2 H); ^{13}C NMR 209.5, 130.1, 130.0, 129.4, 129.2, 128.9, 126.9, 126.8, 126.7, 126.1, 123.3, 122.7, 40.5, 38.2, 25.9 ppm; UV 301 nm (ϵ 1360), 258 (15 412); MS, *m/z* 246 (M^+).

Anal. Calcd for $C_{18}H_{14}O$: C, 87.80; H, 5.69. Found; C, 87.63; H, 5.79.

(8b*α*,8c*β*,11a*S)-(±)-8b,8c,10,11-Tetrahydro-9*H*-cyclopenta[1,3]cyclopropa[1,2-*l*]phenanthren-9-one (10):** light yellow crystals from ether–hexane (0.98 g, 3.98 mmol); mp 109–110 °C; IR ($CHCl_3$) 1718 cm^{-1}; ^{1}H NMR δ 8.06 (m, 2 H), 7.72 (m, 1 H), 7.50–7.24 (complex, 5 H), 3.16 (d, J = 4 Hz, 1 H), 3.08 (m, 1 H), 2.35 (m, 3 H), 1.11 (d, J = 4 Hz, 1 H); ^{13}C NMR 212.4, 132.8, 131.7, 129.7, 129.0, 127.8, 127.1, 127.0, 126.9, 125.7, 123.3, 123.1, 37.9, 37.1, 34.0, 32.5, 24.5 ppm; UV 310 nm (ϵ 1815), 270 (7296), 244 (11 497); MS, *m/z* 246 (M^+).

Anal. Calcd for $C_{18}H_{14}O$: C, 87.80; H, 5.69. Found: C, 87.69; H, 5.72.

Preparative thick layer chromatography of the crude photolysate from the irradiation of **9** yielded three bands. The second band was recovered starting material (1.09 g, 3.80 mmol). The first and third bands, in order of elution, were the following.

(3a*R,14b*R**,14c*R**)-(±)-2,3,9,10,14b,14c-Hexahydrodibenzo[*a*,*e*]cyclopenta[1,3]cyclopropa[1,2-*c*]cyclononen-1-(8*H*)-one (12):** white crystals from hexane (1.12 g, 3.89 mmol); mp 115–116 °C; IR ($CHCl_3$) 1720 cm^{-1}; ^{1}H NMR δ 7.24–6.94 (complex, 7 H), 6.81 (d, J = 7 Hz, 1 H), 2.76 (d, J = 8 Hz, 1 H), 2.60 (d, J = 8 Hz, 1 H), 2.58–2.32 (complex, 5 H), 2.17 (m, 1 H), 2.06 (m, 2 H), 1.92 (m, 2 H); ^{13}C NMR 214.9, 143.2, 142.7, 142.6, 134.1, 130.9, 130.8, 127.1, 127.0, 126.3, 126.1, 125.1, 124.9, 45.8, 40.5, 39.4, 39.3, 34.3, 30.5, 30.0, 26.6 ppm; UV 308 nm (ϵ 31), 265 (500), 216 (8544); MS, *m/z* 288 (M^+).

Anal. Calcd for $C_{21}H_{20}O$: C, 87.50; H, 6.95. Found: C, 87.38; H, 6.99.

(3a*R,14b*S**,14c*R**)-(±)-2,3,9,10,14b,14c-Hexahydrodibenzo[*a*,*e*]cyclopenta[1,3]cyclopropa[1,2-*c*]cyclononen-1-(8*H*)-one (13):** white crystals from ether–hexane (0.28 g, 1.00 mmol); mp 162–163 °C; IR ($CHCl_3$) 1722 cm^{-1}; ^{1}H NMR δ 6.99 (m, 4 H), 6.85 (m, 4 H), 3.24–2.86 (complex, 7 H), 2.59–2.32 (complex, 4 H), 1.70 (m, 1 H); ^{13}C NMR 213.5, 143.3, 143.0, 136.5, 133.2, 130.6, 129.7, 128.5, 127.5, 127.3, 127.2, 125.8, 125.7, 44.6, 37.4, 36.4, 35.3, 35.2, 35.1, 33.7, 30.0 ppm; UV 310 nm (ϵ 35), 265 (381), 214 (9630); MS, *m/z* 288 (M^+).

Anal. Calcd for $C_{21}H_{20}O$: C, 87.50; H, 6.95. Found: C, 87.36; H, 7.01.

