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Hydrocarbon Analogues of the Type II Photoeliminations of Ketones. Photochemistry of 1-Substituted 4-Phenyl-4-pentenes[1]

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Abstract: Direct irradiation of 1,4-diphenyl-4-penten-1-ol produces mainly 2-methyl-2,5-diphenyltetrahydrofuran, while benzophenone-sensitized photolysis gives α-methylstyrene, acetophenone, and 1,4-diphenyl-1-pentanone. The direct irradiation is postulated to proceed via the radical anion of the alkene. A mechanism for the inefficient triplet state reaction ($\Phi = 0.0005$) is proposed which involves initial hydrogen abstraction by the methylene carbon of the excited alkene to give a 1,4 biradical, which then produces the observed products. The mechanism is analogous to the accepted mechanism for the type II photofragmentation of ketones. The mechanism is supported by solvent effects and deuterium-labeling studies. Two related alkenes, 4-phenyl-4-penten-1-ol and 1,4-diphenyl-4-pentene, show similar photochemical behavior, although they react even less efficiently than 1,4-diphenyl-4-penten-1-ol.

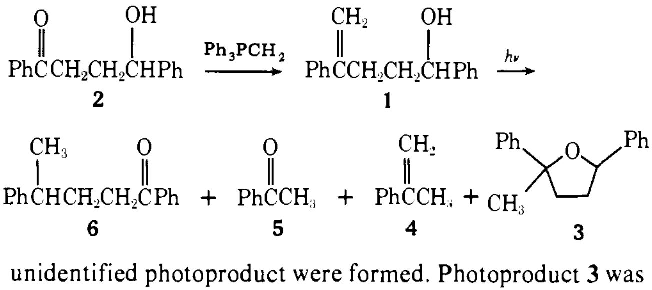
There are now a number of reports in the literature describing the photoinduced abstraction of hydrogen atoms by carbon which occurs in various molecules containing carbon–carbon double or triple bonds. Some examples include intermolecular abstractions by acyclic alkenes,[2-4] cyclic alkenes,[5,6] α,β-unsaturated ketones,[7,8] α,β-unsaturated esters,[9] and acetylenes.[10] Intramolecular abstractions by alkenes,[1,11-17] α,β-unsaturated enones,[18] and α,β-unsaturated amides[19] have also been observed. We report here the full details of our study of the photochemistry of substituted phenylpentenes. These compounds undergo intramolecular hydrogen abstractions very similar to the type II reaction of ketones,[20] although much less efficiently.

Results

For our initial studies we chose to investigate the photochemistry of 1,4-diphenyl-4-penten-1-ol (**1**), for two reasons. Based on the reported substituent effects on the type II reaction of ketones,[20a] we felt that both the phenyl and hydroxyl groups on carbon 1 would increase the rate of hydrogen abstraction. In addition, if **1** were to undergo a type II reaction, the 1,4 biradical which would result could also be generated by irradiation of 1,4-diphenyl-1-pentanone (**6**), and thus an independent check on the behavior of this biradical would be available.

The synthesis of **1** was readily accomplished by a Wittig reaction of 1,4-diphenyl-4-hydroxy-1-butanone[21] (**2**), with excess methylenetriphenylphosphorane. The photochemistry of **1** depended on both the solvent employed and the multiplicity of the excited state. The photoproducts observed under various conditions are summarized in Table I.

The major product from the direct irradiation of **1** in either hexane or benzene was 2-methyl-2,5-diphenyltetrahydrofuran (**3**), obtained as a mixture of stereoisomers. In addition, small amounts of α-methylstyrene (**4**), acetophenone (**5**), and an unidentified photoproduct were formed. Photoproduct **3** was identified by comparison of its spectral properties with those of an authentic sample prepared by acid-catalyzed cyclization of **1**. Direct irradiation of **1** in *tert*-butyl alcohol gave the same products, although the relative percentages changed. The ef-



2 **1**
6 **5** **4** **3**

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Table I. Photoproducts of 1,4-Diphenyl-4-penten-1-ol

solvent	% conversion	percentage of products[a] 3	4	5	6
hexane	54	22	trace	trace	
hexane[b]	37	15			
benzene	34	31	2	2	
benzene[c]	40		21	19	5
tert-butyl alcohol	48	7	3	12	
tert-butyl alcohol[c]	79		7	29	

