of General Education, Kyushu University) for providing their X-ray crystallographic programs.

Registry No. **1a**, 16691-79-5; **1b**, 26307-17-5; **1c**, 479-33-4; **1d**, 32683-51-5; **1e**, 5660-91-3; **1f**, 13177-38-3; **2a**, 2955-79-5; **2b**, 17870-94-9; **3**, 74947-87-8; **3a**, 72001-25-3; **4a**, 74947-88-9; **5′**, 74947-89-0; **5a**, 72003-84-0; **5d**, 70363-69-8; **6**, 74947-90-3; **8**, 26536-34-5; **9**, 106-99-0.

Supplementary Material Available: Listings of interatomic distances (Table X, **3a**; Table XI, **5a**; Table XII, **5d**), intermolecular angles (Table XIII, **3a**, Table XIV, **5a**; Table XV, **5d**), atomic and anisotropic thermal parameters (Table XVI, **3a**; Table XVII, **5a**; Table XVIII, **5d**), and hydrogen atomic parameters (Table XIX, **3a**; Table XX, **5a**; Table XXI, **5d**) (12 pages). Ordering information is given on any current masthead page.

Photocycloaddition Chemistry of 2-(Trimethylsilyl)cyclopentenone and 5-(Trimethylsilyl)uracil. The Utility of a Trimethylsilyl Group as a Removable Directing Group in Photochemistry

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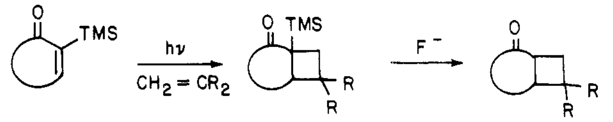
The photocycloaddition reactions of 2-(trimethylsilyl)cyclopentenone with isobutylene, methylenecyclohexane, isopropenyl acetate, propylene, and propyne were investigated. In the first three cases, a regiospecific reaction giving the head-to-tail photoadduct was observed while with propylene and propyne a mixture of head-to-head and head-to-tail isomers was produced. The directing effect of the 5-trimethylsilyl group in uracil photocycloaddition chemistry was dramatic; isobutylene, methylenecyclohexane, and even propylene gave only the head-to-tail adduct in high yield. These photoaddition products may be desilylated to adducts of cyclopentenone and uracil by potassium fluoride dihydrate in dimethyl sulfoxide. The reactions of 2-(triethylsilyl)- and 2-(triphenylsilyl)-cyclopentenone with propene were briefly examined to evaluate the effect of silicon substituents on the regioselectivity of the photocycloaddition reaction. The reaction of the former system with propene gives approximately the same ratio of photocycloaddition products as 2-(trimethylsilyl)cyclopentenone. Attempted photochemical reactions with 2-(triphenylsilyl)cyclopentenone led to decomposition of the starting enone. Finally, the use of a stannous chloride filter solution or a uranium glass filter for cyclopentenone photocycloaddition reactions minimizes the problem of secondary irradiation products being formed in these additions.

Introduction

Since the early observations of intramolecular photoaddition of cyclic enones to double bonds[3] and the extension of these reactions to intermolecular examples,[4,5] such cyclobutane-forming reactions have been of extensive value in organic syntheses. Thus, key steps in the synthesis of caryophyllene,[5] α-caryophyllene alcohol,[6] β-himachalene,[7] bourbonene,[8] loganin,[9] and ormosanine[10] involved photocycloaddition of an α,β-unsaturated ketone to olefin systems. Besides these classic examples, the recent literature is replete with new applications of these reactions in organic synthesis.

In spite of much effort in this area, there is still no clear picture of all the factors involved in determining the stereochemistry of the cyclobutane-ring fusion or the regioselectivity of cycloaddition reactions on unsymmetrical substrates.[11] However, the absence of mechanistic understanding of these reactions is countered by a wealth of literature examples[12] which allows certain generalizations to be made. First, the photocycloaddition reactions of cyclohexenones to oxygenated olefins (i.e., enol acetates, enol ethers, and ketene acetals) usually proceed in a highly selective head-to-tail manner. Second, the photocycloaddition reactions of cyclic enones with olefins bearing certain conjugating groups [i.e., $>C{=}CR(CO_2CH_3)$] give predominantly head-to-head products. However, the reactions of cycloalkenones (cyclohexenone, cyclopentenone) with simple unsymmetrical olefins often give rise to complications. While examples of such reactions are less numerous in the literature—presumably due to complications involved in the separation and characterization of the products—an ample number of reports attests to the low regioselectivity of the reaction.[5,8,12,13] In spite of the problem of mixtures of regioisomers encountered in some reactions, the utility of these reactions in some lengthy synthetic procedures[5] attests to the power of the synthetic method.

Scheme I. Proposed Sequence for Regiospecific Photocycloaddition



The development of methods for effecting high-yield, regiospecific photocycloadditions of cyclic enones to simple unsymmetrical olefins is an old but important problem. In general α-substituents (i.e., acetoxy,[14] fluoro,[15] methyl[16])

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[1] Abstracted in part from M.S. theses of E. L. Fritzen, 1978, and Chuan Shih, 1979, The Ohio State University.

[2] A preliminary report has appeared: Fritzen, E. L.; Swenton, J. S. *Tetrahedron Lett.* **1979**, 1951–1954.

[3] Ciamician, G.; Silber, P. *Chem. Ber.* **1908**, *41*, 1928–1935. Sernaggiotto, E. *Gazz. Chim. Ital.* **1917**, *47*, 153–159; *Ibid.* **1918**, *48*, 52–60. Büchi, G.; Goldman, I. M. *J. Am. Chem. Soc.* **1957**, *79*, 4741–4748.

[4] (a) Eaton, P. E. *J. Am. Chem. Soc.* **1962**, *84*, 2344–2348; (b) *Ibid.* **1962**, *84*, 2454–2455.

[5] (a) Corey, E. J.; Mitra, R. B.; Uda, H. *J. Am. Chem. Soc.* **1963**, *85*, 362–363; *Ibid.* **1964**, *86*, 485–492. (b) Corey, E. J.; Bass, J.; LeManiew, R.; Mitra, R. *Ibid.* **1964**, *86*, 5570–5583.

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[12] For a review, see: Meier, H. *Methoden Org. Chem.* (*Houben-Weyl*) **1975**, *4/5b*, 898–941.

[13] Eaton, P. E. *Acc. Chem. Res.* **1967**, *1*, 50–57.

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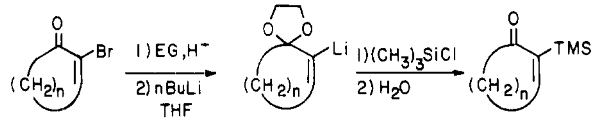
and β-substituents (acetoxy,[17] chloro,[18] cyano,[18] methyl,[16] methoxy[18]) on the enone appear to exert little control over the regioselectivity of the cycloaddition reaction to simple olefins. Ideally, a substitutent is desired which (a) controls the regioselectivity of the photocycloaddition and (b) can be replaced by hydrogen and/or other functional groups. An investigation of α-trimethylsilyl-substituted α,β-unsaturated systems was initiated since if photocycloaddition were regiospecific, then treatment with fluoride ion would result in replacement of the trimethylsilyl substituent by hydrogen (Scheme I). We report here the utility of the trimethylsilyl group as a removable directing group in photocycloaddition chemistry.

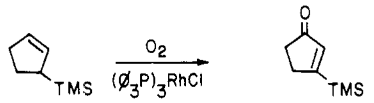
Synthesis of the Silylated Systems

The synthesis of the α-(trimethylsilyl)cyclopentenones and -cyclohexenones involved ketalization of the known α-bromo enones followed by metal–halogen exchange and silylation.[19–21] The chemistry proceeds smoothly except



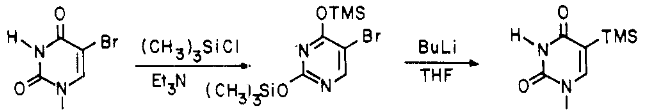
1 2 3

for the ketalization of the 2-bromocyclopentenone which under standard conditions could not be carried to completion. The best results were to allow ketalization to proceed to ca. 70% conversion and to separate the ketal from unreacted ketone by chromatography. The β-(trimethylsilyl)cyclopentenone was prepared by oxidation of the corresponding allyl silane.[22]



4 5

The 5-(trimethylsilyl)uracil was conveniently prepared from 5-bromouracil as outlined below.[23]



6 7 8

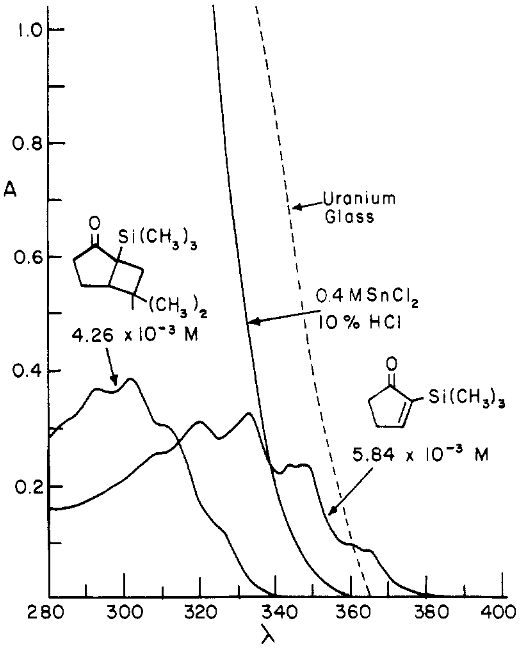
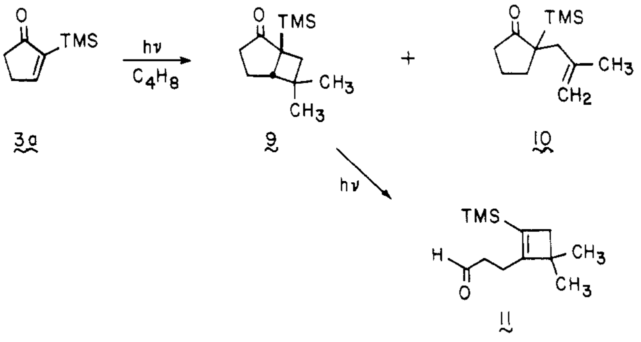


Figure 1. UV spectra of **3a**, **5**, $SnCl_2$ solution, and uranium glass filter (*Ace Bull.* **1980**, *19(2)*, 19).

