Copper(I) Catalysis in Photocycloadditions. II. Cyclopentene, Cyclohexene, and Cycloheptene

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Abstract: Copper(I) triflate catalyzes the photodimerization of the simple nonconjugated unstrained olefins, cyclopentene, cyclohexene, and cycloheptene, but not cyclooctene or acyclic olefins. The major products from cyclohexene and cycloheptene are the thermodynamically less stable trans fused [2 + 2] cyclodimers. The remarkable stereochemistry of the adducts was examined by carbon-13 magnetic resonance, and the structure of the cyclohexene photodimer was established by X-ray crystallography. A mechanism which accords a special significance to ring size and predicts the unreactivity of cyclooctene and acyclic olefins must be operative. A process is favored involving the photoinduced cis–trans isomerization of the copper–olefin complex to a highly strained and reactive *trans*-cyclohexene and *trans*-cycloheptene followed by a thermal $[2_{\pi_a} + 2_{\pi_s}]$ cycloaddition to another olefin. A similar preference for the formation of trans-fused cyclobutane is exhibited in the triplet-sensitized dimerization of cyclohexene and suggests related pathways. However, epimerization of tricyclic cyclobutanes in the presence of triplet sensitizer must be considered.
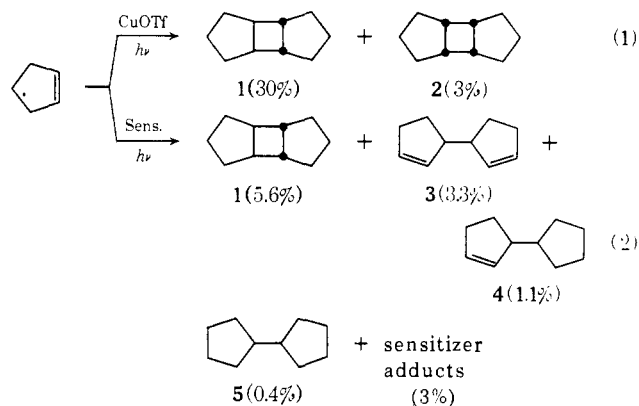
Photodimerizations of simple nonconjugated monoolefins are generally considered to be limited to strained cyclic systems.[1] The ability of olefins to coordinate with metals is enhanced by the strain inherent in the double bonds of norbornene,[2,3] for example, and is reflected in the copper(I)-catalyzed photodimerization of its derivatives as described in the foregoing paper.[4] Since copper(I) triflate is able to coordinate olefins much more strongly than copper(I) halides, the possibility of effecting photodimerization of simple unstrained cycloolefins with this catalyst was examined. Indeed, we find that CuOTf readily catalyzes the photodimerization of cyclopentene, cyclohexene, and cycloheptene but significantly, not cyclooctene. Moreover, the formation of the [2 + 2] cycloadducts occurs with appreciable stereospecificity. The copper(I)-catalyzed photodimerizations under these conditions are compared to the triplet-sensitized reactions studied previously.[5,6] However, the stereochemistries of the photoadducts were not previously determined, owing to the inapplicability of the usual physical methods (such as ir and pmr spectra) to saturated hydrocarbons which lack functionality. Knowledge of the stereochemistry of the [2 + 2] cycloadducts would allow an evaluation of the stereoelectronic factors, such as orbital symmetry, in formulating a mechanism for these metal-catalyzed photocycloadditions. In this study we have employed carbon-13 magnetic resonance (cmr) and X-ray crystallography to establish the stereochemistry of the photodimers, and propose a mechanism which accounts for the unique stereospecificity observed in the photodimerization of cycloolefins.

Results and Discussion

Photodimerization of Cyclopentene. The major

product derived from the CuOTf-catalyzed photodimerization of cyclopentene is *cis-anti-cis*-tricyclo[5.3.0.0²·⁶]decane (1), together with small amounts of the cis-syn-cis isomer 2 and an unidentified dimeric product. The structure of 1 was examined previously.[5]

(1)

(2)

For comparison, the acetone-sensitized photodimerization of cyclopentene afforded the cyclodimer 1 in diminished yields and a mixture of eight other products including the cyclopentyl and cyclopentenyl dimers shown in eq 2.[5]
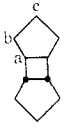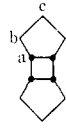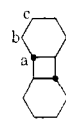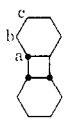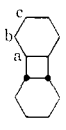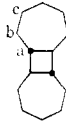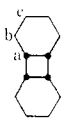
Photodimerization of Cyclohexene. The CuOTf catalyzed photodimerization of cyclohexene afforded one principal cyclodimer 6, *trans-anti-trans*-tricyclo[6.4.0.0²·⁷]dodecane, and a minor amount of the cis-trans isomer 7. A significant amount of the ene product 8, 1-cyclohexylcyclohexene, was also formed as shown in eq 3.

In contrast, the sensitized reaction using methyl acetoacetate[6] afforded only small amounts of the cyclodimers 6 and 7 together with an epimer 9 and other dimers listed in eq 4.

Photodimerization of Cycloheptene. Cycloheptene was readily converted to a single cyclodimer 12, *trans-anti-trans*-tricyclo[7.5.0.0²·⁸]tetradecane, upon irradiation in the presence of CuOTf (see eq 5).

Photolysis of Cyclooctene and 1-Hexene in the Presence of CuOTf. Photodimerization of *cis*-cyclooctene and 1-hexene was attempted under reaction conditions

(1) D. J. Trecker, *Org. Photochem.*, 2, 63 (1969).
(2) (a) J. G. Traynham and J. R. Olechowski, *J. Amer. Chem. Soc.*, 81, 571 (1959); (b) M. A. Muhs and F. T. Weiss, *ibid.*, 84, 4697 (1962).
(3) (a) R. B. Turner, W. R. Meador, and R. E. Winkler, *J. Amer. Chem. Soc.*, 79, 4116 (1957); (b) R. C. Lord and R. W. Walker, *ibid.*, 76, 2518 (1954).
(4) R. G. Salomon and J. K. Kochi, *J. Amer. Chem. Soc.*, 96, 1137 (1974).
(5) H.-D. Scharf and F. Korte, *Chem. Ber.*, 97, 2425 (1964).
(6) M. Tada, T. Kokubo, and T. Sato, *Bull. Chem. Soc. Jap.*, 43, 2162 (1970).

Table I. Carbon-13 Resonance Spectra of Cyclobutyl Products^a

Carbon resonance	1	2	6	7	9	12	13	15
a	150.9	154.7	142.5	148.6, 151.2 153.5, 155.6	158.5	144.5	142.4	158.0
b	159.6	166.2*	161.8*	8 resonances 161.9–170.6	165.7	159.1*	167.7	169.8*
c	167.8	164.3*	166.3*		169.7	166.8*		170.1*
d						164.7		

^a An asterisk indicates assignments may be reversed.