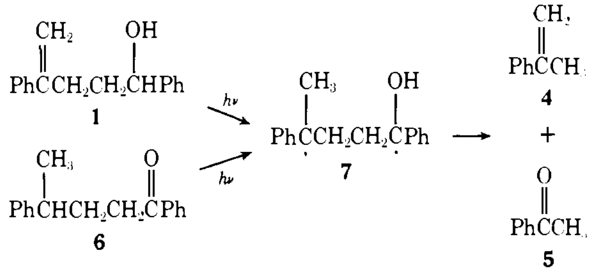
[a] Based on reacted **1**. [b] Containing 1,4-dimethoxybenzene. [c] Containing benzophenone.

ficiency of formation of **3** decreased, allowing the production of **4** and **5** to compete more effectively. When **1** was irradiated in hexane containing 1,4-dimethoxybenzene as an electron donor sensitizer,[22] **3** was again the major product.

Benzophenone-sensitized irradiation of **1** provided several contrasting features when compared with the direct irradiation. In both benzene and *tert*-butyl alcohol, the major products were now **4** and **5**; no **3** was detected in either solvent. An important observation was that a small amount of 1,4-diphenyl-1-pentanone (**6**) was produced in benzene, but not in *tert*-butyl alcohol. Triphenylene was also effective as a sensitizer.[23]

Both direct and sensitized irradiations of **1** produce products very inefficiently. The quantum yield for the production of acetophenone from **1** upon benzophenone-sensitized irradiation in benzene was 0.0005. As a consequence of this, the long irradiation times resulted in significant decomposition of the photoproducts, and made quantitative studies difficult.

α-Methylstyrene and acetophenone are two of the products that would be expected from the 1,4 biradical **7**. In addition, such 1,4 biradicals often cyclize to form cyclobutanols. Since no cyclobutanol-type product was observed upon irradiation of **1**, it was important to determine if the behavior of **7**, generated by a known method, was consistent with these results. As pointed out previously, ketone **6** is expected to produce biradical **7** by the well-known type II reaction.[20a] In the event,

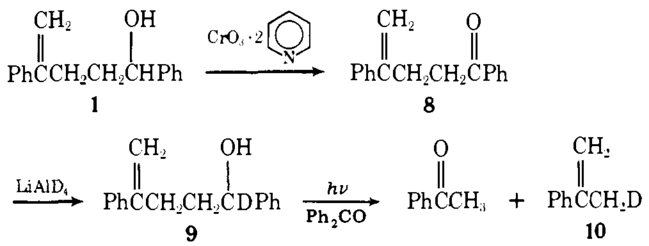


$$\underset{\mathbf{1}}{Ph\overset{CH_2}{\overset{\|}{C}}CH_2CH_2\overset{OH}{\overset{|}{C}}HPh} \xrightarrow{h\nu} \underset{\mathbf{7}}{Ph\overset{CH_3}{\overset{|}{\dot{C}}}CH_2CH_2\overset{OH}{\overset{|}{\dot{C}}}Ph} \xleftarrow{h\nu} \underset{\mathbf{6}}{Ph\overset{CH_3}{\overset{|}{C}}HCH_2CH_2\overset{O}{\overset{\|}{C}}Ph}$$

$$\mathbf{7} \longrightarrow \underset{\mathbf{4}}{Ph\overset{CH_2}{\overset{\|}{C}}CH_3} + \underset{\mathbf{5}}{Ph\overset{O}{\overset{\|}{C}}CH_3}$$

6 produced **4** and **5** in virtually quantitative yield upon irradiation in benzene. Only a minor amount (ca. 2%) of a photoproduct that could be the cyclobutanol was produced.

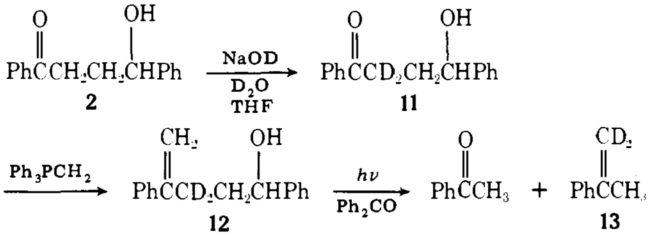
Although the above observations are consistent with a mechanism involving biradical **7** in the photochemistry of **1**, other mechanisms can also be envisioned. We therefore investigated the photochemistry of two deuterium-labeled derivatives of **1** to help delineate the mechanism for the formation of **4** and **5**. Oxidation of **1** with chromium trioxide-pyridine complex[25] gave 1,4-diphenyl-4-penten-1-one (**8**). Reduction of **8** with lithium aluminum deuteride gave **9**. The presence of the deuterium on carbon 1 of **9** had a dramatic effect on the rate of formation of acetophenone and α-methylstyrene upon irradiation. Sensitized irradiation of **1** and **9** revealed a large deuterium isotope effect ($\Phi_1/\Phi_9 = 5.0 \pm 0.6$)[26] on the production of acetophenone. Because of this isotope effect, the yield of α-methylstyrene from irradiation of **9** was quite small, and NMR analysis was not successful. However, GC-mass