Photochemical Cycloaddition Studies

Initial photochemical cycloaddition studies with **3a** using standard Pyrex-filtered light from a Hanovia medium-pressure source gave problems due to secondary irradiation of **9** to afford **11**. This problem, which has complicated the product mixtures from other cyclopentenone photocycloadditions,[4b,14,24] can be solved by proper filtering of the excitation source. When a standard Hanovia immersion-type apparatus is used, a uranium glass filter can be used.[25] For some of the work here, a Rayonet RPR-3500Å source was used, and filtering this light through a 0.4 M stannous chloride solution achieves the same effect as the uranium glass filter (see Figure 1). With light filtered in either way, the reaction of **3a** and isobutylene afforded **9** and **10** in the ratio 5.4:1 with no trace of **11**. Either of these methods improves the yield and reduces the formation of secondary products in other cyclopentenone additions also. The structure of **9** was established by desilylation followed by comparison of this with an authentic sample.[14c] Similarly, desilylation of **10** gave a product identical with the ketone prepared from reaction of the morpholine enamine of cyclopentanone with methallyl iodide followed by hydrolysis. The structure of **11** rests totally on spectroscopic



3a 9 10 11

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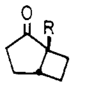
(25) Agosta, W. C.; Smith, A. B. *J. Am. Chem. Soc.* **1971**, *93*, 5513–5520. A number of workers, initially including ourselves, apparently have been unaware of the expediency of a uranium glass filter in cyclopentenone work.

data (IR, ^{1}H and ^{13}C NMR) and should be considered tentative.

The reaction of **3a** with ethylene, methylenecyclohexane, and isopropenyl acetate afforded the adducts **12**–**14a** in



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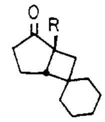
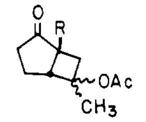


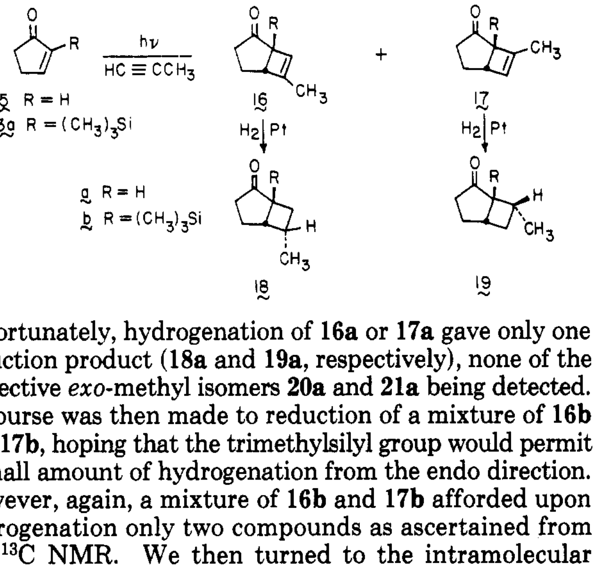
13a R = $(CH_3)_3Si$
b R = H



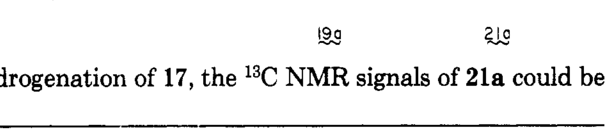
14a R = $(CH_3)_3Si$
b R = H

yields of 71, 76, and 74%, respectively. For **14** two epimers were expected, but one compound of unknown stereochemistry was formed predominantly. The homogeneity of **13a** and **14a** was rigorously established by ^{13}C NMR. Desilylation of adducts **13a** and **14a** with potassium fluoride dihydrate in dimethyl sulfoxide at room temperature smoothly gave the parent ketones **13b** (66%) and **14b** (75%). ^{13}C NMR spectroscopy again established the homogeneity of the compounds.

While highly regiospecific photocycloadditions were observed for the above olefins, propylene provided a more stringent test for the directive effect of a trimethylsilyl group. Reaction of **3a** with propene gave in 90% distilled yield a mixture of cycloaddition products. All attempts to separate the mixture into its pure components failed. The broadband-decoupled ^{13}C NMR of this distilled reaction mixture showed the expected number of lines for three compounds. Desilylation of this mixture again afforded by ^{13}C NMR spectroscopy a mixture of three compounds. The reduction of the cyclobutene double bonds of the separable propyne cycloaddition products of cyclopentenone, **16a** and **17a**, would furnish at least two—perhaps all four—of the stereoisomeric cycloadducts.



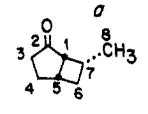
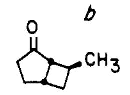
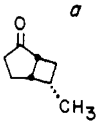
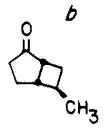
Unfortunately, hydrogenation of **16a** or **17a** gave only one reduction product (**18a** and **19a**, respectively), none of the respective *exo*-methyl isomers **20a** and **21a** being detected. Recourse was then made to reduction of a mixture of **16b** and **17b**, hoping that the trimethylsilyl group would permit a small amount of hydrogenation from the endo direction. However, again, a mixture of **16b** and **17b** afforded upon hydrogenation only two compounds as ascertained from the ^{13}C NMR. We then turned to the intramolecular photocycloaddition[26] of the dienol below. This reaction afforded a mixture of two alcohols which after Jones oxidation gave in 35% overall yield a mixture of **19a** (1 part) and **21a** (2.2 parts). With a pure sample of **19a** from the



19a **21a**

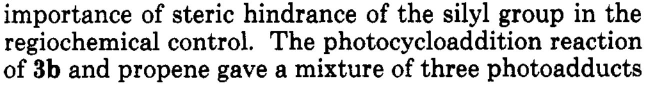
hydrogenation of **17**, the ^{13}C NMR signals of **21a** could be determined from the ^{13}C NMR spectrum of the mixture above. Thus, the ^{13}C NMR spectra of three (**18a**, **19a**, and **21a**) of the four possible cycloaddition products from the cyclopentenone–propene reaction were available.

Table I. Comparison of ^{13}C NMR Shifts of Cyclopentenone Propene Cycloadducts

carbon assignment	 [a]	 [b]	 [a]	 [b]
C-2	221.93	221.93	222.17	223.26
C-1	49.58	52.74	42.36	43.94
C-3	38.48	37.32	38.23	41.57
C-6	33.13	33.26	37.38	36.84
C-5	32.65	32.16	31.68	33.68
C-7	28.28	31.74	29.43	30.34
C-4	28.10	27.92	20.94	26.88
C-8	17.36	22.64	16.64	21.73

[a] These assignments were made with the benefit of off-resonance and gaited decoupling experiments. [b] Because these signals were observed in mixtures, off-resonance experiments were not possible; thus, assignments here must be considered tentative.

Interestingly, examination of the ^{13}C NMR spectrum of the desilylated irradiation mixture of **3a** and propene indicated **19a** to be unequivically absent, with both **18a** and **21a** being present. The third photoaddition product in the reaction mixture was then assigned as **20a**. This was unexpected since **19a** has been reported as a product from the cyclopentenone/propylene addition,[13] and it was surprising that a trimethylsilyl group would markedly effect the formation of this stereoisomer. When the photocycloaddition of cyclopentenone and propylene with stannous chloride-filtered light was reexamined, again only three cycloadducts were observed by ^{13}C NMR. Thus, under these conditions, the isomer with the *endo*-methyl group is absent from both reactions. However, when the cyclopentenone/propylene reaction was performed with Pyrex-filtered light, four cycloaddition products, **18a**–**21a**, in addition to large amounts of an aldehyde, were detected by ^{13}C NMR (see Table I). Apparently, **19a** is a secondary irradiation product in this reaction.[27]



3a R = $Si(CH_3)_3$	**18a** (20%)	**20a** (47%)	**21a** (33%)
15 R = H	**18b** (9%)	**20b** (34%)	**21b** (57%)
3b R = $Si(CH_2CH_3)_3$	**18c** (16%)	**20c** (49%)	**21c** (35%)

The absence of complete regiochemical control with the trimethylsilyl group suggested the photocycloaddition chemistry of 2-(triethylsilyl)cyclopentenone. The regiochemistry observed with this system would evaluate the importance of steric hindrance of the silyl group in the regiochemical control. The photocycloaddition reaction of **3b** and propene gave a mixture of three photoadducts

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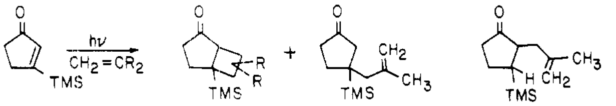
(26) Salomon, R. G.; Coughlin, D. J.; Easter, E. M. *J. Am. Chem. Soc.* 1979, *101*, 3961–3963.

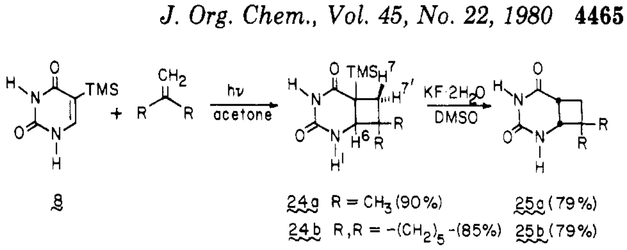
(27) Compound **19a** could arise from the reaction sequence shown below.

(95%), and a desilylation (67%) gave virtually the same **18a**:**20a**:**21a** mixture as was observed from the trimethylsilyl system. A further attempt to probe the influence of silicon substituents on the regioselectivity of the photocycloaddition was thwarted when 2-(triphenylsilyl)cyclopentenone underwent photodecomposition under the reaction conditions. Since VPC conditions were not found to completely separate the three cycloaddition products when propene was used as an olefin, the product proportions given are based on the area of the methyl absorptions in the ^{13}C NMR spectrum. While such areas are not precise measures of the relative amounts of each isomer present, they should approximate the ratios.[28]

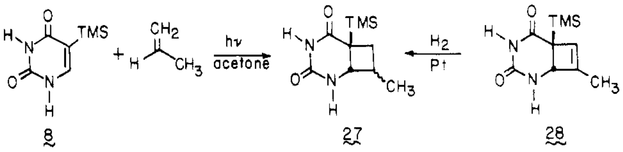


The effect of an α-trimethylsilyl group in directing head-to-tail regioselectivity prompted examination of β-(trimethylsilyl)cyclopentenone, **5**. While the reaction of **5** with ethylene gave a 91% yield of one cycloadduct, **22a**, the corresponding reaction with isobutylene gave one major and one minor product (90%, 7:1 ratio). The major isomer showed bands in the IR spectrum at 3060 (olefinic CH), 1640 (double bond), and 900 (exocyclic methylene) cm^{-1} and in the ^{1}H NMR spectrum two olefinic hydrogens at δ 4.80 and 4.70 in addition to an allylic methyl group at δ 1.78. This, together with the exact molecular weight, indicates an ene-type product. For differentiation of **23a** from the alternate ene product **23b**, the compound was treated with potassium carbonate and deuterium oxide.[29] This resulted in clean exchange by mass spectrometry of four hydrogens for deuterium, thus establishing the ene product as **23a**. In view of the low yield of the photocycloaddition product, its structure proof was not pursued further. We were further discouraged in pursuing the chemistry of **5** when photocycloaddition to methylenecyclohexane gave at least four products as judged by VPC analysis.