6(49%) + 7(8%) +

8(24%) (3)

sens. hv

6(1%) + 7(1.5%) +

9(0.6%) (4)

10(0.9%) + 11(0.9%) + sensitizer adducts

CuOTf hv

12(57%) (5)
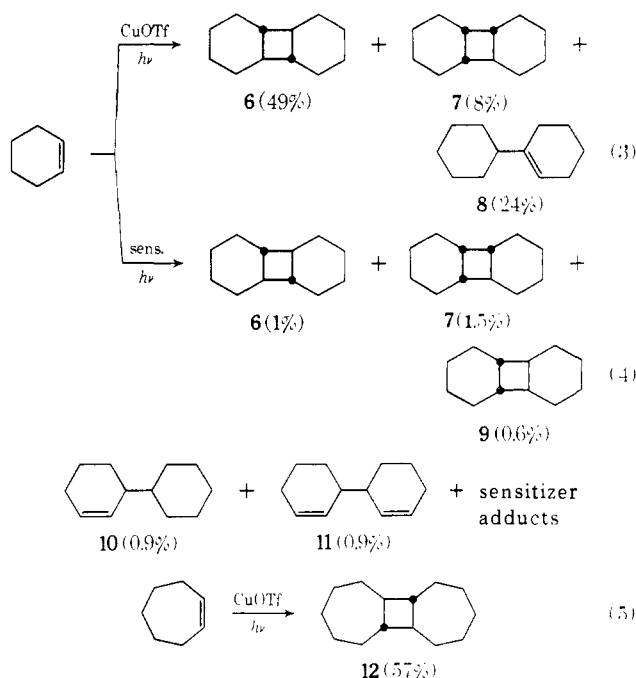
which readily promoted dimerization of cyclopentene, cyclohexene, and cycloheptene. The starting olefins were recovered undimerized in each case, although with cis-cyclooctene some isomerization to the trans isomer had occurred. Similar cis–trans photoisomerizations catalyzed by copper(I) halides have been reported for cyclooctene,[7] 1,5-cyclooctadiene,[8] cyclododecene,[9] and 1,5,9-cyclododecatriene.[9]

Structures of the Photodimers by Carbon-13 Magnetic Resonance. The usual physical methods do not afford sufficient information to establish the stereochemistry of the cycloadducts formed by [2 + 2] photodimerization. However, the simplicity of the carbon-13 magnetic resonance (cmr) spectra for these compounds has provided a basis for the structure elucidation as described below.

The cmr spectra are recorded in Table I for all the cyclobutane products listed in eq 1–5. For comparison, the cmr spectra of the related tricyclo[3.3.0.0^{2,6}]octane (13)[1] and cis-syn-cis-tricyclo[6.4.0.0^{2,7}]dodecane (15) were also examined and included in the table. The tricyclic cyclobutane 13 was prepared from 1,5-cycloocta-

(7) J. A. Deyrup and M. Bethouski, J. Org. Chem., 37, 3561 (1972).
(8) G. M. Whitesides, G. L. Goe, and A. C. Cope, J. Amer. Chem. Soc., 91, 2608 (1969).
(9) H. Nozaki, Y. Nisikawa, M. Kawanisi, and R. Noyari, Tetrahedron, 23, 2173 (1967).

CuOTf hv

13

diene. The cyclodimer 15 was obtained by catalytic hydrogenation of the corresponding cis-syn-cis-tricyclo-[6.4.0.0^{2,7}]dodeca-3,11-diene (14).[10]

14 → 15
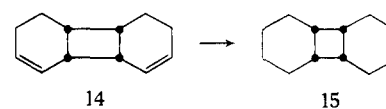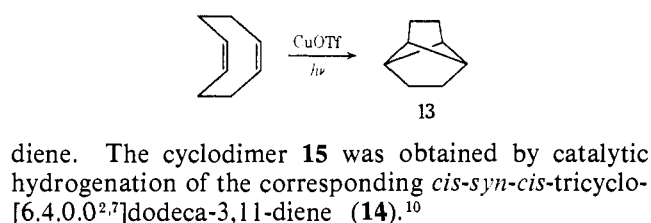
The methine carbons attached to the cyclobutyl ring in each compound listed in Table I were differentiated from the methylene carbons by single frequency off resonance decoupling.

Four of the five possible tricyclo[6.4.0.0^{2,7}]dodecane stereoisomers (i.e., dimers from cyclohexene) were obtained in these studies. The fifth, the trans-syn-trans stereoisomer 16, remains unknown. The axial cyclobutylcarbinyl hydrogens are severely crowded in the cis-syn-cis stereoisomers 2 and 15 as shown schematically in 17. This steric compression results in upfield shifts[11]

16   17
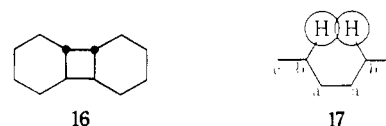
of more than 4 ppm of the cyclobutylcarbinyl (b carbons) carbon resonances compared to the cis-anti-cis stereoisomers 1 and 9 respectively in accord with the assigned structures. The cyclobutyl "a" carbon resonances of the cis-fused cyclohexene dimers 9 and 15 are nearly identical. The cyclobutyl carbon resonance of the trans-fused isomer 6 comes at appreciably lower field. The 16 ppm difference in chemical shift is apparently related to the different conformations of the cyclobutyl rings in these compounds. The cyclobutyl rings in both cis-fused isomers 9 and 15 are flat, whereas the cyclobutyl ring in the trans-fused isomer 6 is puckered. The cyclobutyl ring in the alternative trans-fused isomer 16 is flat. This interpretation is supported by the chemical shift observed for the cyclobutyl carbons in 13. The conformation of the cyclobutyl ring in 13 is identical with that in 6. Moreover, each carbon is monosubstituted with –CH$_2$–. The chemical shifts

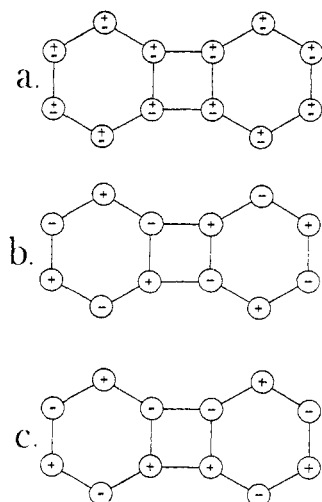(10) D. Valentine, N. J. Turro, Jr., and G. S. Hammond, J. Amer. Chem. Soc., 86, 5202 (1964).
(11) D. M. Grant and B. V. Cheney, J. Amer. Chem. Soc., 89, 5315 (1967).

Figure 1. Schematic representation of disorder: (+) indicates an atom above the plane and (−) indicates an atom below the plane of the paper; (a) the observed arrangement in the disordered crystal structure; (b) trans-anti-trans configuration of tricyclo[6.4.0.0²,⁷]-dodecane; (c) trans-syn-trans configuration.

Figure 2. Bond distances and bond angles in *trans-anti-trans*-tricyclo[6.4.0.0²,⁷]dodecane.

Figure 3. Perspective view of an undisordered molecule of *trans-anti-trans*-dodecane. The numbering system for the atoms is shown.

of the cyclobutyl carbons of both **6** and **13** are *identical*. These data provide presumptive evidence for the choice of structure **6** rather than **16** for the major cyclohexene dimer from the CuOTf catalyzed photocycloaddition.