$$\underset{\mathbf{1}}{Ph\overset{CH_2}{\overset{\|}{C}}CH_2CH_2\overset{OH}{\overset{|}{C}}HPh} \xrightarrow{CrO_3\cdot 2\,C_5H_5N} \underset{\mathbf{8}}{Ph\overset{CH_2}{\overset{\|}{C}}CH_2CH_2\overset{O}{\overset{\|}{C}}Ph} \xrightarrow{LiAlD_4} \underset{\mathbf{9}}{Ph\overset{CH_2}{\overset{\|}{C}}CH_2CH_2\overset{OH}{\overset{|}{C}}DPh} \xrightarrow[Ph_2CO]{h\nu} Ph\overset{O}{\overset{\|}{C}}CH_3 + \underset{\mathbf{10}}{Ph\overset{CH_2}{\overset{\|}{C}}CH_2D}$$

spectroscopic analysis showed the presence of one deuterium per molecule in the α-methylstyrene (parent at m/e 119). A strong peak at m/e 103 (parent minus 16) can be attributed to the loss of monodeuteriomethyl and suggests that the deuterium is located in the methyl group as shown in **10**.

Another labeled derivative of **1** confirmed the position of the deuterium in **10** and provided additional insight into the mechanism. Ketone **2** was deuterated in the α position and the resulting ketone **11** converted to **12** by a Wittig reaction. Since



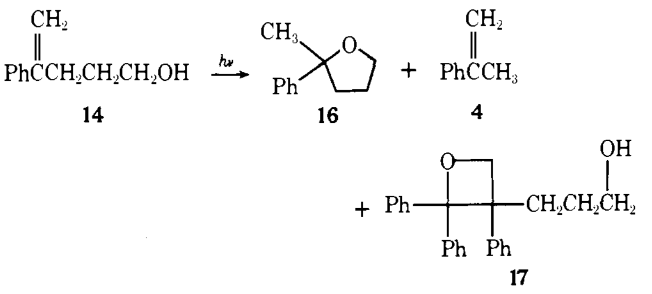
$$\underset{\mathbf{2}}{Ph\overset{O}{\overset{\|}{C}}CH_2CH_2\overset{OH}{\overset{|}{C}}HPh} \xrightarrow[D_2O,\ THF]{NaOD} \underset{\mathbf{11}}{Ph\overset{O}{\overset{\|}{C}}CD_2CH_2\overset{OH}{\overset{|}{C}}HPh} \xrightarrow{Ph_3PCH_2} \underset{\mathbf{12}}{Ph\overset{CH_2}{\overset{\|}{C}}CD_2CH_2\overset{OH}{\overset{|}{C}}HPh} \xrightarrow[Ph_2CO]{h\nu} Ph\overset{O}{\overset{\|}{C}}CH_3 + \underset{\mathbf{13}}{Ph\overset{CD_2}{\overset{\|}{C}}CH_3}$$

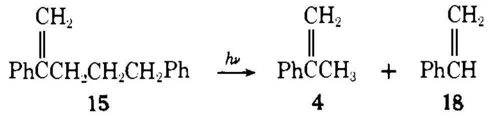
there was no complication by a deuterium isotope effect in this case, it was possible to determine by NMR that the deuterium in the α-methylstyrene produced upon sensitized irradiation of **12** was located in the vinyl positions, as shown in structure **13**.

It would be very interesting to know the rate constant for the type II reaction of **1** so that it might be compared with the rate constants observed for the type II reaction of similar ketones. Stern–Volmer quenching studies,[27] which have proven so useful in determining the kinetics of carbonyl photochemistry, are less easily applied to alkene photochemistry because the quencher will compete with the alkene for the light in direct irradiations, and will competitively quench the sensitizer if one is used. Cristol[28] has developed an elegant method to circumvent these problems by using a sensitizer and a constant ratio of substrate to quencher. An attempt to use this method, with benzophenone as the sensitizer and 1,3-cyclohexadiene[29] as the quencher, failed in the case of **1**. In fact, the amount of acetophenone increased slightly with increasing quencher concentration. The probable reason for this increase is that there is less light-induced decomposition of the acetophenone as the concentrations of both **1** and cyclohexadiene were increased.