Photocycloadditions of 5-(Trimethylsilyl)uracil, 8. The photocycloaddition chemistry of pyrimidinediones has been extensively studied and 5-substituents have been shown in two cases (5-F and 5-CF$_3$) to markedly favor the formation of the head-to-tail orientation in the products.[30] However, neither the 5-fluoro nor the 5-trifluoromethyl substituents is conveniently replaced by hydrogen to afford products of the parent ring system. In view of the aforementioned results with cyclopentenones, the chemistry of 5-(trimethylsilyl)uracil was examined. The acetone-sensitized photocycloaddition of **8** to isobutylene and methylenecyclohexane gave the products **24a** and **24b** in excellent yields. The ^{1}H NMR spectra of these compounds in Me$_2$SO-d_6 or pyridine[31] were sufficient to establish the head-to-tail orientation shown. As an illustration, for **24a**, H^6 appears as a doublet (J = 4 Hz) which collapses to a singlet after shaking with deuterium oxide, while H^7 and H$^{7'}$ appear as a clean AB quartet (J = 12 Hz). The absence of the other regioisomers was established by ^{13}C NMR spectroscopy since both **24a** and **24b** exhibited only the required number of carbons in the broadband-decoupled spectra. In contrast to the room-temperature desilylation of the previous systems, desilylation of **24a** and **24b** at a convenient rate required heating at >100 °C for 4 h. The desilylated compounds **25a** and **25b** exhibited spectroscopic properties in full agreement with the assigned structures.



Finally, the reaction of **8** with propylene was studied since this would provide a more stringent test for the directing effect of a trimethylsilyl group. Gratifyingly, **8** reacts with propene to give a mixture of two cycloaddition products (ca. 15:85, exo/endo) in 87% yield as deduced from the ^{13}C NMR spectrum. The assignment of these two isomers as the two head-to-tail cycloadducts was made on the basis of the chemistry outlined below. The cycloadduct of **8** and propyne formed in 68% yield was established as **28** by desilylation to the known uracil–propyne adduct.[32] Catalytic hydrogenation of **28** gave a major and minor product (ca. 2:98, exo/endo). The major product is assigned as the endo isomer while the minor material is assigned as the exo isomer. The IR and ^{1}H NMR spectra of the hydrogenation products of **28** were nearly identical with those of the irradiation mixture of **8** and propene. Definitive proof for the presence of the same two compounds was obtained from comparison of the ^{13}C NMR of the two samples. Except for the relative intensities, the chemical shifts in the two spectra were identical to within 0.04 ppm. Thus, the trimethylsilyl group in uracil directs nearly exclusive head-to-tail regioselectivity not only for isobutylene and methylenecyclohexane but also for propene.



Discussion

The results in the cyclopentenone and uracil systems demonstrate the directing effect of the trimethylsilyl group on regioselectivity of cyclobutane-ring formation. The separation of regioisomeric products is often a tedious, time-consuming proposition in photocycloaddition chemistry. Since the trimethylsilyl group can be readily removed from the adducts, the use of these silylated reagents serves as an indirect method for achieving regiospecific head-to-tail cycloadducts in selected cases. Furthermore, in the cyclopentenone systems, the use of 2-trimethylsilyl derivative **3a** and filtered light decreases the formation of secondary products and/or improves the yield of the reaction relative to cyclopentenone. This arises because **3a** dimerizes about a factor of four times slower than cyclopentenone and because the absence of light below 340 nm

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[28] In one case (the mixture of **19a** and **21a**), it was possible to compare the product ratio determined by integration of the methyl carbon resonances in the ^{13}C NMR vs. the methyl hydrogen resonances in the ^{1}H NMR; the ratios were within experimental error (±5%).

[29] Kinstle, T. H.; Stark, R. E. *J. Org. Chem.* **1967**, *32*, 1318–1322.

[30] Swenton, J. S.; Grimm, F.; Fritzen, E. L. "Division of Petroleum Chemistry Abstracts: Symposium on Photochemistry as a Route to Chemicals", Joint Meeting of the American Chemical Society and Chemical Society of Japan, Honolulu, HI, April 1979; American Chemical Society: Washington, DC; p 121–129.

[31] The NMR spectrum of these pyrimidinedione systems in pyridine is often markedly simplified relative to the spectrum in Me$_2$SO-d_6.

[32] Comber, R. N.; Swenton, J. S.; Wexler, A. J. *J. Am. Chem. Soc.* **1979**, *101*, 5411–5412.

minimizes the problem of secondary irradiation of photocycloaddition products. We have found Pyrex-filtered light quite acceptable for cyclohexenone and uracil photocycloadditions; however, we strongly affirm Agosta's recommendation[25] that uranium glass-filtered (or $SnCl_4$-filtered) light be used for cyclopentenone photocycloadditions.

The advantages of using **3a** relative to cyclopentenone itself rest with the difficulty of separating the product mixture relative to the preparation of the silylated compound in three steps from cyclopentenone. Where the olefin is somewhat precious and the separation of regioisomers difficult, the efficient regiospecific photochemistry of **3a** more than compensates for its preparation from cyclopentenone. Unfortunately, the chemistry of 2-(trimethylsilyl)cyclopentenone cannot be extended to the cyclohexenone analogue since this compound undergoes photocycloaddition very slowly, if at all, with even isobutylene, a result not completely unexpected in view of the known photochemistry of 2-methylcyclohexenone.[5b] In the pyrimidinedione system, the 5-(trimethylsilyl)uracil, **8**, affords nearly completely regioselective photocycloaddition even with propylene. Past experience has shown that it is very difficult to separate even the regioisomers of uracil and isobutylene by conventional chromatography.[33] While we have not extensively studied the yields of photocycloadditions of **8** vs. uracil, one example is especially pertinent. Uracil reacts with propyne to give a 43% yield of cycloadduct after a lengthy chromatography[32] while **8** reacts with propyne to give a 61% yield of cycloaddition product **28** after a simple filtration through silica gel. While these silylated cycloaddition products have been subject only to desilylation here, the rapid advances in synthetic organosilicon chemistry may present methods that would allow the trimethylsilyl group to be replaced by other functionalities.

The regioselectivity observed in photocycloaddition reactions of cyclic enones with olefins is a function not only of substituents on the carbonyl component but also of substituents on the nonexcited olefin. It is generally believed[34] that the steps outlined in Scheme II are involved in photochemical cycloadditions to olefins. If indeed this is the general mechanism, then the regiochemistry can be influenced at two stages of the reaction sequence. A preferred orientation in the excited-state complex could lead to formation of one isomeric biradical, giving rise eventually to one observed cycloaddition product. Second, if isomeric biradicals are formed in the reaction, their fragmentation-to-closure ratio will determine the observed product ratio in the system. Little is known of how silicon influences exciplex orientation or the effect of silicon substituents in influencing closure vs. cleavage product ratios of biradicals. The ability of silicon to stabilize a β-radical is known;[35] if such stabilization favors formation of biradical **29** vs. **30**, this could be a factor in the regiochemistry observed here. Experiments are currently in progress to answer the two questions noted above, and any further mechanistic discussion is deferred until this work is complete.

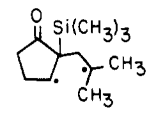
Scheme II. Abbreviated Mechanism for Photocycloaddition

$$K^{*3} + O \rightarrow [\text{exciplex}]$$

$$[\text{exciplex}] \rightarrow \text{biradical}$$

$$\text{biradical} \rightarrow K + O$$

$$\text{biradical} \rightarrow \text{products}$$



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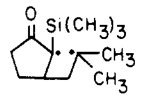

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Experimental Section[36]

2-Bromo-2-cyclohexenone Ethylene Ketal. A solution containing 5 g (0.05 mol) of 2-cyclohexenone in 45 mL of CCl_4 was cooled to 10 °C in an ice bath, and 2.8 mL (0.05 mol) of bromine in 45 mL of CCl_4 was added rapidly. When addition was complete, 15 mL of pyridine was added at once. A thick, white precipitate formed, and the reaction was allowed to stir at room temperature for 3 h. The reaction was then filtered, and the filtrate was added to 150 mL of ether. The resulting solution was washed with 10% aqueous HCl (2 × 50 mL) and saturated aqueous $NaHCO_3$ (2 × 50 mL). The extracts were washed with brine (50 mL), dried, and concentrated in vacuo until crystallization began. After the solution was cooled for 2 h at −10 °C, filtration gave 6.28 g (69%) of 2-bromo-2-cyclohexenone, mp 72.5–75 °C (lit.[37] mp 74 °C). A second crop was obtained, 0.93 g, mp 63–72 °C.

A solution containing 19.1 g (0.11 mol) of the enone, 9 g (0.15 mol) of ethylene glycol, and 0.10 g (0.5 mmol) of *p*-toluenesulfonic acid in 300 mL of benzene was refluxed under a water separator for 24 h. After 200 mL of benzene was distilled off, the residue was washed with 5% aqueous NaOH (2 × 20 mL) and H_2O (2 × 20 mL). Workup and concentration afforded 23 g (96%) of the ketal which was used without further purification: IR (neat) 2940 (s), 2890 (s), 1635 (m), 1435 (m), 1353 (m), 1180 (s), 1160 (s), 1115 (s), 1075 (s), 1029 (s), 954 (s), 820 (m), 790 (m), 742 (m) cm^{-1}; ^1H NMR δ 1.64–2.26 (br str m, 6 H), 3.70–4.34 (m, 4 H), 6.21 (t, J = 4 Hz, 1 H); exact mass calcd for $C_8H_{11}BrO_2$ m/e 217.9942, obsd m/e 217.9947.

2-(Trimethylsilyl)-2-cyclohexenone. A solution of 1.0 g (4.46 mmol) of the ketal in 20 mL of tetrahydrofuran was cooled to −72 °C and 2.2 mL of 2.42 M *n*-butyllithium in hexane added dropwise over 5 min. After the solution was stirred for an additional 5 min, 0.92 g (8.44 mmol) of trimethylsilyl chloride in 5 mL of tetra-

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[33] Wexler, A. J.; Hyatt, J. A.; Raynolds, P. W.; Cottrell, C.; Swenton, J. S. *J. Am. Chem. Soc.* **1978**, *100*, 512–520.

[34] Wagner, P. J.; Bucheck, D. J. *J. Am. Chem. Soc.* **1969**, *91*, 5090–5097; *Ibid.* **1970**, *92*, 181–185. deMayo, P.; Loutfy, R. O. *Ibid.* **1977**, *99*, 3559–3565. For a somewhat different viewpoint, see: Shaik, S.; Epiotis, N. D. *Ibid.* **1978**, *100*, 18–29.

(35) Wilt, J. W.; Aznovoorian, P. M. *J. Org. Chem.* **1978**, *43*, 1285–1286 and references cited therein.