Confirmation of the structure for the cyclodimer **6** is unambiguously provided by the X-ray crystal structure presented in the next section. The assignment of a cis-trans structure **7** for the minor cyclohexene dimer from the CuOTf catalyzed photocycloaddition follows unambiguously from its unique cmr spectrum. All 12 carbon atoms of this isomer are magnetically nonequivalent. As expected, the chemical shifts of the four different cyclobutyl carbons lie between those found for the cis-fused isomers **9** and **15** and the trans-fused isomer **6**. The assignment of a trans-anti-trans structure **12** to the cycloheptene photodimer follows from the chemical shift of the cyclobutyl carbons. This resonance is found at relatively low field near those of the puckered cyclobutyl derivatives **6** and **13**.

The structures of some of the other photodimers obtained in this study were reported previously. Thus, the products of the acetone-sensitized photodimerization of cyclopentene were characterized previously, and the yields of products in this reaction were calculated from published data.⁵ Compounds **1**, **8**, and **9** were identified by spectral comparison with authentic samples.¹⁰,¹² Compound **11** was the only fully characterized dimer reported in a previous study of the methyl acetoacetate sensitized photodimerization of cyclohexene.⁶ A sample of 3-cyclohexylcyclohexene (**10**) was obtained by the reaction of cyclohexylmagnesium bromide with 3-bromocyclohexene.

X-Ray Crystal Structure of Photodimer 6. The foregoing structural assignment by cmr for the major photoproducts **6** and **12** rests on the hypothesis that the chemical shifts of the cyclobutyl carbons are predictably dependent on the conformation of the four-membered ring. In order to substantiate this assumption and to establish the unusual stereochemistry, an investigation of the X-ray crystal structure of **6** was undertaken.

(12) (a) P. E. Eaton, *J. Amer. Chem. Soc.*, **84**, 2454 (1962); (b) F. K. Signaigo and P. L. Cramer, *ibid.*, **55**, 3326 (1933).
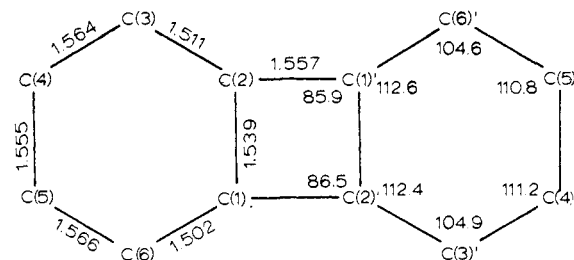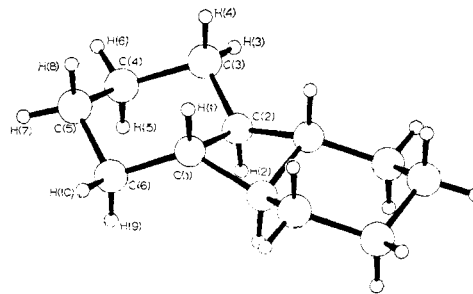
The most suitable crystal of **6** was grown from a melt, but was crystallographically disordered as shown schematically in Figure 1 where (+) and (−) indicate an atom above and below the plane, respectively. The structure resulting from the X-ray diffraction study is shown in Figure 1a which could result from the trans-anti-trans configuration in Figure 1b superimposed on its mirror image or from the trans-syn-trans configuration in Figure 1c superimposed on its enantiomer. Although this ambiguity cannot be resolved crystallographically, the correct assignment is clearly evident from a consideration of bond lengths. Several X-ray structure determinations have been carried out on fused ring systems containing a cyclobutane ring. There is abundant evidence that in structures of this type the *inter* ring bonds are always longer than the *intra* ring bonds, as shown in Table II. The bond lengths calculated for the assignment in Figure 1b would be consistent with this observation. The cyclobutane ring bond lengths for the trans-anti-trans configuration are 1.539 Å for the intra cyclohexane bond and 1.557 Å for the inter cyclohexane bond. On the other hand, the bond lengths for the trans-syn-trans model (Figure 1c) are 1.539 Å for the intra cyclohexane bond and only 1.505 Å for the inter ring bond. Moreover, a carbon–carbon bond length of 1.505 Å is unprecedented for all the cyclobutanes for which we have compiled X-ray crystal data. Indeed, carbon–carbon single bond lengths in substituted cyclobutanes generally are *longer* than the normal value of 1.537 Å (Table VII, see paragraph at end of paper regarding supplementary material). The trans-anti-trans model (Figure 1b) is therefore adopted.

The atomic coordinates and thermal parameters are given in Tables III and IV in the microfilm edition of the journal. The final bond distances and angles are listed in Table V and shown in Figure 2. Figure 3 shows a perspective view of the molecule and the num-
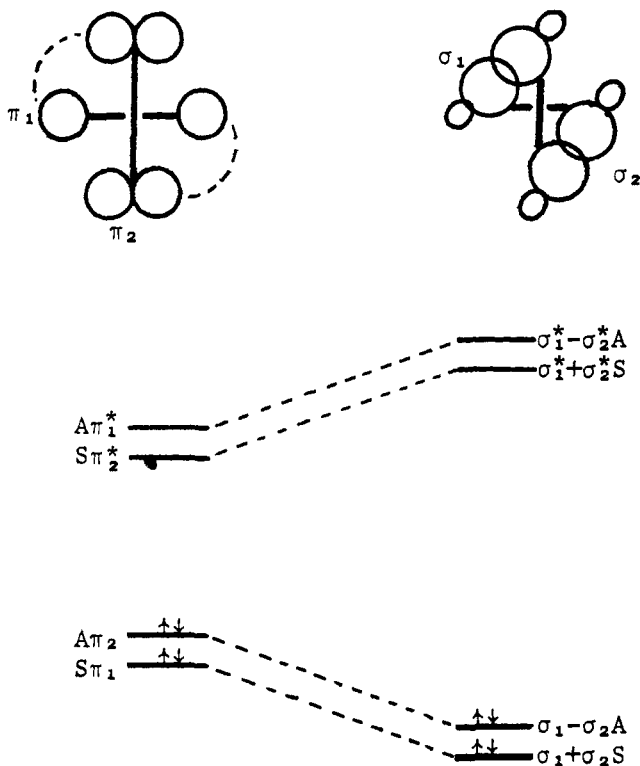
Figure 4. Correlation diagram for a $[2_{\pi_a} + 2_{\pi_s}]$ cycloaddition: $\pi_1 = \pi_s$, $\pi_2 = \pi_a$.

bering system used in the tables. Torsion angles for the molecule are also given in Table VI in the microfilm edition.

Although not required by the space group the molecular symmetry is approximately 222, with one twofold axis coinciding with the one in the space group, a second twofold axis going through the midpoints of C-(1)–C(2) and C(4)–C(5), and the third through the midpoints of C(1)–C(2)' and C(2)–C(1)'.