A second type of quenching study was also attempted. If the direct irradiation of **1** produces **3** from the singlet excited state and **4** and **5** from the triplet excited state (produced by intersystem crossing of the singlet), the presence of a quencher might affect the formation of the products differently. As the quencher concentration is increased, it will absorb more of the light. This should cause an equal decrease in the amount of all three photoproducts. Any additional triplet quenching by energy transfer would result in a further decrease in the amount of **4** and **5**. In this event, no difference in the amount of "quenching" of **3** and **5** could be detected using 1,3-cyclohexadiene concentrations of up to 0.04 M.[32] Unfortunately, it is not possible to determine whether this negative result is due to the triplet of **1** having such a short lifetime that it cannot be quenched or whether it is due to **4** and **5** being produced from the singlet excited state upon direct irradiation.

Two other alkenes, 4-phenyl-4-penten-1-ol (**14**) and 1,4-diphenyl-4-pentene (**15**), were prepared from the corre-





sponding ketones by a Wittig reaction. Both of these alkenes exhibited photochemical behavior similar to that of **1**. Thus, upon direct irradiation in benzene, **14** gave 29% of 2-methyl-2-phenyltetrahydrofuran (**16**) and 1% of α-methylstyrene. Benzophenone-sensitized irradiation of **14** in benzene gave 3% of **4** and 38% of 3-(3-hydroxypropyl)-2,2,3-triphenyloxetane (**17**). Oxetane **17** was identified by its spectral properties (see Experimental Section). Especially informative was the mass spectrum of **17**, which showed a highest mass peak at *m/e* 314, corresponding to loss of CH_2O from the molecular ion. This is a common fragmentation of oxetanes.[33] Benzophenone-sensitized irradiation of **15** gave 8% of **4** and 13% of styrene (**18**). Comparative irradiations of **1**, **14**, and **15** showed that **1** produced α-methylstyrene 24 times as efficiently as **14** and 2.6 times as efficiently as **15**.

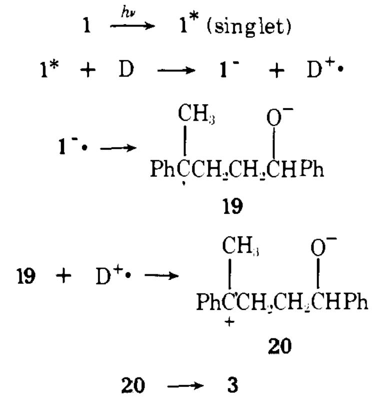
Discussion

Direct irradiation of **1** and **14** yields products resulting from formal Markownikoff addition of the alcohol group to the carbon-carbon double bond. Numerous examples of the photochemical addition of alcohols and other nucleophiles to acyclic alkenes have been reported in the recent literature.[24,34-38] These reactions have been postulated to occur from the singlet excited state by electron-transfer mechanisms; radical cations give anti-Markownikoff addition products and radical anions give Markownikoff addition products. Thus, a reasonable mechanism for the formation of **3** from **1**, patterned after that proposed by Arnold and Maroulis[22a] for the Markownikoff addition of methanol to 1,1-diphenylethylene, involves the interaction of the singlet excited state of **1** with an electron donor to give the radical anion of **1** and the radical cation of the donor (or perhaps an exciplex with substantial charge-transfer character). The identity of the electron donor is not clear at this point. Subsequent steps leading to **3** are similar to those in the Arnold and Maroulis mechanism (see Scheme I). This mechanism is supported by the observation that irradiation of a solution of 1,4-dimethoxybenzene, a known electron donor sensitizer,[22] and **1** also results in the formation of **3**. In this case the radical ions are produced by the interaction of the singlet excited state of dimethoxybenzene with **1**.