(36) Melting points below 200 °C were taken with a Thomas-Hoover capillary melting-point apparatus and are uncorrected. Melting points >200 °C were determined on a hot-stage apparatus. Measurements of standard samples indicated that the observed melting points were probably 1–2 °C lower than the corrected values. Infrared spectra were recorded on a Perkin-Elmer Model 467 grating spectrometer. ^1H NMR spectra were taken at 60 MHz (in CCl_4 unless otherwise noted) with a Varian EM-360 instrument. ^{13}C NMR spectra were recorded on a Bruker HX-90 instrument at 20 MHz by Dr. C. Cottrell in $CDCl_3$ unless otherwise noted. Mass spectra and exact mass measurements were obtained by Mr. C. R. Weisenberger on a Consolidated Electronics MS-9 double-focusing mass spectrometer. Analytical samples were determined by Scandinavian Microanalytical Laboratory, Herlev, Denmark. Aluminum oxide and silica gel were from E. Merck Co. Medium-pressure chromatography was performed at 20–30 psi, using a silica gel 60 prepacked column (Lobar) made by E. Merck, Darmstadt, available from EM Laboratories. Tetrahydrofuran was distilled from benzophenone ketyl directly into the reaction flask. Reactions run in an inert atmosphere made use of a three-way stopcock with a $^{14}/_{20}$ standard-taper joint which allowed the flask to be flame dried under vacuum and filled with purified nitrogen. Butyllithium in hexane (Ventron) was titrated in tetrahydrofuran with 1,10-phenanthroline or HMPA–Ph_3CH (−78 °C) as indicator. Workup as usual refers to extraction with ether, washing of the ether layers with saturated brine solution, drying over calcium sulfate, and concentration in vacuo. In chromatography, E refers to ether, while PE refers to petroleum ether, bp 35–50 °C. Commercial pentane was washed twice with concentrated H_2SO_4 and once with brine solution and then distilled.

(37) Bordwell, F. G.; Wellman, K. M. *J. Org. Chem.* **1963**, *28*, 2544–2550.

hydrofuran was added via syringe. The reaction was warmed to room temperature and worked up as usual to afford 0.56 g (72%) of white crystals, mp 34–39 °C. A recrystallized sample (PE) had mp 40–41.5 °C: IR (KBr) 2939 (m), 1665 (s), 1592 (w), 1495 (w), 1460 (w), 1253 (s), 1172 (w), 1144 (w), 870 (m), 850 (s), 820 (w), 765 (m), 710 (s) cm^{-1}; ^{1}H NMR δ 0.00 (s, 9 H); UV (pentane) 223 nm (ϵ 10 000), 342 (52).

Anal. Calcd for $C_9H_{16}OSi$: C, 64.23; H, 9.58. Found: C, 63.97; H, 9.52.

Irradiation of 2-(Trimethylsilyl)-2-cyclohexenone with Isobutylene. A Pyrex irradiation vessel was equipped with a dry ice condenser and gas inlet. The vessel was charged with 0.64 g (3.31 mmol) of **3b** and 130 mL of purified pentane. The vessel was attached to the Hanovia immersion well, and isobutylene was condensed into the reaction mixture until the volume had increased by 20 mL. The solution was then irradiated with Pyrex-filtered light and the reaction monitored by VPC (7 ft × $^1/_8$ in. 5% SE-30 on 60–80 Chromosorb G at 120 °C). After 8 h of irradiation, no evidence of reaction was seen by VPC. Removal of the solvent in vacuo left 0.61 g of unchanged starting material, as identified by VPC retention time and NMR.

2-Bromo-2-cyclopentenone Ethylene Ketal. A solution containing 20.4 g (0.25 mol) of 2-cyclopentenone in 200 mL of CCl_4 was cooled to 0 °C. To the stirred solution was added 12.7 mL (0.25 mol) of bromine in 200 mL of CCl_4 over a period of 45 min. When the addition was complete, 40 g (0.40 mol) of triethylamine in 200 mL of CCl_4 was added dropwise, maintaining the reaction temperature at 0 °C. During the addition, a thick, white precipitate formed. When the addition was complete, the reaction was stirred at room temperature for 1.5 h and filtered. The filtrate was washed with 10% aqueous HCl (3 × 50 mL) and H_2O (2 × 50 mL), decolorized with charcoal, filtered, and washed with 100 mL of brine. Drying and concentration afforded a residue which was triturated at 0 °C with ether/hexane until crystallization was initiated. After the mixture stood at ca. −10 °C overnight, 25.1 g (63%) of 2-bromo-2-cyclopentenone was obtained as white crystals, mp 35–36 °C (lit.[38] mp 39–39.5 °C).

A benzene solution (150 mL) containing 13 g (80.7 mmol) of the enone, 30 g (0.48 mol) of ethylene glycol, and 10 mg of *p*-toluenesulfonic acid was refluxed and the water collected via a Dean–Stark trap. As the reaction proceeds, the solution changes from colorless to orange; the reaction should be stopped before the color of the solution turns dark brown. After refluxing for 4.5 h (VPC analysis, 7 ft × $^1/_8$ in. column, 5% SE-30 on 60/80 Chromosorb G at 130° C, indicated 70% conversion to product), the reaction mixture was cooled and washed with saturated $NaHCO_3$ (2 × 50 mL) and then water (2 × 50 mL). Standard workup afforded 15.5 g of a brownish oil which was chromatographed on activity III neutral aluminum oxide (5 × 17 cm column). Elution with 2% E/PE proceeded as follows: 300 mL, nil; 400 mL, 10.8 g of the bromo ketal; 200 mL, nil; 1100 mL, 3.61 g (28%) of starting ketone. Molecular distillation of the product [bath 60 °C (1.5 mm)] afforded 10.0 g (83% based on recovered starting material) of pure bromo ketal. Runs at somewhat lower (ca. 50%) conversion gave 68–75% of the bromo ketal: IR (neat) 2980 (s), 2940 (s), 2880 (s), 1620 (m), 1472 (m), 1445 (w), 1428 (w), 1322 (s), 1220 (sh), 1175 (s, br), 1050 (s), 1035 (s), 1005 (s), 952 (s), 940 (sh), 923 (s), 890 (s), 850 (s), 775 (m) cm^{-1}; ^{1}H NMR δ 1.88–2.52 (str m, 4 H), 3.69–4.30 (str m, 4 H), 6.00 (t, J = 3 Hz, 1 H); exact mass calcd for $C_7H_9BrO_2$ *m/e* 203.9786, obsd *m/e* 203.9791.

2-(Trimethylsilyl)-2-cyclopentenone (3a). To a −70 °C solution of 20.4 g (0.10 mol) of bromo ketal and 80 mL of ether was added 65 mL of 1.63 M *n*-butyllithium in hexane over a period of 30 min. Upon warming to room temperature, the solution turned cloudy. The solution was then cooled to −70 °C, 21 g (0.20 mol) of trimethylsilyl chloride was added, and the reaction mixture warmed to room temperature. A white precipitate was present which dissolved when 20 mL of water was added. Standard workup and distillation of the solvent through a 15-cm Vigreux column followed by vacuum distillation gave 13.15 g (88%) of **3a**: bp 60–62 °C (5 mm); IR (neat) 2940 (s), 1690 (s), 1580 (s), 1440 (s), 1405 (m), 1300 (m), 1285 (s), 1252 (s), 1241 (s), 1180 (s), 1005 (s), 952 (m), 922 (m), 845 (s), 795 (m), 770 (s), 762 (s), 700 (m) cm^{-1}; ^{1}H NMR δ 0.00 (s, 9 H), 1.93–2.20 (m, 2 H), 2.35–2.65 (m, 2 H), 7.50 (t, J = 3 Hz, 1 H); UV λ_{max} (pentane) 225 nm (ϵ 68 000), 332 (53); exact mass calcd for $C_8H_{14}OSi$ *m/e* 154.0813, obsd *m/e* 154.0817.

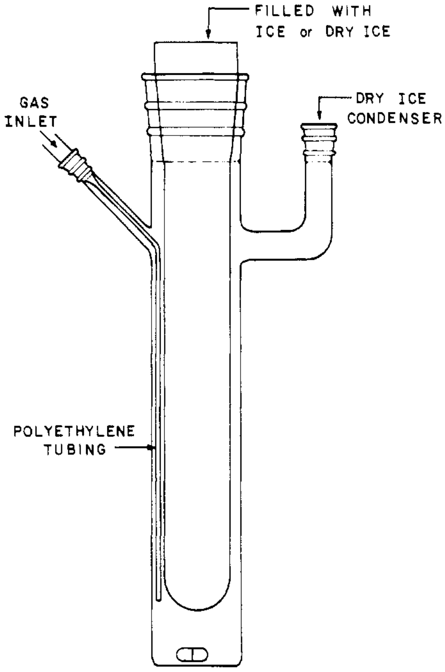

Figure 2. Dummy immersion well used in tin(II) chloride filtered irradiations.

Photoaddition Reactions of 3a and Isobutylene with Unfiltered Light. A solution of 0.62 g of **3a** in 150 mL of purified pentane was placed in a Pyrex well (Figure 2) equipped with a dry ice condenser. Isobutylene was then condensed into the solution until the volume increased by 20 mL. The solution was irradiated in a Rayonet reactor with 350-nm light for 3.5 h. Preparative VPC (2 ft × 1/4 in., 5% SE-30 on 60/80 Chromosorb G at 100 °C) gave pure samples of the three photoproducts with the product ratios indicated.

Aldehyde 11 (19%): IR (neat) 2960 (s), 2720 (m), 1725 (s), 1610 (s), 1465 (m), 1440 (m), 1412 (m), 1365 (m), 1255 (s), 1062 (m), 890 (sh), 845 (s), 760 (s), 698 (m) cm^{-1}; ^{1}H NMR ($CCl_4/CHCl_3$) δ 0.06 (s, 9 H), 1.16 (s, 6 H), 2.06 (s, 2 H), 2.44 (m, 4 H), 9.72 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 201.76, 166.56, 140.16, 45.31, 43.55, 42.52, 25.77 (two carbons), 21.89, 1.18; exact mass calcd for $C_{12}H_{22}OSi$ *m/e* 210.1439, obsd *m/e* 210.1443.

Ene Product 10 (21%): IR (neat) 3080 (w), 2960 (s), 1710 (s), 1645 (w), 1450 (m), 1415 (m), 1380 (w), 1325 (w), 1260 (s), 1160 (s), 900 (m), 850 (s), 765 (m), 730 (w), 695 (w) cm^{-1}; ^{1}H NMR ($CCl_4/CHCl_3$) δ 0.05 (s, 9 H), 1.35 (s, 3 H), 1.55–2.75 (br m, 8 H), 4.55 (br d, 2 H); exact mass calcd for $C_{12}H_{22}OSi$ *m/e* 210.1439, obsd *m/e* 210.1441.