The cyclohexane ring is in the expected chair conformation. The average bond distance of 1.54 Å and average angle of 109.4° appear normal; X-ray mean values observed in cyclohexane[13] are 1.523 Å and 111.-34°. Both of the exocyclic (relative to the cyclobutane ring) bonds, C(2)–C(3) and C(6)–C(1), are shorter than normal C–C single bonds. The angles C(2)–C(3)–C(4) and C(5)–C(6)–C(1) are also smaller than normal.

The cyclobutane ring is quite puckered with a dihedral angle of 139 ± 2°, defined as the angle between the normals to the planes of C(2), C(1)', and C(2)' and C(2), C(1), C(2)'. This value for the trans-fused ring structure of **6** is outside the range of 147–178° found in cis-fused ring compounds (see Table II, supplementary material). The strain in the cyclobutane ring is also evident in the endocyclic angles of 85.9 and 86.5°. There appears to be nothing unusual in the molecular packing, intermolecular contacts being determined by normal van der Waals contacts.

Mechanisms of CuOTf Catalyzed and Triplet-Sensitized Photodimerizations. The stereochemical course of the CuOTf catalyzed photodimerizations of cyclohexene and cycloheptene are remarkable. Doubly trans-fused cyclobutanes **6** and **12** are selectively formed

in spite of a thermodynamic preference for the cis-fused isomers. This preference is evident, for example, in the isomerization of **18** to **19** under equilibrating conditions.[14]
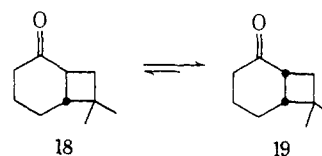
Formation of **6** and **12** necessitates a formal twisting of the C=C bonds of *both* of the cycloalkene monomers. The overall transformations are formally $[2_{\pi_a} + 2_{\pi_a}]$ cycloadditions. Such cycloadditions conserve orbital symmetry in a concerted photoexcited-state
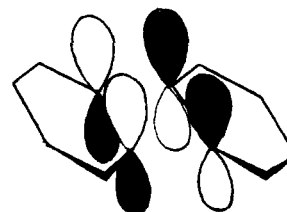
process. However, it is not clear how such a concerted process could avoid serious unfavorable steric interference. A more readily acceptable mechanism for the copper(I) triflate promoted photodimerizations of cycloheptene and cyclohexene involves initial copper(I) catalyzed photoisomerization to trans cycloolefins. The latter may be coordinated with copper(I) and thereby derive a degree of stabilization.[8] Cyclohexyne and cycloheptyne which, like trans-cyclohexene and trans-cycloheptene, are highly strained unsaturated carbocycles, form isolable complexes with Pt(0).[15] Such a mechanism accords a special significance to ring size and can explain the unreactivity of acyclic olefins. Thus, eight-membered or larger trans-cycloalkenes are relatively stable, isolable compounds.[16] Copper(I) salts catalyze the photochemical production of these compounds from their cis-isomeric counterparts. trans-Cycloheptene has been generated thermally and trapped but never isolated.[17] Both trans-cyclohexene and trans-cycloheptene have been suspected as reactive intermediates in photosensitized ionic addition reactions of the corresponding cis-cycloalkenes.[18]

A second cis-olefinic reaction partner must also undergo a twisting of its C=C bond during the dimerization. This process can be efficiently achieved by the stereoelectronic control of a concerted thermal $[2_{\pi_a} + 2_{\pi_s}]$ cycloaddition of a reactive trans-cycloalkene with another molecule of cis-cycloalkene. Such a process conserves orbital symmetry as indicated in the correlation diagram shown in Figure 4. One face of the trans-cycloalkene C=C bond is shielded by a polymethylene bridge, and the other face is quite exposed. Hence, the trans-cycloalkene is both ideally suited for and sterically restricted to a suprafacial reaction. There-

(13) R. Kahn, R. Fourme, D. Andre, and M. Renaud, *Acta Crystallogr., Sect. B*, **29**, 131 (1973).

(14) E. J. Corey, J. D. Bass, R. Le Mahieu, and R. B. Mitra, *J. Amer. Chem. Soc.*, **86**, 5570 (1964).

(15) M. A. Bennett, G. B. Robertson, P. O. Whimp, and T. Yoshida, *J. Amer. Chem. Soc.*, **93**, 3797 (1971).

(16) K. Ziegler and H. Wilms, *Justus Liebigs Ann. Chem.*, **567**, 1 (1950).

(17) E. J. Corey, F. A. Carey, and R. A. E. Winter, *J. Amer. Chem. Soc.*, **87**, 934 (1965).

(18) J. A. Marshall and R. D. Carroll, *J. Amer. Chem. Soc.*, **88**, 4092 (1966); (b) P. J. Kropp and H. J. Krauss, *ibid.*, **89**, 5199 (1967); (c) J. A. Marshall, *Accounts Chem. Res.*, **2**, 33 (1969).
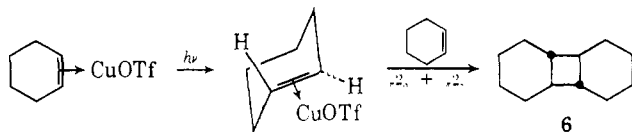
fore, *cis*-cycloalkene must be the antarafacial partner in the reaction. Such a process is sterically unencumbered, and could lead to either of two possible doubly trans-fused isomers. The selective production of the less sterically congested trans-anti-trans isomer **6** rather than the trans-syn-trans isomer **16** is a reasonable consequence of "product development control."

As with larger ring cycloalkenes, cis–trans isomerization of acyclic alkenes does not yield unusually reactive products. Moreover, the twisting of the C=C bond associated with excitation to the first singlet or triplet excited states[19] may provide a pathway for energy loss[1] which would be most efficient for systems in which twisting is not accompanied by the creation of torsional strain.

The availability of a *trans*-cycloalkene intermediate is not a necessary condition for the Cu(I)-catalyzed photodimerization. Clearly, cis–trans isomerization of norbornene derivatives or cyclopentene is structurally prohibited and the reaction takes a different course giving cis-fused isomers. These olefins should give rise to highly strained and reactive[18c] singlet or triplet first excited states which may be expected to have relatively long lifetimes.[1]

For comparison we have determined the stereochemical course of the triplet-sensitized dimerization of cyclohexene. Methyl acetoacetate sensitized photolysis of cyclohexene was reported to yield two stereoisomeric cyclobutanes[6] which were incorrectly assumed to be the cis-fused isomers **9** and **15**.[20] We isolated and characterized three cyclobutane stereoisomers. The two major products correspond to those found previously. They are the *trans-anti-trans*- and *cis-trans*-tricyclo[6.4.0.0²,⁷]dodecane (**6** and **7**), respectively. In addition, minor amounts of another dimer, *cis-anti-cis*-tricyclo[6.4.0.0²,⁷]dodecane (**9**) were also found. No trace of the cis-syn-cis isomer **15** was detected. Other products included 3,3′-bicyclohexenyl (**11**) and 3-cyclohexylcyclohexene (**10**). Analogous products were reported for the acetone-sensitized photodimerization of cyclopentene.[5] The latter gives the cis-fused cyclobutane **1** as well as 3,3′-bicyclopentenyl **3**, 3-cyclopentylcyclopentene **4**, and bicyclopentyl **5**.