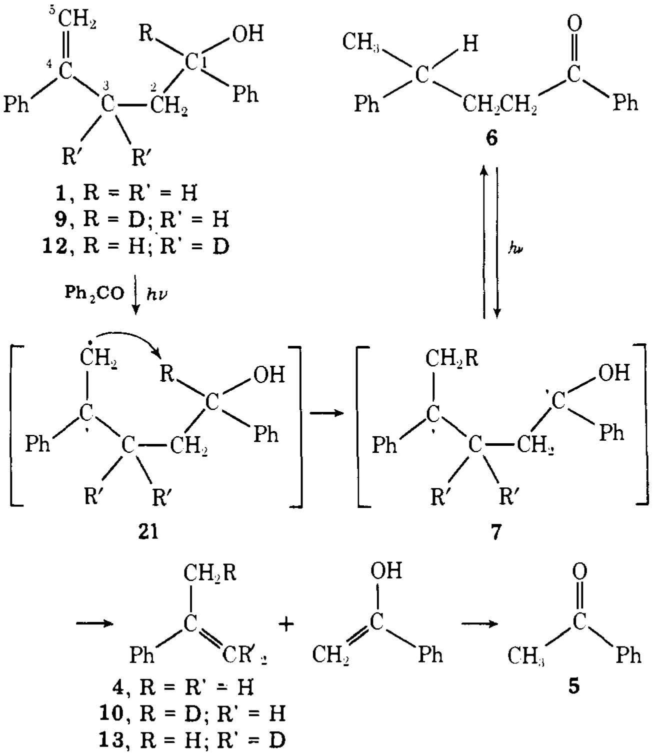
A mechanism analogous to that accepted[20] for the type II reaction of ketones accounts well for the behavior of the triplet excited state of **1** (see Scheme II). Energy transfer from triplet benzophenone produces **21**, the triplet excited state of **1**. A hydrogen atom is transferred from carbon 1 to carbon 5 in triplet **21**, via a cyclic, six-membered transition state, to produce 1,4 biradical **7**. Biradical **7** then undergoes a fragmentation to produce α-methylstyrene and the enol of acetophenone.

Biradicals related to **7** are intermediates in the type II reaction of ketones. When **7** is generated from irradiation of ketone **6**, its behavior is identical with that when it is generated from **1**, that is, α-methylstyrene and acetophenone are the major products. Further support for the presence of **7** as an intermediate in the reaction is provided by the observation that sensitized irradiation of **1** produces **6** in benzene, but not in *tert*-butyl alcohol. Exactly such behavior has been observed for similar 1,4 biradicals when generated by irradiation of ketones.[20a] In benzene solution the hydroxyl hydrogen of **7** is transferred to carbon 4 to give **6** in competition with fragmentation. In *tert*-butyl alcohol, hydrogen bonding of the hydroxyl hydrogen to solvent effectively suppresses its transfer and fragmentation only is observed.

Scheme I



Scheme II



The deuterium-labeling studies fully support the mechanism shown in Scheme II. Irradiation of **9** gives **10** with the deuterium in the methyl group, while irradiation of **12** gives **13** with deuterium in the vinyl positions. The large deuterium isotope effect observed in the case of **9** indicates a rather symmetrical transition state for the reaction of **21** (R = D) to give **7**. Wagner[39] has reported a deuterium isotope effect of 4.8 for the type II reaction of 1-phenyl-1-nonanone, and Lewis[40] has reported an isotope effect of 1.7 for the type II reaction of **2**, the ketone analogue of **1**. However, it is not surprising that the transition state for abstraction in the case of **1** (carbon abstracting a hydrogen on carbon) is more symmetrical than in the case of **2** (oxygen abstracting a hydrogen from a carbon).

These results firmly establish that biradical **7** is an intermediate in the sensitized reaction of **1**. However, it is possible that **7** is not produced by hydrogen abstraction in the triplet excited state of **1**, but by some other mechanism. A referee has suggested that **7** is produced from ketone **6** and that **6** is produced from **1** by some unspecified mechanism. We believe that the observation that **6** is produced when **1** is irradiated in benzene, but not in *tert*-butyl alcohol, argues against this possibility. This demonstrates that the type II reaction of **6** is slow enough under these conditions so that **6** can be detected if formed. Since no **6** was detected in *tert*-butyl alcohol, it cannot be an intermediate in this solvent, and therefore it is not a major intermediate in benzene either. Another suggestion is that benzophenone is acting as a chemical sensitizer, that is, the benzophenone triplet abstracts the hydrogen from carbon 1 and delivers it to carbon 5, thus generating biradical **7**. The observation that the reaction can also be sensitized by triphenylene makes this possibility seem unlikely. Overall we feel that the results are best explained by the mechanism outlined in Scheme II.

The triplet excited state photochemistry of acyclic alkenes is usually dominated by cis–trans isomerization.[41] This is probably also the case with **1**, although the isomerization process is invisible in this case. Thus, hydrogen abstraction competes inefficiently with deactivation by rotation about the π bond and this "free rotor effect"[42] accounts for the low quantum yield for hydrogen abstraction. In fact, Padwa[11] has recently reported several examples of a type II reaction for cyclopropenes where the quantum yields are quite high.