Cycloadduct 9 (60%): IR (neat) 2960 (s), 2870 (m), 1710 (s), 1450 (m), 1415 (m), 1385 (w), 1372 (m), 1323 (w), 1303 (w), 1275 (m), 1255 (s), 1222 (w), 1213 (m), 1201 (w), 1165 (m), 1085 (m), 1002 (m), 971 (m), 922 (m), 860 (s), 845 (s) cm^{-1}; ^{1}H NMR ($CCl_4/CHCl_3$) δ 0.00 (s, 9 H), 0.98 (s, 3 H), 1.04 (s, 3 H), 1.55–2.60 (m, 7 H); ^{13}C NMR δ (off-resonance decoupling multiplicities) δ 225.42 (s), 49.01 (d), 42.94 (undetermined), 42.40 (t), 39.60 (t), 37.12 (s), 30.56 (q), 24.01 (q), 20.24 (t), 3.85 (q); UV λ_{max} (pentane) 305 nm (ϵ 90); exact mass calcd for $C_{12}H_{22}OSi$ *m/e* 210.1439, obsd *m/e* 210.1443.

Photocycloaddition Reactions of 2-(Trimethylsilyl)-cyclopentenone. General. These reactions were performed by using a dummy immersion well held within ca. 2 cm of a 450-W Hanovia medium-pressure source (Figure 2). The light from the Hanovia source was filtered through a 5-cm solution of 0.4 M $SnCl_2$ solution in 10% hydrochloric acid. For volatile olefins the dummy well was equipped with a dry ice/isopropyl alcohol condenser and the desired amount of olefin condensed into the irradiation solution. Preliminary studies were performed by immersing both

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[38] Dunn, G. L.; DiPasquo, V. J.; Hoover, J. R. E. *J. Org. Chem.* **1968**, *33*, 1454–1459.

light source and irradiation assembly in a 0 °C bath. Later runs were performed at ambient temperature with no marked difference in results.

Isobutylene. Isobutylene was condensed into a solution of 1.07 g (6.96 mmol) of **3a** in 200 mL of pentane until the solution volume increased by 20 mL. The solution was then irradiated for 6 h, the reaction being monitored by VPC (7 ft × 1/8 in., 5% SE-30 on 60/80 Chromosorb G, 130 °C). Removal of the solvent in vacuo left 1.35 g of a light yellow liquid which was molecularly distilled [bath 70 °C (1 mm)] to afford 1.30 g (89%) of a mixture of photoproducts (**9**/**10**, 5.4:1).

Methylenecyclohexane. A solution of 0.50 g (3.24 mmol) of **3a** and 3.24 g (33.7 mmol) of methylenecyclohexane in 150 mL of pentane was irradiated for 20 h. Removal of the bulk of solvent first by distillation and then the remaining traces under vacuum gave 0.96 g of a yellow liquid which was molecularly distilled [bath 60 °C (1 mm)] to afford 0.62 g (76%) of pure cycloadduct **13a**: IR (neat) 2929 (s), 2850 (s), 1709 (s), 1450 (m), 1412 (m), 1414 (m), 1255 (s), 1210 (m), 1170 (m), 1000 (m), 850 (str s) cm^{-1}; ^{1}H NMR δ 0.08 (s, 9 H), 0.98–2.55 (str m, 17 H).

Anal. Calcd for $C_{15}H_{26}OSi$: C, 71.93; H, 10.46. Found: C, 71.38; H, 10.27.

Ethylene. The irradiation vessel was charged with 1.22 g (7.9 mmol) of **3a** and 175 mL of purified pentane. The dummy well was filled with dry ice/isopropyl alcohol and ethylene was bubbled through the reaction mixture for 15 min. The solution was then irradiated, with ethylene slowly being bubbled through the solution, and the reaction was monitored by VPC (7 ft × 1/8 in., 5% SE-30 on 60/80 Chromosorb G at 120 °C). After 16 h, reaction was complete, and the solvent was removed in vacuo, leaving 1.21 g of a light yellow liquid. A 1.13-g sample of the product was chromatographed on a prepacked silica gel column and eluted with 10% ether/hexane under medium pressure. The elution proceeded as follows: 200 mL of 10% ether/hexane, nil; 280 mL of 10% ether/hexane, 1.03 g (71%) of cycloadduct. The spectral properties were as follows: IR (neat) 2950 (s), 1710 (s), 1255 (s), 850 (s) cm^{-1}; ^{1}H NMR δ -0.10 (s, 9 H), 1.7–2.5 (m, 9 H); exact mass calcd for $C_{10}H_{18}OSi$ *m/e* 182.1126, obsd *m/e* 182.1129.

Isopropenyl Acetate. A solution containing 1.00 g (6.5 mmol) of **3a** and 6.6 g (0.07 mol) of isopropenyl acetate in 10 mL of acetonitrile was irradiated in a quartz irradiation tube with tin chloride filtered light for 30 h. Removal of the solvent in vacuo left 1.76 g of a light yellow liquid. This was crystallized at low temperature and recrystallized five times from PE at low temperature to afford 1.22 g (74%) of a white solid: mp 48.5–50 °C; IR 2950 (s), 1745 (s), 1715 (s), 1550 (br, m), 1375 (s), 1255 (s), 1230 (s, br), 1170 (s), 840 (s) cm^{-1}; ^{1}H NMR δ 0.00 (s, 9 H), 1.45 (s, 3 H), 1.90 (s, 3 H), 2.10–2.90 (m, 7 H); ^{13}C NMR δ 223.48, 169.59, 81.30, 50.47, 41.54, 39.12, 24.80, 21.94, 20.43, 3.73 (one carbon not detected): exact mass calcd for $C_{13}H_{22}O_3Si$ *m/e* 254.1338, obsd *m/e* 254.1342.

1-Pentene. In a manner similar to other irradiations, a solution of 0.51 g (3.3 mmol) of **3a** and 3.5 g (66 mmol) of 1-pentene in 200 mL of pentane was irradiated for 6.5 h, using the assembly shown in Figure 2. Workup and molecular distillation gave 0.62 g (84%) of product mixture. The ^{13}C NMR spectrum showed three saturated carbonyl absorptions at δ 224.84, 223.99, and 223.81 in addition to three trimethylsilyl groups at δ -1.88, -3.70, and -4.19. This suggested a product mixture similar to the propene reaction; thus, no separations were attempted.

Propene. Propene was condensed into a solution of 0.485 g (3.15 mmol) of **3a** in 190 mL of pentane until the volume increased by 10 mL. The irradiation progress was monitored by VPC (7 ft × 1/8 in., 5% SE-30 on 60/80 Chromosorb G at 130 °C) and terminated after 5 h. Removal of the solvent in vacuo left 0.66 g of slightly yellow liquid which was molecularly distilled [bath 60 °C (0.4 mm)] to give 0.56 g (90%) of colorless liquid: UV λ_{max} (MeOH) 292 nm (ε 84.5); IR (neat) 2970 (s), 2885 (m), 1710 (s), 1450 (m), 1410 (m), 1255 (s), 1200 (m), 1160 (m), 1145 (m, br), 995 (m), 850 (s), 765 (m), 702 (m) cm^{-1}; ^{1}H NMR δ 3.00–1.43 (m, 8 H), 1.27–0.83 (str m, 3 H), -0.03 to -0.10 (3 sharp s, 9 H); ^{13}C NMR ($CDCl_3$/Me_4Si, 20 MHz) showed a mixture of three cycloadducts which had three saturated carbonyl absorptions (δ 224.84, 224.36, 224.17) and three trimethylsilyl absorptions (δ -2.00, -3.70, -4.13); exact mass calcd for $C_{11}H_{20}OSi$ *m/e* 196.1283, obsd *m/e* 196.1288.

Propyne. A mixture of 0.56 g (3.63 mmol) of **3a** and 5.8 g of propyne in 200 mL of pentane was irradiated and the progress of the reaction followed by VPC (26 ft × 1/8 in., 5% SE-30 on 60/80 Chromosorb G at 150 °C). After 3.5 h, two products were formed with very close retention times in the ratio 1:1. Removal of the solvent in vacuo and molecular distillation [bath 40 °C (0.5 mm)] of the crude residue gave 0.597 g (85%) of clear, yellow liquid: IR (neat) 3040 (w), 2960 (s), 2878 (m), 1710 (vs), 1630 (w), 1458 (m), 1445 (m), 1420 (m), 1378 (w), 1330 (w), 1260 (vs), 1210 (m), 1180 (m), 1158 (m), 1140 (w), 1060 (w), 1020 (m), 997 (m), 955 (w), 930 (sh), 848 (vs), 793 (m), 760 (m), 698 (m) cm^{-1}; ^{1}H NMR δ 5.75 (br s), 5.62 (br s), 3.10–1.55 (m, 8 H), 0.05 and 0.00 (2 s, 9 H); exact mass calcd for $C_{11}H_{18}OSi$ *m/e* 194.1127, obsd *m/e* 194.1132. ^{13}C NMR showed two cycloadducts present in an almost equal ratio, their chemical shifts tentatively assigned as follows: (**17b**) δ 217.98, 149.96, 60.81, 44.54, 36.53, 19.60, 14.81, -3.03; (**16b**) δ 217.44, 150.32, 131.87, 54.37, 49.10, 37.02, 22.45, 15.47, -2.73.

Irradiation of Cyclopentenone and Propyne. By use of the same apparatus as for the photocycloadditions of **3a**, 1.58 g (19.23 mmol) of **15** and 10.5 g of propyne were irradiated with filtered light for 8 h [the reaction was monitored by VPC (7 ft × 1/8 in., 5% SE-30 on 60/80 Chromosorb G at 130 °C)]. The solution was filtered to remove dimers and the filtrate concentrated to give 1.71 g of yellow liquid which was molecularly distilled [bath 60 °C (1.5 mm)] to afford 1.59 g (68%) of a mixture of **17a** and **16a**. A 0.50-g portion of this mixture was separated by medium-pressure chromatography on a Lobar silica gel column size B, using 5% E/PE as solvent. Elution proceeded as follows: 250 mL, nil; 60 mL, 300 mg of **17a**; 20 mL, 50 mg of a mixture of **17a** and **16a**; 70 mL, 80 mg of pure **16a**.

Irradiation of Cyclopentenone and Propylene. The photochemical assembly described in Figure 2 was charged with 1.48 g of cyclopentenone in 200 mL of pentane and propylene bubbled through the solution until the volume increased by 20 mL. The solution was irradiated for 4.5 h with $SnCl_2$-filtered light. Concentration left 1.44 g of yellow oil of which 0.72 g was molecularly distilled to give 0.633 g of slightly yellow, clear liquid. The ^{13}C NMR spectrum of this liquid showed the presence of three cycloadducts as well as some unreacted cyclopentenone.

Catalytic Hydrogenation of 16a. To a solution of 72.8 mg (0.6 mmol) of **16a** in 5 mL of ethyl acetate was added 5 mg of platinum oxide, and the solution was stirred under a hydrogen atmosphere at atmospheric pressure for 2 h. The mixture was filtered, and the solvent was removed in vacuo to afford 70 mg (94%) of a colorless liquid: IR (neat) 2945 (s), 2860 (m), 1735 (s), 1455 (w), 1417 (w), 1383 (w), 1175 (m) cm^{-1}; NMR ($CDCl_3$) δ 3.10–1.55 (str m, 9 H), 1.00 (d, *J* = 6 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 222.17, 42.36, 38.23, 37.38, 31.68, 29.43, 20.94, 16.63; exact mass calcd for $C_8H_{10}O$ *m/e* 124.0888, obsd *m/e* 124.0892.