We anticipated the photodimeric cyclobutanes such as **6**, **7**, and **9** to be unstable and interconverted by epimerization under the reaction conditions, since hydrogen atom abstraction from hydrocarbons such as cyclohexane by triplet state ketones is well documented.[21] Epimerization of tertiary centers by the reversible generation of free radicals is also known as in the example involving the photoepimerizations in the presence of HgBr₂.[22] A solution of the cyclobutane **6** in

acetone was irradiated with 350-nm light to afford a complex mixture of products including all three of the cyclobutanes **6**, **7**, and **9**. The free radical photoepimerization of **6** in the presence of HgBr₂ was also examined. As expected, **6** was slowly converted into **7** upon irradiation of a cyclohexane solution with 254-nm uv light in the presence of HgBr₂. In control experiments, no photoepimerization of **6** occurred in the presence of CuOTf.

Conclusion

The stereochemical course of the CuOTf catalyzed photodimerizations of cyclohexene and cycloheptene is remarkable. The thermodynamically less stable transfused tricyclododecanes and tricyclotetradecanes are formed preferentially. The stereoselectivity of these dimerizations as well as the reluctance of cyclooctene and acyclic olefins to undergo photodimerization may indicate a concerted orbital-symmetry controlled process involving formation of reactive CuOTf complexed trans cycloolefin intermediates.

The corresponding triplet-sensitized photodimerizations of cyclopentene and cyclohexene are of limited preparative value since yields of dimers are low and accompanied by numerous side products which are difficult to separate. Moreover, the dimerization of cyclohexene is nonstereospecific, although the actual stereospecificity of the reaction may be greater than observed since the cyclobutane products are epimerically unstable toward uv irradiation in the presence of a triplet sensitizer. A reactive trans cyclohexene intermediate may also be involved in the triplet sensitized dimerization, since trans-fused tricyclododecanes are formed preferentially.

Experimental Section

Elemental microanalysis was performed by Spang Microanalytical Laboratory, Ann Arbor, Mich. Proton magnetic resonance spectra were obtained on a Varian HR-220 or A-60 spectrometer. Carbon magnetic resonance spectra were recorded on a Varian DP-60 Fourier transform spectrometer with proton decoupling. In addition, off-resonance decoupled spectra were recorded to aid in differentiation of carbon resonances due to methylene and methine carbons. All cmr spectra are reported in ppm upfield from CS₂, and were measured in CCl₄ solution taking the CCl₄ resonance at 96.7 as an internal standard. All pmr spectra are reported in ppm downfield from tetramethylsilane, and were measured in CCl₄ solution with TMS as an internal standard. Infrared spectra were recorded on a Perkin-Elmer 137 G spectrometer using neat liquids between KBr disks or solids fused into KBr disks. Ultraviolet spectra were recorded with a Cary 14 spectrophotometer. All reactions with copper trifluoromethanesulfonate complexes or other air-sensitive organometallics as well as all photoreactions were conducted in an atmosphere of dry nitrogen. Vapor phase chromatography (vpc) was performed on a Varian A-90 or Aerograph Hi Fy chromatograph.

Copper(I) Triflate Catalyzed Photodimerization of Cyclopentene. A solution of (CuOTf)₂–C₆H₆ (0.4 g) in cyclopentene (7 ml, 5.4 g) was irradiated in a quartz tube for 120 hr with 254-nm light. The mixture was then taken up in pentane and washed with aqueous KCN (30 ml of 2.5 M) to remove copper(I). Pentane and unreacted cyclopentene were removed by distillation. The crude dimer was distilled under reduced pressure to yield 1.9 g of dimers, bp 40–58° (10 mm). Analysis of the distillate by vpc revealed the presence of three products. The relative retention times of these products on a 10 ft × 0.25 in. Apiezon J on Firebrick column were 14, 17, and 21 min and the relative yields were 85, 6, and 9%, respectively. Samples of the first and last products were isolated by preparative vpc and characterized as follows.

cis-anti-cis-Tricyclo[5.3.0.0²,⁶]decane (**1**). A mixture of *cis-anti-cis*-tricyclo[5.3.0.0²,⁶]decan-3-one[12] (3.0 g, 20 mmol), KOH (2.6 g, 2.2 equiv), 85% hydrazine (hydrate) (2.6 ml, 3.6 equiv), and tri-

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ethylene glycol (26 ml) was boiled under reflux for 1.5 hr to form the hydrazone. Water, excess hydrazine, and most of the hydrocarbon product were removed by distillation until the temperature of the pot rose to 200°. Boiling was continued for 3 more hr. The cooled solution was diluted with 26 ml of water and extracted with pentane. The distillate was extracted with the same pentane. The organic extract was washed with water and then saturated aqueous NaCl and dried (MgSO₄). After removal of pentane by distillation, the residual oil was distilled under reduced pressure: bp 56° (10 mm); ir 1460, 1435, 1300, 1255, 1220, 1175, 1020, 957, 936, 900, 858, 828 cm⁻¹; pmr (220 MHz) δ 1.94 (4 H, d, J = 6 Hz), 1.73 (4 H, m), 1.53 (4 H, m), 1.39 (4 H, m); cmr see Table I. *Anal.* Calcd for C₁₀H₁₆: C, 88.16; H, 11.84. Found: C, 88.16; H, 11.88. This hydrocarbon was identical by cmr spectroscopy and vpc retention time with the major product of the copper(I) catalyzed photodimerization of cyclopentene; *i.e.*, relative retention time 14 min (see above).

cis-syn-cis-Tricyclo[5.3.0.0²,⁶]decane (2). The product of relative retention time 21 min (see above) exhibits: pmr (220 MHz) δ 2.66 (4 H, s), 1.45 (12 H, m); cmr see Table I. *Anal.* Calcd for C₁₀H₁₆: C, 88.16; H, 11.84. Found: C, 87.92; H, 11.89.

cis-syn-cis-Tricyclo[6.4.0.0²,⁷]dodecane (15). 1,3-Cyclohexadiene was photodimerized.[10] A sample of *cis-syn-cis*-tricyclo[6.4.0.-0²,⁷]dodeca-3,11-diene was separated from the mixture of photodimers by spinning band distillation. The diene (0.39 g) was stirred under H₂ with a suspension of 100 mg of 5% Pd/C in 6 ml of ethanol until hydrogen absorption ceased. The catalyst was removed by filtration and washed with pentane (30 ml). The combined filtrate and washings were washed with water and then dried (Na₂SO₄) and concentrated by rotary evaporation. Last traces of solvent were removed by evacuation through a Dry Ice–acetone trap to yield 0.39 g of crude product. Final purification was accomplished by preparative vpc on a 10 ft × 0.25 in. column containing Apiezon J on Firebrick at 210°: ir 2900, 1460, 1445, 980, 915, 810 cm⁻¹; pmr (220 MHz) δ 2.37 (4 H, s), 1.59 (12 H, m), 1.25 (4 H, broad s); cmr see Table I, exact mass, 164.1563 (calcd for C₁₂H₂₀, 164.1565).

cis-anti-cis-Tricyclo[6.4.0.0²,⁷]dodecane (9). The hydrocarbon 9 was prepared from the corresponding diene as described previously.[10] It exhibited: ir 2900, 2820, 1445, 1350, 928, 878, 847, 813 cm⁻¹; pmr (220 MHz) δ 2.00 (4 H, s), 0.91–1.68 (16 H); cmr see Table I.