The products formed from **14** and **15** upon sensitized irradiation can also be explained by a mechanism similar to that outlined in Scheme II. The observation that both of these compounds react less efficiently than **1** is similar to the effect of these substituents on the type II reaction of ketones.[20] The formation of **17** has precedent in the literature. Triplet benzophenone is known to add to conjugated dienes to form oxetanes in a reaction that competes very inefficiently with energy transfer.[43] The very low efficiency for fragmentation of **14** allows oxetane formation to predominate in this case. We did not detect a similar product in the photosensitized reaction of **1**, although we cannot rule out the presence of a small amount of oxetane. However, since **1** underwent fragmentation about 24 times more efficiently than **14**, oxetane formation would be expected to be only a minor process.

Experimental Section

General. Boiling points are uncorrected; melting points are corrected. Nuclear magnetic resonance spectra were obtained on Varian EM-360 and HA-100 spectrometers. Ultraviolet spectra were obtained on a Beckman Acta V spectrophotometer. Infrared spectra were obtained with a Perkin-Elmer 337 or 710 A spectrophotometer. Mass spectra were obtained on a AEI MS-12 spectrometer. Elemental analyses were obtained from Spang Microanalytical Laboratory, Ann Arbor, Mich., and from Atlantic Microlab, Inc., Atlanta, Ga.

Gas-liquid partition chromatography was performed with a Hewlett-Packard 5750 chromatograph coupled to a Columbia Scientific Industries CSI 38 digital integrator. The following columns were used: column A, 1.8 m × 3.2 mm, 10% Silicone Gum Rubber UCW-982 on 60/80 Chromosorb W; column B, 3 m × 3.2 mm, 20% Carbowax 20M on 80/100 Chromosorb P; column C, 1.5 m × 3.2 mm, 10% butanediol succinate on 80/100 Chromosorb P; column D, 1.5 m × 3.2 mm, 3% SE-52 on 80/100 Chromosorb G; column E, 1.5 m × 3.2 mm, 3% SE-30 on 80/100 Chromosorb G; column F, 1.5 m × 3.2 mm, 15% FFAP on 60/80 Chromosorb W; column G, 1.8 m × 3.2 mm, 3% OV-17 on 100/200 Chromosorb W. Preparative GLC employed an Aerograph A-700 chromatograph.

1,4-Diphenyl-4-penten-1-ol (1). To a stirring suspension of 52.5 g (0.147 mol) of methyltriphenylphosphonium bromide in 450 mL of dry tetrahydrofuran, maintained under an atmosphere of dry nitrogen, 66.5 mL (0.148 mol) of 2.34 M *n*-butyllithium solution was added via a syringe. This solution was stirred for 4 h at room temperature; then 10.0 g (0.0416 mol) of 1,4-diphenyl-4-hydroxy-1-butanone (**2**)[21] in 100 mL of dry tetrahydrofuran was added dropwise over a period of 30 min. The solution was refluxed for 3 days. After cooling, the solution was poured into 1 L of water. The organic phase was separated and the aqueous phase was extracted with three 300-mL portions of ether. The combined extracts were washed four times with water and dried over anhydrous magnesium sulfate. The solvent was removed in vacuo and the residue chromatographed on silica gel (3.5 × 83 cm column) using 10% ether in hexane as eluent. The following fractions were obtained: fraction 1, 1340 mL, discarded; fraction 2, 2000 mL, 9.43 g of product. Distillation gave 8.19 g (82.5%) of **1**, bp 150-151 °C (0.25 mm). Redistillation gave an analytical sample which crystallized on standing in the cold: mp 31-32.5 °C; NMR ($CDCl_3$) τ 2.9 (m, 10 H, aromatics), 4.83 (d, J = 1.2 Hz, 1 H, C=CH), 5.07 (d, J = 1.2 Hz, 1 H, C=CH), 5.58 (t, J = 6.4 Hz, 1 H, CH), 6.91 (s, 1 H, OH), 7.6 (m, 2 H, CH_2), 8.2 (m, 2 H, CH_2); λ_{max} (ethanol) 239 nm (ϵ 9940). Anal. ($C_{17}H_{18}O$) C, H.