Catalytic Hydrogenation of 17a. To a solution of 250 mg (2.05 mmol) of **17a** in 15 mL of methyl alcohol was added 30 mg of platinum oxide, and the resulting solution was then stirred under a hydrogen atmosphere. The reaction was complete after 3 h. The mixture was filtered, and the solvent was removed in vacuo to afford 238 mg (95%) of colorless liquid. This sample was further purified by preparative VPC (2 ft × 1/4 in., 5% SE-30 on 60/80 Chromosorb G, 100 °C) to give satisfactory spectroscopic data: IR (neat) 2955 (s), 2960 (m), 1725 (s), 1455 (m) 1411 (w), 1379 (w), 1295 (w), 1231 (w), 1160 (m), 1110 (w), 1062 (w) cm^{-1}; ^{1}H NMR ($CDCl_3$/Me_4Si) δ 3.27–1.36 (str m, 9 H), 0.90 (d, *J* = 7 Hz, 3 H); ^{13}C NMR δ 221.93, 49.58, 38.48, 33.13, 32.65, 28.28, 28.10, 17.36; exact mass calcd for $C_8H_{12}O$ *m/e* 124.0888, obsd *m/e* 124.0892.

(*E*) and (*Z*)-Octa-2,7-dien-4-ols. The Grignard reagent was formed from 1.46 g (61 mmol) of magnesium turnings and 7.49 g (61 mmol) of 1-bromopropene (Aldrich; bp 58-59.5 °C) in 25 mL of tetrahydrofuran at 40–50 °C. After the solution was refluxed for 1 h, the reagent was cooled to 10 °C (at this stage a brown, viscous precipitate formed), and 3.7 g (44 mmol) of 4-pentenal[39] in 10 mL of tetrahydrofuran was added dropwise. After the mixture was stirred for 2 h at room temperature, workup gave ca. 4 g of orange oil which was molecularly distilled [bath 44–46 °C (0.7 mmHg)] to give 3.23 g (58%) of the dienol as a colorless

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(39) Webb, R. F.; Dieke, A. J.; Parsons, J. A. *J. Chem. Soc.* **1961**, 4092–4095.

liquid. This crude material was used directly for the irradiation.

***exo*- and *endo*-7-Methylbicyclo[3.2.0]heptan-2-ones (19a and 21a).** The hydroxy diene from above, 1.0 g (7.9 mmol), and 0.1 g of $(CuOTf)_2 \cdot C_6H_6$[40] in 200 mL of ether was irradiated through quartz for 16 h with a 450-W Hanovia medium-pressure source. (A metallic copper mirror was deposited on the walls of the irradiation flask as the reaction proceeded.) The resulting solution was poured into a mixture of ice (10 g) and concentrated ammonium hydroxide (10 mL). Workup as usual gave 1.08 g of colorless liquid which was oxidized directly with Jones reagent to give the ketones **19a** and **21a** (2.2:1). A purified sample (2 ft × $^1/_4$ in., 5% SE-30 on 60/80 Chromosorb G, 110 °C) showed the expected spectral properties of a mixture. Especially diagnostic were the *exo*-methyl group (δ 1.2, J = 7 Hz) of **21a** and the *endo*-methyl group of **19a** (δ 0.97, J = 7 Hz).

2-(Triethylsilyl)cyclopentenone (3b). This compound was prepared similarly to **3a** from 1.96 g (9.55 mmol) of the bromo ketal, 5.9 mL of 1.65 M *n*-BuLi, and 4.3 g (28.5 mmol) of chlorotriethylsilane. The crude product, 2.59 g of an orange oil, was chromatographed on a 3 × 24 cm silica gel column with elution as follows: 500 mL of 3% E/PE, nil; 1300 mL of 6% E/PE, 0.93 g (49%) of **3b** as a colorless liquid. **3b**: IR (neat) 2960 (s), 2920 (s), 2880 (s), 1695 (s), 1575 (m), 1465 (m), 1442 (m), 1420 (m), 1286 (m), 1244 (m), 1176 (m), 1014 (m), 860 (br m) cm^{-1}; NMR δ 7.64 (t, J = 2 Hz, 1 H), 2.85–2.50 (m, 2 H), 2.4–2.0 (m, 2 H), 1.1–0.4 (complex m, 15 H); exact mass calcd for $C_{11}H_{20}OSi$ *m/e* 196.1283, obsd *m/e* 196.1286.

Photocycloaddition and Desilylation Reactions of 3b. These reactions were performed as for **3a** except that the photochemical reaction was performed on 0.449 g of **3b** for 8.5 h, using uranium glass-filtered light from a 450-W Hanovia medium-pressure source.

Photocycloaddition Reactions of 5-(Trimethylsilyl)uracil (8). General. Irradiations were conducted with a standard Hanovia 450-W immersion apparatus, using a Corex filter at ambient temperature. For volatile olefins the apparatus was equipped with a dry ice/isopropyl alcohol condenser. The reactions were conveniently followed by TLC on silica gel, using 10% methanol/chloroform as the eluant.

Isobutylene. Isobutylene was bubbled through a solution of 207.7 mg (1.13 mmol) of **8** in 180 mL of acetone equipped with a dry ice/acetone condenser until the volume of the solution increased by 20 mL (100-fold excess olefin) and the solution irradiated for 3 h. The acetone was removed in vacuo, and the resulting residue was washed with hexane, filtered, and dried to yield 270 mg of white solid, mp 204–206 °C. Recrystallization from methanol gave 244 mg (90%) of pure cycloadduct as white crystals: mp 209–211 °C; UV λ_{max} (MeOH) 226 nm (ϵ 1700); IR (KBr) 3230 (m, br), 3080 (m), 2970 (m), 1710 (vs), 1495 (m), 1374 (m), 1242 (m), 860 (s) cm^{-1}; ^{1}H NMR (Me_2SO-d_6) δ 9.71 (br s, 1 H), 7.53 (br s, 1 H), 3.44 (d, J = 4 Hz, 1 H, overlapping with water absorption), 1.89 (s, 2 H), 0.97 (s, 6 H), 0.15 (s, 9 H); ^{1}H NMR (pyridine) δ 3.92 (d, J = 4 Hz, 1 H), 2.21 (AB q, J = 12 Hz, $\Delta\nu$ = 20 Hz, 2 H), 1.13 (s, 3 H), 1.00 (s, 3 H), 0.25 (s, 9 H) [after shaking with deuterium oxide δ 3.91 (s, 1 H), 2.12 (AB q, J = 12 Hz, $\Delta\nu$ = 20 Hz, 2 H), 1.20 (s, 6 H), 0.20 (s, 9 H)]; ^{13}C NMR (Me_2SO-d_6) δ 175.87, 153.06, 55.72, 42.41, 38.72, 33.97, 27.75, 21.93, 4.15.

Anal. Calcd for $C_{11}H_{20}N_2O_2Si$: C, 54.96; H, 8.39. Found: C, 55.08; H, 8.37.

Methylenecyclohexane. A solution of 103.6 mg (0.56 mmol) of **8** and 2.70 g (28 mmol) of methylenecyclohexane in 200 mL of acetone was irradiated for 1.5 h. The acetone was removed in vacuo and the crude residue washed with hexane, filtered, and dried. Recrystallization from methanol afforded 134 mg (85%) of fine white crystals: mp 240–241 °C; UV λ_{max} (MeOH) 225 nm (ϵ 1080); IR (KBr) 3226 (m, br), 3085 (m), 2940 (m), 1705 (vs), 1485 (m), 1445 (m), 1378 (m), 1258 (m), 1240 (m), 1186 (m), 905 (m), 855 (s) cm^{-1}; ^{1}H NMR (Me_2SO-d_6) δ 9.53 (br s, 1 H), 7.47 (br d, J = 4 Hz, 1 H), 3.37 (d, J = 4 Hz, 1 H, overlapping by water absorption), 1.83 (AB q, J = 12 Hz, $\Delta\nu$ = 15 Hz, 2 H), 1.33 (br s, 10 H), 0.05 (s, 9 H); ^{1}H NMR (pyridine) δ 3.88 (d, J = 4 Hz, 1 H), 2.17 (AB q, J = 12 Hz, $\Delta\nu$ = 27 Hz, 2 H), 1.80–1.90 (br s, 10 H), 0.28 (s, 9 H) [after shaking with deuterium oxide the doublet at δ 3.88 collapsed to a singlet]; ^{13}C NMR (Me_2SO-d_6) δ 175.92, 153.01, 55.81, 46.35, 42.66, 36.64, 33.92, 30.76, 25.23, 22.02, 21.39, 4.10.

Anal. Calcd for $C_{14}H_{24}N_2O_2Si$: C, 60.00; H, 8.57. Found: C, 59.58; H, 8.53.

Propylene. Propylene was bubbled into a solution of 0.159 g (0.86 mmol) of **8** in 200 mL of acetone until the volume increased by 10 mL. Irradiation for 3 h followed by concentration of the solution afforded a crude, solid resiude. This material was washed with hexane and recrystallized from methanol to give 170 mg (87%) of an endo/exo mixture (ca. 85:15 by ^{13}C NMR) as a white solid: mp 227–235 °C dec; UV λ_{max} (MeOH) 222 nm (ϵ 2828); IR (KBr) 3230 (br m), 3080 (m), 2960 (m), 1708 (vs), 1485 (m), 1377 (m), 1280 (m), 1255 (m), 1227 (m), 1187 (m), 950 (m), 850 (s) cm^{-1}; ^{1}H NMR (Me_2SO-d_6) δ 9.68 (br s), 7.61 (br s), 7.33 (br m), 4.10–3.70 (m), 3.40–3.10 (m), 2.30–1.20 (m), 1.00 (d, J = 6 Hz), 0.02 (s), 0.01 (s); ^{13}C NMR (Me_2SO-d_6) δ 176.12, 175.68, 153.44, 152.72, 54.55, 48,72, 45.76, 35.81, 35.03, 32.36, 31.54, 18.92, 18.04, 14.89, −2.25 −3.95.

Anal. Calcd for $C_{10}H_{18}N_2O_2Si$: C, 53.06; H, 8.02. Found: C, 53.13; H, 7.91.

Propyne. Propyne (2.1 g, 52 mmol) was introduced through a dry ice/isopropyl alcohol cooled condenser to a solution of 105 mg (0.57 mmol) of **8** in 200 mL of acetone and the solution irradiated for 2 h. Concentration afforded 143 mg of brownish solid which was chromatographed on silica gel (3 × 20 cm column), using 8% methanol/chloroform as eluant. Elution proceeded as follows: 100 mL, nil; 125 mL, yellow oil; 75 mL, 77 mg (61%) of cycloadduct as a fine white solid. Cycloadduct: mp 238–240 °C; IR (KBr) 3230 (br m), 3080 (m), 2960 (w), 1700 (vs), 1490 (br m), 1440 (m), 1360 (m), 1275 (m), 1255 (m), 1245 (m), 1186 (m), 850 (s) cm^{-1}; ^{1}H NMR (Me_2SO-d_6) δ 9.57 (br s, 1 H), 7.62 (br s, 1 H), 5.82 (d, J = 1 Hz, 1 H), 3.75 (poorly resolved d, J = 4 Hz, I H), 1.60 (d, J = 1 Hz, 3 H), 0.02 (s, 9 H); exact mass calcd for $C_{10}H_{16}N_2O_2Si$ *m/e* 224.0981, obsd *m/e* 224.0987.