Copper(I) Triflate Catalyzed Photodimerization of Cyclohexene. A solution of (CuOTf)₂–C₆H₆ (0.2 g) in cyclohexene (4 ml, 3.2 g) and THF (1 ml) was sealed into a quartz tube (0.8 cm i.d.) and irradiated for 108 hr with 254-nm light in a Rayonet Photochemical reactor. The mixture was then taken up in pentane, washed with aqueous KCN (30 ml of 2.5 N) to remove copper(I), and dried (MgSO₄). Solvent and unreacted cyclohexene (1.4 ml, 1.1 g) were removed by careful distillation. The residual oil was distilled under reduced pressure to yield a total of 1.7 g (81%) of products boiling in the range 96–98° (10 mm). The distillate was shown to consist of three dimers by vpc on a 5 ft × 0.25 in. column containing 20% SF96 on 60–80 Firebrick. Samples of each product were isolated by preparative vpc. Relative retention times and yields were 1.00 (60%), 1.11 (10%), and 1.29 (30%). The product of longest retention time was identified as 1-cyclohexylcyclohexene by comparison of its pmr and cmr spectra with those of an authentic sample prepared by the method of Signaigo and Cramer.[12b] The major and minor products were assigned the structures 6 and 7, respectively, based, in part, on the following physical measurements.

trans-anti-trans-Tricyclo[6.4.0.0²,⁷]dodecane (6). The major product is a crystalline solid: mp 41–42°; ir 2850, 1450, 1340, 1020, 1035, 950, 910, 817 cm⁻¹; pmr (60 MHz) two broad peaks centered at δ 1.75 and 1.13; cmr see Table I. *Anal.* Calcd for C₁₂H₂₀: C, 87.73; H, 12.27. Found: C, 87.71; H, 12.15.

cis-trans-Tricyclo[6.4.0.0²,⁷]dodecane (7). The smallest product from CuOTf catalyzed photodimerization is an oil: ir 2850, 1450, 1320, 1130, 1060, 985, 920, 870, 845, 820, 805 cm⁻¹; cmr see Table I; exact mass 164.15666 (calcd for C₁₂H₂₀, 164.1565).

Photolysis of Cyclohexene in the Presence of Benzene. A solution of benzene (0.2 ml) in cyclohexene (4 ml) was irradiated at 254 nm in a sealed quartz tube for 120 hr. The mixture was analyzed by vpc for cyclohexene dimers. None were detected. The unreacted cyclohexene and benzene were removed by distillation to leave about 0.2 g of a polymeric residue which again was shown not to contain cyclohexene dimers by vpc analysis.

Copper(I) Triflate Catalyzed Photodimerization of Cycloheptene. A solution of (CuOTf)₂–C₆H₆ (0.2 g) in cycloheptene (4 ml, 3.3 g)

was sealed into a quartz tube (0.8 cm i.d.). The solution was irradiated at 254 nm for 108 hr in a Rayonet Photochemical reactor. The mixture was then taken up in pentane and washed with aqueous KCN (30 ml of 2.5 M) to remove copper(I). Pentane was removed by rotary evaporation and unreacted cycloheptene (1.5 ml, 1.2 g) by distillation. The semicrystalline residue was taken up in pentane. The solution deposited fine needles upon cooling with a Dry Ice–acetone bath. A total of 1.1 g of a single dimer (57%) was isolated which was purified further by sublimation at 110° (0.3 mm). It had a mp 128–130°; ir 1440, 1340, 1275, 1215, 1115, 942, 825, 767, 740 cm⁻¹; pmr (220 MHz) δ 1.80 (4 H, dd, J = 6 Hz), 1.52 (8 H, m), 1.36 (4 H, m), 1.14 (4 H, t, J = 13 Hz), 0.82 (4 H, s); cmr see Table I. *Anal.* Calcd for C₁₄H₂₄: C, 87.42; H, 12.58. Found: C, 87.48; H, 12.72. These data support a *trans-anti-trans*-tricyclo[7.5.0.0²,⁸]tetradecane (12) structure for this dimer which is different from the previously reported cis-syn-cis (mp 53°) and cis-trans (an oil) isomers, or tetradecahydrocyclobuta[1,2:3,4]-dicycloheptene isomers.

Triplet-Sensitized Photodimerization of Cyclohexene. Cyclohexene was irradiated with uv light in the presence of methyl acetoacetate under the reaction conditions previously reported by Tada, Kokubo, and Sato.[6] Thus, methyl acetoacetate (29 g) in cyclohexene (82 g) and benzene (350 ml) was irradiated internally with a 450-W Hanovia medium-pressure mercury lamp through a quartz immersion well for 14 hr. Solvent, unreacted cyclohexene, and sensitizer were removed by distillation and dimers were isolated by distillation under reduced pressure as a broad fraction, bp 40–100° (2–3 mm) (20 g). Sensitizer adducts containing an ester group were removed by stirring this fraction with KOH (20 g) in water (15 ml) and methanol (20 ml) under gentle reflux for 3 hr. After cooling, pentane (100 ml) was added and the organic phase was washed with water. The organic extract was analyzed by vpc on a 6 ft × 0.25 in. column containing 15% Carbowax on 30–60 Chromosorb P at 140°. The following products were obtained and are listed with their relative vpc retention times and estimated absolute yields in Table VIII. Yields were estimated for dimers based on

Table VIII

Product	Retention time, min	Yield, %
trans-anti-trans-Tricyclo[6.4.0.0²,⁷]dodecane (6)	6.9	1.0
cis-trans-Tricyclo[6.4.0.0²,⁷]dodecane (7)	8.5	1.5
cis-anti-cis-Tricyclo[6.4.0.0²,⁷]dodecane (9)	9.3	0.6
Not isolated	11.0	0.8
3-Cyclohexylcyclohexene (10)	12.3	0.9
3,3′-Bicyclohexenyl (11)	15.0	0.9

the weight of product 11 isolated from this organic extract and the relative peak areas of the other dimers *vs.* 11. Product 11 was isolated as follows. The organic extract was treated with AgNO₃ (40 g) in water (100 ml). The aqueous phase was then treated with concentrated aqueous NH₄OH (100 ml), and, after cooling, the mixture was extracted with pentane. The extract was washed with water (2 × 50 ml) and then with saturated aqueous NaCl (50 ml). Rotary evaporation of solvent left 0.7 g of crude oily product which was almost pure 11 by comparison of its pmr spectrum with that of an authentic sample.[6]

The organic phase, after AgNO₃ extraction, was washed with water, and then concentrated by rotary evaporation. The resulting oil was distilled under reduced pressure. The products 6 and 7 were isolated from a fraction bp 85–105° (10 mm) (4 g) by preparative vpc on a 10 ft × 0.25 in. column of Apiezon J on Firebrick at 200°. These products correspond to Tada, Kokubo, and Sato's products VIIa and VIIb, respectively (which were not fully characterized previously), according to retention times relative to 3,3′-bicyclohexenyl and comparison of ir spectra with those reported. In addition, products of greater retention time were collected in a single fraction. Samples of the products 9, 10, and 11 were obtained from this fraction by preparative vpc on the above mentioned Carbowax column at 140°.