General Procedure for Lithium–Liquid Ammonia Reductions. To 40 mL of liquid ammonia (distilled from Na) at −78 °C was added 5.6 mg (0.80 mmol) of freshly cut lithium wire. The solution turned dark blue and 0.36 mmol of the tricyclic ketone (**10**, **12**, or **13**) in 3 mL of dry tetrahydrofuran was added all at once. The solution gradually changed color from blue to white to light brown (10–15 min). Approximately 100 mg of solid ammonium chloride was added and the ammonia was evaporated on a stream of dry nitrogen. The remaining solid was diluted with water and ether extracted. The ether extract was washed with water and saturated sodium chloride, dried over anhydrous $MgSO_4$, and concentrated under vacuum. The oil was purified by preparative thick layer chromatography. The following results were obtained.

Reduction of **10** afforded 60 mg (0.24 mmol, 68%) of **14** and 11 mg (0.04 mmol, 5.5%) of recovered starting material. The physical and spectral data for **14** were as follows: mp 94–95 °C; IR ($CHCl_3$) 1740 cm^{-1}; ^{1}H NMR δ 7.81 (m, 2 H), 7.40 (m, 6 H), 3.10 (d, J = 14 Hz, 1 H), 2.80 (d, J = 14 Hz, 1 H), 2.73 (d, J = 17 Hz, 1 H), 2.38 (d, J = 17 Hz, 1 H), 2.31 (t, J = 6 Hz, 2 H), 1.99 (m, 2 H); ^{13}C NMR 218.3, 141.4, 134.4, 133.9, 133.6, 128.4, 127.6, 127.2, 124.6, 123.6, 123.5, 49.8, 42.8, 41.4, 36.4, 33.4 ppm; MS, *m/z* 248 (M^+).

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[17] Melting points were obtained on a Thomas Hoover melting point apparatus and are uncorrected. IR spectra were recorded with a PE-681 instrument and are referenced to polystyrene. ^{1}H NMR and ^{13}C NMR spectra were measured as solutions in $CDCl_3$ at 300 MHz and 75 MHz, respectively, on a Varian XL-300 superconducting FT instrument; chemical shifts are reported (^{1}H in δ units and ^{13}C in ppm) relative to internal Me_4Si. UV spectra were recorded in 95% ethanol on a Hitachi 100-80A or a PE-3840 spectrophotometer. Mass spectra were recorded at 70 eV on a CEC 21-110B double-focusing mass spectrometer. Microanalytical determinations were performed at Galbraith Laboratories, Knoxville, TN. All reactions were run under an atmosphere of dry nitrogen. *tert*-Butyl alcohol for photochemical reactions was distilled from CaH_2 prior to use and all photochemical reactions were degassed with dry, oxygen-free nitrogen for 1 h prior to and during irradiation. Column chromatography was performed on silica gel (Grace, grade 62, 60–200 mesh) mixed with Sylvania 2282 phosphor and slurry packed into Vycor columns such that band elution could be monitored with a hand-held UV lamp. Preparative thick layer chromatography was performed on Analtech (no. 02015) preparative silica gel uniplates with fluorescent indicator. Reactions were monitored and kinetic measurements were made on a Varian 3400 capillary GC with FI detection.

Table I. Crystal Data for 10, 12, and 13

	10	**12**	**13**
formula	$C_{18}H_{14}O$	$C_{21}H_{20}O$	$C_{21}H_{20}O$
M_r	246.3	288.4	288.4
a, Å	7.506 (2)	20.679 (8)	10.375 (3)
b, Å	17.069 (8)	15.422 (9)	9.278 (4)
c, Å	9.923 (4)	9.777 (2)	16.954 (8)
α, deg	90	90	90
β, deg	95.08 (3)	91.15 (3)	93.84 (3)
γ, deg	90	90	90
V, Å	1266.4 (8)	3117.4 (23)	1628.4 (12)
$F(000)$	520	1232	616
μ(Mo K_α), cm^{-1}	0.73 cm	0.685	0.656
γ(Mo K_α) Å	0.71069	0.71069	0.71069
D_{calcd}, g cm^{-3}	1.292	1.229	1.176
Z	4	8	4
obsd refl	1163	2113	1615
R/R_w, %	5.2/5.0	8.7/10.7	8.8/11.2
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$

Anal. Calcd for $C_{18}H_{16}O$: C, 87.10; H, 6.45. Found: C, 87.04; H, 6.48.

Reduction of **12** yielded 73 mg (0.26 mmol, 70%) of **15** and 8.1 mg (0.03 mmol, 3.5%) of recovered starting material. The physical and spectral data for **15** were as follows: mp 129–130 °C; IR ($CHCl_3$) 1745 cm^{-1}; ^1H NMR δ 7.52 (m, 1 H), 7.32–6.72 (complex, 7 H), 3.26 (d, J = 14 Hz, 1 H), 2.90 (d, J = 14 Hz, 1 H), 2.80–2.24 (complex, 4 H); ^{13}C NMR 219.0, 149.0, 141.7, 140.8, 136.9, 132.0, 131.3, 131.1, 130.0, 127.3, 126.7, 126.1, 125.7, 49.2, 45.1, 39.8, 37.9, 36.0, 30.0, 28.9 ppm; MS, m/z 290 (M^+).