Desilylation of the Cycloadducts. The desilylations were performed in dimethyl sulfoxide, using 2–3 equiv of potassium fluoride dihydrate. For the carbocyclic systems, the reactions were performed at room temperature, while for most of the pyrimidinediones elevated temperatures were required.

9 and 10. A 1.21-g (5.77-mmol) sample of the distilled irradiation mixture was dissolved in 10 mL of dimethyl sulfoxide and 1.085 g (11.54 mmol) of potassium fluoride dihydrate was added. The resulting mixture was stirred for 9 h at room temperature, then poured into 30 mL of water, and extracted with ether (3 × 50 mL). Workup as usual afforded 866 mg of yellow oil which was chromatographed on a medium-pressure Lobar prepacked silica gel column (size B) with 5% E/PE as eluant. Elution proceeded as follows: 150 mL, nil; 50 mL, 96 mg (12%) of the ene product. Ene product: IR (neat) 3070 (m), 2960 (s), 2930 (s), 2870 (s), 1735 (s), 1645 (m), 1450 (m), 1160 (s), 898 (s) cm^{-1}; ^{1}H NMR δ 4.68 (br s, 2 H), 2.60–1.75 (br envelope, 9 H), 1.62 (s, 3 H); exact mass calcd for $C_9H_{14}O$ *m/e* 138.1044, obsd *m/e* 138.1048.

The elution was continued as follows: 50 mL, nil; 400 mL, 0.54 g (68%) of cycloadduct. Cycloadduct: IR (neat) 2950 (s), 1725 (s), 1450 (m), 1415 (m), 1370 (m), 1290 (m), 1165 (br m), 895 (m) cm^{-1}; ^{1}H NMR δ 2.8–1.5 (br envelope, 8 H), 1.20 (s, 3 H), 1.03 (s, 3 H); exact mass calcd for $C_9H_{14}O$ *m/e* 138.1044, obsd *m/e* 138.1048.

13a. A mixture of 0.22 g (0.89 mmol) of cycloadduct and 0.18 g (1.94 mmol) of potassium fluoride dihydrate in 2 mL of dimethyl sulfoxide was stirred at room temperature for 5 h. The reaction mixture was poured into 10 mL of water and extracted with petroleum ether (3 × 15 mL). Standard workup followed by molecular distillation [bath 60 °C (1 mm)] yielded 0.10 g (66%) of pure **13b**. Losses entailed with this small-scale distillation contributed to the low yield: IR (neat) 2920 (s), 2850 (s), 1740 (s), 1450 (m), 1185 cm^{-1}; ^{1}H NMR δ 1.2–2.68 (m, 18 H); ^{13}C NMR δ 222.54, 42.57, 40.17, 39.99, 39.02, 37.89, 35.50, 33.92, 25.92, 22.51 (2 C), 21.30; exact mass calcd for $C_{12}H_{18}O$ *m/e* 178.1357, obsd *m/e* 178.1361.

14a. To a solution of 0.804 g (3.16 mmol) of **14a** in 8 mL of dimethyl sulfoxide was added 0.595 g (6.32 mmol) of potassium

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(40) Salomon, R. G.; Kochi, J. K. *J. Am. Chem. Soc.* **1973**, *95*, 1889–1897.

fluoride dihydrate. After the mixture was stirred at room temperature, TLC analysis (silica gel, 20% E/PE) showed the reaction was complete after 5 h. The reaction mixture was poured into 20 mL of water and extracted with ether (3 × 50 mL). Concentration and drying afforded 0.55 g of light yellow oil which was chromatographed on a 2 × 20 cm silica gel column. Elution proceeded as follows: 400 mL of 10% E/PE, nil; 200 mL of 20% E/PE, 0.43 g (75%) of **14b** as a colorless liquid. **14b**: IR (neat) 2960 (m), 1735 (vs), 1435 (m), 1370 (s), 1260 (s), 1220 (s), 1195 (s), 1160 (s), 1145 (s), 1025 (m) cm^{-1}; ^{13}C NMR δ 219.50, 169.74, 47.03, 39.14, 38.23, 37.99, 25.06, 21.48, 20.57 (one carbon undetected); exact mass calcd for $C_{10}H_{14}O_3$ *m/e* 182.0942, obsd *m/e* 182.0947.

Propene–3a Cycloadducts. To a solution of 215 mg (1.10 mmol) of a mixture of cycloadducts in 10 mL of dimethyl sulfoxide was added 220 mg (2.20 mmol) of potassium fluoride dihydrate. The resulting mixture was then stirred at room temperature for 20 h. After the reaction was complete (checked by NMR), the reaction mixture was quenched with 10 mL of water. The resulting solution was then extracted with ether (3 × 50 mL) and worked up as usual to afford 107 mg (78%) of pale yellow liquid, which was then molecularly distilled [bath 60 °C (0.5 mm)] to give 95 mg (70%) of colorless liquid: IR (neat) 2953 (s), 2965 (m), 1730 (s), 1460 (m), 1451 (m), 1411 (m), 1166 (m) cm^{-1}; ^{13}C NMR ($CDCl_3/Me_4Si$) showed a mixture of three isomers with chemical shifts δ 223.36, 222.36, 221.87, 52.65, 43.85, 42.30, 41.52, 38.18, 37.30, 36.31, 33.60, 33.14, 31.54, 30.29, 29.35, 27.89, 26.83, 22.55, 21.64, 20.85, 16.51 (three carbons not distinct); exact mass calcd for $C_8H_{12}O$ *m/e* 124.0888, obsd *m/e* 124.0892.

24a. A solution of 0.16 g (0.66 mmol) of **24a** in 5 mL of dimethyl sulfoxide and 110 mg (1.32 mmol) of potassium fluoride dihydrate was stirred under nitrogen at 100 °C for 4 h. Concentration and recrystallization of the crude residue from ethanol afforded 87.5 mg (79%) of **25a** as fine white needles: mp 249–250 °C; IR (KBr) 3220 (br m), 3080 (br m), 2976 (m), 1705 (vs), 1480 (br m), 1380 (m), 1375 (m), 1370 (m), 1253 (m); ^{1}H NMR (Me_2SO-d_6) δ 9.82 (br s, 1 H), 7.50 (br s, 1 H), 3.52 (dd, J = 10 Hz, 1 H), 3.60–3.20 (5-line m, 1 H), 2.17 and 2.08 (2 s, 2 H), 1.13 (s, 3 H), 1.05 (s, 3 H) [after shaking with D_2O the NMR spectrum (pyridine) showed that the d of d at δ 3.83 turned into a clean d (J = 10 Hz) and a markedly more complex absorption appeared in the δ 2.30–1.80 region]; ^{13}C NMR (Me_2SO-d_6) δ 173.30, 152.81, 52.00, 40.37, 35.91, 30.57, 28.09, 22.36; exact mass calcd for $C_7H_{12}N_2O_2$ *m/e* 168.0899, obsd *m/e* 168.0903.

24b. A solution of 0.24 g (0.86 mmol) of **24b** in 3 mL of dimethyl sulfoxide and 161 mg (1.71 mmol) of potassium fluoride dihydrate was heated to 140 °C for 4 h. Chromatography of the residue after concentration with 10% $CH_3OH/CHCl_3$ as eluant gave 140 mg (79%) of **25b** as fine, white crystals: mp 253.5–255.5 °C; IR (KB) 3228 (br m), 3100 (m), 2940 (m), 2862 (m), 1710 (vs), 1676 (sh), 1483 (m), 1435 (m), 1387 (m), 1265 (m), 1256 (m); ^{1}H NMR (pyridine) δ 3.87 (dd, J = 4, 10 Hz, 1 H), 3.45 (center of 4-line m, 1 H), 2.13 and 2.00 (2 s, 2 H), 1.50 and 1.33 (overlapping br s, 10 H); exact mass calcd for $C_{11}H_{16}N_2O_2$ *m/e* 208.2624, obsd *m/e* 208.2630.

27. A solution of 0.180 g (0.80 mmol) of **27** in 3 mL of dimethyl sulfoxide and 150 mg (1.6 mmol) of potassium fluoride dihydrate was heated under nitrogen at 130 °C for 4 h. The crude, brown solid obtained upon concentration was chromatographed on silica gel, using 10% $CH_3OH/CHCl_3$ as eluant, to give 90.8 mg (74%) of the desilylated cycloadducts: mp 214–218 °C dec; IR (KBr) 3240 (br m), 3090 (br m), 2960 (m), 1720 (s), 1680 (m), 1490 (m), 1388 (m), 1305 (m), 1273 (m), 1246 (m) cm^{-1}; ^{1}H NMR (Me_2SO-d_6) δ 9.85 (br s), 7.70 (br s), 7.40 (br s), 3.85 (m), 3.10 (m, overlapping with water absorption), 2.30–1.50 (m, overlapping with Me_2SO absorption), 0.95 (m); ^{13}C NMR δ 173.30, 152.81, 52.99, 40.37, 35.71, 30.57, 28.09, 22.36; exact mass calcd for $C_7H_{10}N_2O_2$ *m/e* 154.0742, obsd *m/e* 154.0747.

28. A solution of 0.110 g (0.49 mmol) of **28** in 5 mL of dimethyl sulfoxide and 94 mg (0.98 mmol) of potassium fluoride dihydrate was stirred at room temperature for 24 h. Concentration and recrystallization of the residue from methanol afforded 50 mg (67%) of the desilylated cycloadduct as white crystals: mp 238–240 °C (lit.[28] 241–242 °C); IR 3220 (br m), 3075 (br m), 2960 (br m), 1709 (br s), 1482 (m), 1438 (m), 1365 (m), 1295 (m), 1278 (m), 1251 (m), 1140 (m), 880 (m), 860 (m); ^{1}H NMR (Me_2SO-d_6) δ 9.90 (br s, 1 H), 7.82 (br s, 1 H), 5.95 (s, 1 H), 4.08 (br s, 1 H), 3.54 (br s, 1 H), 1.68 (s, 3 H); exact mass calcd for $C_7H_8N_2O_2$ *m/e* 152.0586, obsd *m/e* 152.0593.