Products 6, 7, and 9 were characterized by comparison of vpc retention times as well as ir or cmr spectra with those of authentic samples (*vide supra*). Product 10 was identified with 3-cyclohexylcyclohexene which was unambiguously synthesized (*vide infra*).

3-Cyclohexylcyclohexene (10). A solution of 3-bromocyclohexene (3.2 g, 20 mmol) in ether (3 ml) was added dropwise to a

solution of cyclohexylmagnesium bromide (30 mmol) in ether (30 mmol). The resulting mixture was boiled under reflux for an additional hour. After cooling, the mixture was poured onto a mixture of ice and concentrated HCl (20 ml). The resulting mixture was extracted with ether. The extract was washed with water and then with saturated aqueous NaCl and dried (Na_2SO_4). Solvent was removed by distillation and the residual oily crude product was distilled under reduced pressure to give the title compound (1.9 g) in 57% yield: bp 112–114° (12 mm); pmr (60 MHz) δ 5.63 (2 H, s), 1.0–2.2 (18 H); exact mass, 164.1573 (calcd for $C_{12}H_{20}$, 164.1565).

Epimerization of *trans-anti-trans*-Tricyclo[6.4.0.0^{2,7}]dodecane (6) with $HgBr_2$. A suspension of $HgBr_2$ (0.1 mmol, 36 mg) in a 0.05 M solution of 6 (16 mg) in cyclohexane (2 ml) was deoxygenated with a stream of N_2 and then irradiated in a quartz tube with 254-nm light. A black deposit formed on the walls of the tube. The deposit was intermittently removed by scraping. After a week of irradiation the solution was analyzed for tricyclododecane isomers by vpc on both a 10 ft × $^1/_8$ in. 15% FFAP on 60–80 Chromosorb P column at 150° and a 7 ft × $^1/_8$ in. 20% PDEAS on 60–80 Chromosorb P (HMDS) column at 140°. The product mixture consisted of two isomers 6 and 7 in a ratio of 2:1. Retention times were 6, 11.6 min and 7, 14.5 min on the FFAP column and 6, 16.0 min and 7, 21.0 min on the PDEAS column.

Acetone-Sensitized Photoepimerization of *trans-anti-trans*-Tricyclo-[6.4.0.0^{2,7}]dodecane. A solution of *trans-anti-trans*-tricyclo[6.4.-0.0^{2,7}]dodecane (6) (40 mg) in acetone (2 ml) was irradiated in a Pyrex tube with 350-nm light for 1 day. Analysis by vpc (10 ft × $^1/_8$ in. 15% FFAP on 60–80 Chromosorb P column at 150°) indicated five components including unreacted 6. Besides 6, two other cyclobutanes were identified. The other products were not characterized. The identities, retention times, and relative yields of the cyclobutane epimers were: 6, 14.8 min, 79%; 7, 18.1 min, 18%; 9, 20.0 min, 3%. The cis-syn-cis isomer 15, retention time 31.0 min, was not detected in the product mixture.

Uv Irradiation of *trans-anti-trans*-Tricyclo[6.4.0.0^{2,7}]dodecane in a Solution of CuOTf in Cycloheptene. A solution of 6 (20 mg) and (CuOTf)$_2$–C_6H_6 (40 mg) in cycloheptene (2 ml) and THF (0.5 ml) was prepared and 0.5 ml was sealed in a quartz tube. Tetradecane (20 μl) was added to the rest of the solution and 0.5 ml was sealed in a quartz tube. Both tubes were irradiated with 254-nm light for 109 hr. Analysis of the products (on a 10 ft × $^1/_8$ in. 15% FFAP on 60–80 Chromosorb P column at 150°) revealed the absence of any traces of 7 or 8 and the same ratio of 6 to *n*-tetradecane as before irradiation.

Crystal Data for *trans-anti-trans*-Tricyclo[6.4.0.0^{2,7}]dodecane. The crystals of the dimer 6 obtained by recrystallization were colorless, transparent plates of poor quality for X-ray diffraction work. A small amount of sample (mp 41–42°) was therefore sealed in a 0.3 mm diameter thin-walled glass capillary and a crystal was grown from the melt. Several attempts to crystallize the sample into a predominant single crystal afforded a fragment representing about 3% of the volume. The main crystal measured 0.3 mm in length and 0.3 mm in diameter. Crystal data: $C_{12}H_{20}$, mol wt, 164.3; monoclinic, a = 9.426 (8), b = 4.791 (5), and c = 11.770 (8) Å; β = 105.07 (4)°, V = 513.2 × 10^{-24} cm^3, Z = 2, ρ_{calcd} 1.063 g cm^{-3}. $F(000)$ = 184, $\mu_{Mo\,K\alpha}$ = 0.632 cm^{-1}. With systematic absences of hkl when $k + l = 2n + 1$ the space group is either $A2/m$, $A2$, or Am.

Data Collection and Reduction. Data were collected at $-140°$ on a Picker FACS-1 diffractometer equipped with a nitrogen cold stream of local design.[23] The unit cell parameters were obtained by a least-squares fit to the angular settings of 18 reflections carefully centered at $\pm 2\theta$. The take-off angle was 2°; a pulse height analyzer and a graphite monochromator were used (λ 0.71069). The crystal-to-aperture (4 × 4 mm) distance was 25 cm, while the distance from the monochromator to the crystal was 14.5 cm. The mosaic spread of the crystal was checked by performing ω scans on several strong reflections. The average half-width was 0.27°. Twofold redundant data $hk \pm l$ and $\bar{h}k \pm l$ were collected in the range $4 \leq 2\theta \leq 55°$ using the moving crystal moving counter technique with a 2θ scan rate of 2°/min and a symmetric scan width of 2.8° + dispersion; 20-sec stationary background counts were measured on each side of the reflection. When the data collection was initiated the space group was thought to be

$P2_1/c$, three standard reflections were collected every 30 measurements, and a total of 3235 intensities were measured. During the data collection it became evident that all reflections hkl for which $k + l = 2n + 1$ were unobserved; the space group was therefore assigned to $A2/m$, $A2$, or Am. A drift in the standards was also observed during data collection; repeated attempts to realign the crystal failed to recover the intensity and a correction for the drift was deemed necessary. The locally written program[24] to correct for the drift takes into account the fact that the decay was anisotropic as determined from a plot of the three standards, which were noncoplanar reciprocal lattice vectors. Data reduction was then carried out in the usual manner[25] resulting in 663 unique reflections of which 212 were considered observed by the criterion $|F_o|^2 \geq 2\sigma(F_o^2)$. No corrections for absorption or extinction were carried out.