Anal. Calcd for $C_{21}H_{22}O$: C, 86.90; H, 7.59. Found: C, 86.72; H, 7.71.

Reduction of **13** yielded 61.3 mg (0.21 mmol, 58.7%) of **15** and 9.7 mg (0.03 mmol, 4.2%) of recovered starting material. The reduction product was identical by TLC, mp, mmp, IR, ^1H NMR, ^{13}C NMR, MS, and elemental analysis with the material isolated from the reduction of **12**.

Reaction Profiles. A solution of 100 mg (0.40 mmol of **6**, 0.35 mmol of **9**) in 400 mL of *tert*-butyl alcohol was irradiated as before in the Hanovia apparatus. The reaction was monitored by GC analysis of 0.2-mL aliquots removed by syringe from the reaction at 5-min intervals during the first hour and at 15-min intervals thereafter. The samples were injected onto a 0.25 mm × 3 m DB-1 column, temperature programmed between 200 and 300 °C; the individual compounds were found to be stable to these thermal conditions. Peak areas were determined from electronic integration of the peaks relative to internal benzophenone standard.

Control Experiment. Photostability of the Photoproducts. In a typical control run, 0.3 mmol of the photoproduct was irradiated as a 0.001 M solution in *tert*-butyl alcohol by using the Hanovia apparatus. The reactions were monitored by GC at 15-min intervals during the first hour and at 30-min intervals thereafter. Compounds **11** and **13** were found to be stable under the irradiation conditions over a 6-h period; compound **10** was found to convert to **11** (40% conversion after 3 h, see Figure 5); and compound **12** was found to rearrange to **13** (40% conversion after 6 h).

Control Experiment. Irradiation of 6 in Benzene. A 325-mL degassed benzene solution of 80 mg (0.33 mmol) of the spirofluorenylcyclohexenone **6** was irradiated as before. The reaction was monitored by GC at 15-min intervals during a period of 1 h (45% conversion). Peak areas were determined as described previously and showed that formation of **10** was slightly retarded (31% of the mixture after 1 h) while **11** was formed at a rate slightly faster (14% of the mixture after 1 h) than that observed when the irradiation was performed in *tert*-butyl alcohol.

Crystallographic Structure Determinations. Crystals of **10**, **11**, and **12** were mounted on a Syntex P3 automated diffractometer. Unit cell dimensions (Table I) were determined by least-squares refinement of the best angular positions for 15 independent reflections ($2\theta > 15°$) during normal alignment procedures using molybdenum radiation (λ = 0.71069 Å). Data were collected at room temperature by using a variable scan rate, a θ–2θ scan mode, and a scan width of 1.2° below $K\alpha_1$ and 1.2° above $K\alpha_2$ to a maximum 2θ value of 60.0°. Backgrounds were measured at each side of the scan for a combined time equal to the total scan time. The intensities of the three standard reflections were remeasured after every 97 reflections and as the intensities of these reflections showed less than 6% variation, corrections for decomposition were deemed unnecessary. Data were collected for Lorentz, polarization, and background effects. After removal of redundant and space group forbidden data, observed data ($I > 3.00\sigma(I)$) were used to solve the structures. MULTAN[18] was used to locate atom positions. Least-squares refinement followed by difference Fourier synthesis allowed location of the hydrogen atom positions.

Refinement of scale factor and positional and anisotropic thermal parameters for all non-hydrogen atoms was carried out to convergence. Hydrogen atom positions and assigned isotropic thermal parameters were included in the final cycles of refinement[19] but were held fixed. Scattering factors were taken from Cromer and Mann.[20]

The final cycle of refinement function minimized $\Sigma(|F_o| - |F_c|)^2$ led to final agreement factors, R = 5.2% (**10**), 8.7% (**12**), 8.8% (**13**), $R = (\Sigma||F_o| - |F_c||/\Sigma|F_o|) \times 100$. A weight equal to $1/\sigma F$ was introduced in the final cycles of refinement: R_w = 5.0% (**10**), 10.7% (**12**), 11.2% (**13**).

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Supplementary Material Available: Tables II–X listing positional parameters, final anisotropic thermal parameters, and bond angles and distances for compounds **10**, **12**, and **13** (11 pages). Ordering information is given on any current masthead page. A listing of calculated and observed structure factors is available from R.A.B.

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