4-Phenyl-4-penten-1-ol (14). Compound **14** was prepared from 105 g (0.294 mol) of methyltriphenylphosphonium bromide, 0.294 mol of *n*-butyllithium, and 15.0 g (0.092 mol) of 1-phenyl-4-hydroxy-1-butanone[44] in dry THF in the same manner as described for the preparation of **1**. Distillation yielded 5.53 g (37%) of **14**: bp 88-93 °C (0.2 mm); NMR ($CDCl_3$) τ 2.80 (m, 5 H, aromatics), 4.80 (d, J = 1.2 Hz, 1 H, C=CH), 5.0 (q, J = 1.2 Hz, 1 H, C=CH), 4.50 (t, J = 7 Hz, 2 H, CH_2O), 7.17 (s, 1 H, OH), 7.46 (m, 2 H, CH_2C=C), 8.36 (m, 2 H, CH_2); λ_{max} (cyclohexane) 238 nm (ϵ 9750). Anal. ($C_{11}H_{14}O$) C, H.

1,4-Diphenyl-4-pentene (15). To a stirring suspension of 8.60 g (0.024 mol) of methyltriphenylphosphonium bromide in 150 mL of anhydrous ether, maintained under an atmosphere of dry nitrogen, 12.6 mL of 1.97 M (0.025 mol) *n*-butyllithium solution was added via a syringe. This solution was stirred for 4 h at room temperature; then a solution of 3.57 g (0.016 mol) of 1,4-diphenyl-1-butanone[45] in 100 mL of anhydrous ether was added and the solution was heated to reflux overnight. After cooling, the solid was removed by filtration and washed with ether. The combined ether solutions were concentrated and the residue was chromatographed on silica gel (3.5 × 86 cm column) using 2% ether in hexane as eluent. The following fractions were obtained: fraction 1, 610 mL, discarded; fraction 2, 440 mL, 3.7 g of oil. Distillation of fraction 2 gave 2.78 g (78%) of **15**: bp 111-112 °C (0.175 mm); NMR ($CDCl_3$) τ 2.9 (m, 10 H, aromatics), 4.79 (d, J = 2 Hz, 1 H, C=CH), 5.02 (m, 1 H, C=CH), 7.53 (m, 4 H, CH_2C=C and CH_2Ph), 8.25 (m, 2 H, remaining CH_2); λ_{max} (ethanol) 238 nm (ϵ 7600). Anal. ($C_{17}H_{18}$) C, H.

2-Methyl-2,5-diphenyltetrahydrofuran (3). A solution of 1.220 g (5.12 mmol) of **1** and 0.084 g of *p*-toluenesulfonic acid in 50 mL of reagent benzene was refluxed for 2 h with a Dean-Stark separator. After cooling, the solution was washed with aqueous sodium bicarbonate solution, then with water, and dried over anhydrous magnesium sulfate. The solvent was removed in vacuo and the residue distilled to give 0.79 g (65%) of **3** as a mixture of stereoisomers, bp 128-133 °C (0.3 mm). An analytical sample was obtained by preparative GC (1.5 m × 6.4 mm, 3% SE-30 at 182 °C) followed by distillation: NMR (CCl_4) τ 2.9 (m, 10 H, aromatics), 5.1 (m, 1 H, CH), 7.9 (m, 4 H, CH_2CH_2), 8.42 and 8.48 (pair of singlets, 3 H total, CH_3). Anal. ($C_{17}H_{18}O$) C, H.

Alternatively, **3** could be prepared by acidic workup of the reaction of methylmagnesium iodide and **2** as described below.

The crude product obtained from 0.021 mol of methylmagnesium iodide and 0.0083 mol of **2** was dissolved in 50 mL of benzene containing 0.05 g of *p*-toluenesulfonic acid and the solution was heated to reflux for 2.5 h with a Dean-Stark separator. After washing with aqueous sodium bicarbonate solution and with water, the solution was dried over anhydrous magnesium sulfate. The solvent was removed in vacuo and the residue distilled to give 0.79 g (40%) of slightly impure **3**, bp 129-133 °C (0.35 mm). The spectral properties of this material were identical with those of **3** obtained from cyclization of **1**.

2-Methyl-2-phenyltetrahydrofuran (16). A solution of 1.01 g (6.24 mmol) of **14** and 0.097 g of *p*-toluenesulfonic acid in 50 mL of benzene was heated to reflux for 1 h. The solution was washed with aqueous sodium bicarbonate solution and with water and dried over anhydrous magnesium sulfate. The solvent was removed in vacuo and the residue distilled to give 0.56 g (56%) of **16**: bp 126-129 °C (39 mm); $n^{21}{}_D$

1.5179 (lit.[45] bp 105-107 °C (20 mm); $n^{21}{}_D$ 1.5179); NMR ($CDCl_3$) τ 2.76 (m, 5 H, aromatics), 6.17 (m, 2 H, CH_2O), 8.15 (m, 4 H, remaining CH_2's), 8.53 (s, 3 H, CH_3).