At the termination of the data collection the small fragment was carefully aligned and sample data were collected for later removal of possible overlap of reflections.

Structure Solution and Refinement. Both the averages of the normalized structure factor magnitudes (E_{hkl}) and the zero-moment test indicated a centrosymmetric space group and the structure solution was therefore approached using the centrosymmetric direct method technique,[26] even though this implied a disordered structure. A three-dimensional E map appeared to indicate even more disorder than had been expected. However, this was resolved as a case of a pseudohomometric structure described by Bürgi and Dunitz.[27] With only two molecules in the unit cell in space group $A2/m$, having the equivalent positions $(0,0,0; 0, ^1/_2, ^1/_2) \pm (x, y, z; x, \bar{y}, z)$, molecular symmetry $2/m$ is imposed. Consequently a superposition of the molecule and its mirror image was observed. This structure consisting of six half-weight carbon atoms was refined using full-matrix least-squares methods varying positional and isotropic thermal parameters for all atoms. Hydrogen atoms were initially included, but not varied, in calculated positions with an isotropic B of 3.0, and reestimated after every two cycles of refinement. The hydrogen atom positions were confirmed in a final difference Fourier where only the carbon atoms were used in the structure factor calculation. The hydrogen atoms on the cyclobutane ring which were the most difficult to estimate showed up particularly well, since they were well removed from the plane of disorder. Anisotropic refinement was not attempted in view of the disorder and the close proximity of some of the atoms to the mirror plane. At convergence the average parameter shift was 0.01σ and the maximum was 0.04σ. The final values of $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_w = [\Sigma w (F_o^2 - F_c^2)^2/\Sigma w F_o^4]^{1/2}$ were 0.056 and 0.111, respectively. The standard error of an observation of unit weight $[\Sigma w (F_o^2 - F_c^2)^2/NO - NV]^{1/2}$ was 0.95 for NO = 212 and NV = 25. The quantity minimized was $\Sigma w (F_o^2 - F_c^2)^2$ where $w = 1/\sigma^2(F_o)^2$. The final residual R_w for 663 unique reflections was 0.122 and no anomalies were observed for the "unobserved" data. The atomic scattering factor for carbon was taken from the "International Tables for Crystallography"[28] and the one for hydrogen from Stewart, et al.[29]

The atomic parameters, for carbon and hydrogen in the photodimer 6, are listed in Tables III and IV, respectively, as are the bond lengths and angles in Tables V and VI (supplementary material).

Supplementary Material Available. Tables II–VII and a tabular listing of h, k, l, 10 $|F_o|$, and 10 F_o in electrons will appear following

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(24) In addition to local programs for the CDC 6600 and XDS Sigma 2 used in this work, local versions of the following programs were employed: SAYEQ, direct methods program of Long; FORDAP, Fourier program of Zalkin; ORFFE, function and error program of Busing and Levy; ORTEP, thermal ellipsoid plot of Johnson; LINUS, full-matrix least-squares program of Hamilton; this program closely resembles the ORFLS program of Busing and Levy.

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Photoisomerization of 4-Pyridones to 2-Pyridones

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Abstract: Irradiation of 1,2,6-trimethyl-3,5-diphenyl-4-pyridone or 1-ethyl-2,6-dimethyl-3,5-diphenyl-4-pyridone with a medium-pressure mercury lamp yielded their isomers, 1,4,6-trimethyl-3,5-diphenyl-2-pyridone or 1-ethyl-4,6-dimethyl-3,5-diphenyl-4-pyridone, respectively. However, photolysis of 1-n-propyl-2,6-dimethyl-3,5-diphenyl-4-pyridone or 1-methyl-2,3,5,6-tetraphenyl-4-pyridone produced no reaction. This photoisomerization was shown to proceed via the singlet state with moderate quantum efficiency. Mechanistic aspects of the reaction were discussed.
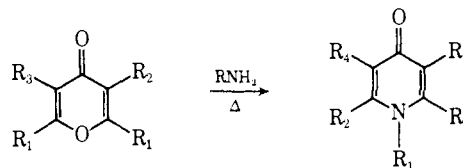
The photochemistry of cyclohexadienones bearing a heteroatom in the ring has been studied extensively.[2] In most cases the known photoreactions of these compounds are restricted to dimerization and isomerization. In 2-pyridones photodimerization was described about 10 years ago,[3-5] and the [4 + 4] cycloadducts were obtained. The photoisomerization of 1-methyl-2-pyridone to N-methyl-2-aza-3-oxabicyclo[2.2.0]hex-5-ene[6] was accomplished by low-temperature photolysis, and the generality of this photoisomerization of 2-pyridones[7] was recently established. A kinetic analysis of photoisomerization of 1-methyl-2-pyridone by quenching and sensitization has shown[8] that the lowest singlet state is involved in the formation of the products. On the other hand, relatively little attention has been given to the photochemical reaction of 4-pyridones. Sugiyama and his group[9] reported that ultraviolet irradiation of 1,2,6-trimethyl-4-pyridone and 1,2-diphenyl-6-methyl-4-pyridone resulted in recovery of the starting materials.

Formation of the photodimer from 4-pyrones[10] and 4-thiopyrones[11] is well known. However, we recently found that introduction of a phenyl group into the C-3 and C-5 positions of 4-pyrone and 4-thiopyrone prevents the formation of the photodimer and that photolysis of these hindered 4-pyrones[12] and 4-thiopyrones[13] afforded 2-pyrones and cyclopentadienones, respectively. While the nature of the substituent effect upon photoisomerization of hindered 4-pyrones was not fully understood, it was anticipated that introduction of the phenyl substituent into the C-3 and C-5 positions of 4-pyridones might increase the photoreactivity of 4-pyridones. In this respect 1,2,6-trimethyl-3,5-diphenyl-4-pyridone (1), 1-ethyl-2,6-dimethyl-3,5-diphenyl-4-pyridone (2), 1-n-propyl-2,6-dimethyl-3,5-diphenyl-4-pyridone (3), 1-methyl-2,3,5,6-tetraphenyl-4-pyridone (4), and 1,2,6-trimethyl-3-phenyl-4-pyridone (5) were prepared as the hindered 4-pyridones and their photochemistry was studied. The present paper[14] deals with the photoisomerization of these hindered 4-pyridones to 2-pyridones as well as comparison of the photoreactivity of these compounds with that of hindered 4-pyrones.[12]

Results

Preparative Photochemistry and Product Structure Proof. The synthesis of hindered 4-pyridones (1–5) utilized the condensation[15] of the corresponding 4-pyrones (6–8) with alkylamines. The structure assigned

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6, R_1 = Me; R_2 = R_3 = Ph

7, R_1 = R_2 = R_3 = Ph

8, R_1 = Me; R_2 = Ph; R_3 = H

1, R_1 = R_2 = Me; R_3 = R_4 = Ph

2, R_1 = Et; R_2 = Me; R_3 = R_4 = Ph

3, R_1 = n-Pr; R_2 = Me; R_3 = R_4 = Ph

4, R_1 = Me; R_2 = R_3 = R_4 = Ph

5, R_1 = R_2 = Me; R_3 = Ph; R_4 = H