Hydrogenation of 28. A solution of 40 mg (0.18 mmol) of **28** and 10 mg of platinum oxide in 10 mL of methanol was stirred under a hydrogen atmosphere for 2 h. The reaction mixture was then filtered through Celite and the methanol removed in vacuo. Recrystallization of the residue from methanol afforded 35.7 mg (88%) of a mixture of endo and exo isomers (ca. 2:98 by ^{13}C NMR) as white crystals: mp 229–237 °C dec; IR (KBr) 3210 (m, br), 3080 (m), 2960 (m), 1710 (vs), 1485 (m), 1377 (m), 1280 (m), 1250 (m), 1227 (m), 1187 (m), 850 (s) cm^{-1}; ^{1}H NMR (Me_2SO-d_6) δ 9.68 (br s), 7.61 (br s), 7.33 (br m), 4.10–3.70 (m), 3.40–3.10 (m), 2.30–1.20 (m), 1.00 (d, J = 6 Hz), 0.02 (s), 0.01 (s); exact mass calcd for $C_{10}H_{18}N_2O_2Si$ *m/e* 226.1137, obsd *m/e* 226.1142.

Photocycloaddition of 5 with Ethylene. A Pyrex irradiation vessel was equipped with a dry ice/acetone condenser and charged with 0.3826 g (2.57 mmol) of 3-(trimethylsilyl)cyclopentenone in 200 mL of pentane. A steady flow of ethylene was bubbled into the solution while the solution was irradiated with Pyrex-filtered light from a Hanovia 450-W medium-pressure mercury arc lamp. The reaction was monitored by VPC (7 ft × $^1/_4$ in., 5% SE-30 on Chromosorb G, 130 °C) and was completed in 1 h. Removal of the solvent in vacuo left 0.4124 g (91%) of yellow oil. Molecular distillation [60 °C (0.5 mm)] afforded 0.397 g (85%) of colorless liquid: IR (neat) 2960 (s), 2880 (m), 1730 (s), 1450 (m), 1410 (m), 1270 (sh), 1257 (s), 1175 (m), 1092 (m), 1030 (m), 993 (m), 930 (m), 890 (s), 850 (s), 760 (m), 702 (m) cm^{-1}; ^{1}H NMR ($CDCl_3/Me_4Si$) δ 2.80–1.70 (m, 9 H), 0.03 (s, 9 H); exact mass calcd for $C_{10}H_{18}OSi$ *m/e* 182.1127, obsd *m/e* 182.1132.

Photocycloaddition of 5 with Isobutylene. The reactor was charged with a solution of 0.3853 g (2.5 mmol) of 3-(trimethylsilyl)cyclopentenone in 200 mL of prepurified pentane. A dry ice/acetone condenser was attached to the reaction flask, and isobutylene was bubbled into the solution through the nitrogen inlet until the volume of the solution increased by 20 mL (100-fold excess in olefin). The resulting solution was then irradiated through Pyrex-filtered light (Hanovia 450-W medium-pressure mercury arc lamp). The reaction was monitored by VPC (7 ft × $^1/_4$ in., 5% SE-30 on 60/80 Chromosorb G, 130 °C), and the starting enone disappeared completely after 1 h of irradiation, with two new products being formed in the ratio 7:1. Removal of the solvent in vacuo followed by molecular distillation [70 °C (1 mm)] gave 0.474 g (90%) of pale yellow oil. The IR and NMR spectra of this crude mixture indicated both cycloadduct and an ene product were present. Every effort tried to separate this mixture by normal chromatography (silica gel, ether–petroleum ether) failed. Finally, this mixture was separated on a 2 ft × $^1/_4$ in. 5% SE-30 on 60/80 Chromosorb G, 100 °C, preparative VPC column. The cycloadduct was found to be the minor product with shorter retention time: IR 2940 (s), 2903 (s), 2845 (m), 1730 (s), 1254 (s), 1163 (m), 835 (s) cm^{-1}; ^{1}H NMR ($CCl_4/CHCl_3$) δ 2.40–1.73 (str m, 7 H), 1.20 (s, 3 H), 1.04 (s, 3 H), 0.06 (s, 9 H); exact mass calcd for $C_{12}H_{22}OSi$ *m/e* 210.1440, obsd *m/e* 210.1444. The major product proved to be the ene product: IR (neat) 3060 (m), 2940 (s), 1740 (s), 1640 (m), 1462 (m), 1458 (m), 1408 (m), 1375 (m), 1368 (sh), 1270 (sh), 1268 (s), 1163 (s), 1049 (m), 1020 (m), 990 (m), 943 (m), 900 (s), 840 (vs) cm^{-1}; NMR δ 4.80 (br, 1 H), 4.70 (br, 1 H), 2.20–1.90 (a series of peaks, 8 H), 1.78 (br s, 3 H), 0.00 (s, 9 H); exact mass calcd for $C_{12}H_{22}OSi$ *m/e* 210.1440, obsd *m/e* 210.1444.

Deuteration of 22. To a solution of 96 mg (0.457 mmol) of 3-(β-methylallyl)-3-(trimethylsilyl)cyclopentenone in 8 mL of deuterium oxide was added 20 mg (0.144 mmol) of potassium carbonate. The resulting solution was heated at reflux temperature for 4 days. The cooled solution was then extracted with ether (2 × 50 mL); the ether extracts were washed with brine (10 mL), dried over calcium sulfate, and concentrated to give 85 mg (87%) of yellow oil; exact mass calcd for $C_{12}H_{18}D_4OSi$ *m/e* 214.1691, obsd *m/e* 214.1695.

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72162-99-3; **8**, 59523-07-8; **9**, 72163-08-7; **10**, 72163-09-8; **11**, 72163-00-9; **12**, 72163-02-1; **13a**, 72163-01-0; **13b**, 72163-01-0; **14a**, 74855-11-1; **14b**, 65961-30-0; **15**, 930-30-3; **16a**, 36269-80-4; **16b**, 74855-12-2; **17a**, 74855-13-3; **17b**, 74855-14-4; **18a**, 72163-04-3; **18b**, 74892-16-3; **18c**, 74855-15-5; **19a**, 74892-17-4; **20a**, 74957-64-5; **20b**, 74892-18-5; **20c**, 74892-19-6; **21a**, 74892-13-0; **21b**, 74892-14-1; **21c**, 74855-01-9; **22a**, 74855-02-0; **22b**, 74877-67-1; **23a**, 74855-03-1; **24a**, 74855-04-2; **24b**, 74855-05-3; **25a**, 59137-83-6; **25b**, 74855-06-4; *exo*-**27**, 74855-07-5; *endo*-**27**, 74892-15-2; **28**, 74855-08-6; 2-bromo-2-cyclohexenone ethylene ketal, 70156-98-8; 2-cyclohexenone, 930-68-7; 2-bromo-2-cyclopentenone ethylene ketal, 68241-78-1; 2-cyclopentenone, 930-30-3; isobutylene, 115-11-7; methylenecyclohexane, 1192-37-6; ethylene, 74-85-1; isopropenyl acetate, 108-22-5; 1-pentene, 592-41-6; propene, 115-07-1; propyne, 74-99-7; (*E*)-octa-2,7-dien-4-ol, 74855-09-7; (*Z*)-octa-2,7-dien-4-ol, 74855-10-0; 1-bromopropene, 590-14-7; 4-pentenal, 2100-17-6.

Photochemistry of Cycloalkenes. 9. Photodimerization of Cyclohexene[1]

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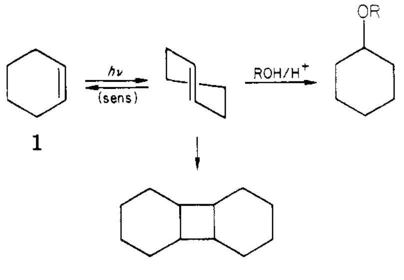
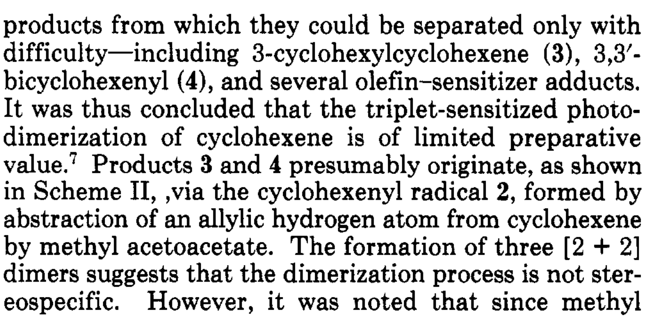
The photodimerization of cyclohexene has been restudied. Either direct or triplet-sensitized irradiation produced a stereoisomeric mixture of [2 + 2] dimers **6–8**, respectively, as primary products with the cis,trans isomer **7** predominating. The direct-irradiation process was complicated by the accompanying formation of the radical-derived products **3–5**. Dimerization is interpreted in terms of initial light-induced cis → trans isomerization of cyclohexene, followed by a nonstereospecific ground-state $[2_s + 2_a]$ addition of *trans*-cyclohexene to the cis isomer. By contrast, cycloheptene showed little tendency to undergo photodimerization; attempted *p*-xylene-sensitized dimerization afforded instead principally the sensitizer–olefin adduts **10** and **11**. Comparison is made with the copper(I) triflate catalyzed photodimerization of cyclohexene and cycloheptene.

Usually the only consequence of sensitized irradiation of alkenes in various media, either protic or aprotic, is cis ⇄ trans isomerization about the double bond. A notable exception is the behavior of cyclohexenes and cycloheptenes, which undergo protonation on sensitized irradiation in protic media—a phenomenon not shared by either acyclic, exocyclic, or larger ring cyclic olefins, on one hand, or smaller ring cyclic olefins, on the other hand.[3,4] It has been proposed that photoprotonation involves an initial light-induced cis → trans isomerization of the olefin, followed by ground-state protonation of the resulting highly strained *trans*-cycloalkene intermediate (Scheme I), rather than protonation of an excited state of the olefin.[3] This proposal has recently been supported by studies with cycloheptene and 1-phenylcyclohexene and -heptene, which show the involvement of an intermediate in the photoprotonation process having a lifetime much longer than would be expected for an excited state.[5]

Scheme I



Scheme II



On sensitized irradiation in aprotic media cyclohexenes undergo instead [2 + 2] cyclodimerization.[3,6,7] Two reports on the photodimerization of cyclohexene have appeared; in both cases methyl acetoacetate was employed as photosensitizer.[6,7] A mixture of three [2 + 2] dimers (**6–8**) was obtained in low yield, along with a number of other products from which they could be separated only with difficulty—including 3-cyclohexylcyclohexene (**3**), 3,3′-bicyclohexenyl (**4**), and several olefin–sensitizer adducts. It was thus concluded that the triplet-sensitized photodimerization of cyclohexene is of limited preparative value.[7] Products **3** and **4** presumably originate, as shown in Scheme II, ,via the cyclohexenyl radical **2**, formed by abstraction of an allylic hydrogen atom from cyclohexene by methyl acetoacetate. The formation of three [2 + 2] dimers suggests that the dimerization process is not stereospecific. However, it was noted that since methyl acetoacetate is capable of abstracting hydrogen atoms, the actual stereospecificity of the reaction may be greater than that observed due to secondary epimerization. Indeed,

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