1,4-Diphenyl-1-pentanone (6). To a slurry of 3.31 g (0.0768 mol) of a 56% dispersion of sodium hydride in mineral oil (the oil was removed by washing with hexane) in 100 mL of dry Me_2SO, maintained under an atmosphere of dry nitrogen, was added a solution of 14.99 g (0.078 mol) of ethyl benzoylacetate in 25 mL of dry Me_2SO over a period of 15 min. After the resulting yellow solution had stirred at room temperature for 15 min, a solution of 15.56 g (0.078 mol) of 1-bromo-2-phenylpropane in 20 mL of dry Me_2SO was added. The resulting solution was heated to 60-65 °C for 4 days. The solution was poured into 1 L of water and extracted with three 250-mL portions of ether. The combined extracts were washed twice with water and dried over anhydrous magnesium sulfate. The solvent was removed in vacuo to leave 23.5 g of oil.

This oil was heated to reflux for 45 min in 200 mL of 48% aqueous hydrobromic acid. After cooling, the solution was poured into water and ether extracted. The combined extracts were washed with water, twice with 5% aqueous sodium bicarbonate solution, and again with water and dried over anhydrous magnesium sulfate. The solvent was removed in vacuo to leave 18.6 g of dark oil. This oil was chromatographed on silica gel (3.5 × 85 cm column) using 2% ether in hexane as the eluent to give 6.80 g of a mixture of **6** and 1-bromo-2-phenylpropane. This material was rechromatographed as described above using 1% ether in hexane as eluent to give 4.52 g of **6**. This material was distilled to give 3.39 g (18%) of **6**, bp 137-142 °C (0.25 mm). This material crystallized on standing and was recrystallized from hexane to give an analytical sample: mp 40-41 °C; NMR ($CDCl_3$) τ 2.6 (m, 10 H, aromatics), 7.2 (m, 3 H, CH and CH_2), 8.0 (m, 2 H, CH_2), 8.8 (d, J = 7 Hz, 3 H, CH_3); λ_{max} (ethanol) 241 nm (ϵ 12 000), 278 (ϵ 810). Anal. ($C_{17}H_{18}O$) C, H.

1,4-Diphenyl-4-penten-1-one (8). To a stirring solution of 8.25 g (0.104 mol) of pyridine in 150 mL of dichloromethane was added 5.31 g (0.053 mol) of chromium trioxide and the solution was stirred at room temperature for 15 min. A solution of 2.01 g (0.0085 mol) of **1** in 10 mL of dichloromethane was added to the now burgundy-colored solution and the mixture was stirred at room temperature for 45 min. The solution was decanted from the tarry residue and the residue was washed with 200 mL of ether. The combined organic phases were washed three times with 5% aqueous sodium hydroxide solution, with 5% aqueous hydrochloric acid solution, and with 5% aqueous sodium bicarbonate solution, then dried over anhydrous magnesium sulfate. The solvent was removed in vacuo to leave an oil which crystallized on standing. Recrystallization from hexane gave 1.79 g (90%) of **8**; mp 57-58 °C; NMR ($CDCl_3$) τ 2.15 (m, 2 H, aromatics ortho to C=O), 2.68 (m, 8 H, remaining aromatics), 4.73 (broad s, 1 H, C=CH), 4.90 (broad s, 1 H, C=CH), 6.97 (broad singlet with shoulders, 4 H, CH_2's). Anal. ($C_{17}H_{16}O$) C, H.

1,4-Diphenyl-1-deuterio-4-penten-1-ol (9). A solution of 1.494 g (6.33 mmol) of **8** in 25 mL of anhydrous ether was added dropwise to a stirring slurry of 0.425 g (10.1 mmol) of lithium aluminum deuteride in 50 mL of anhydrous ether. After the solution had stirred at room temperature for 3.5 h, 1.7 mL of water was carefully added and the solution was stirred overnight. The solids were removed by filtration and washed well with ether. After the combined ether solutions were dried with anhydrous magnesium sulfate, the solvent was removed in vacuo to leave an oil. Distillation of this oil gave 1.36 g (90%) of **9**, bp 147-150 °C (0.25 mm). Analysis by NMR showed the triplet at τ 5.58 to be entirely absent.

1,4-Diphenyl-3,3-dideuterio-4-penten-1-ol (12). Ten milliliters of a solution of NaOD in deuterium oxide (prepared by reacting 0.2 g of sodium with 20 mL of deuterium oxide) was added to a solution of 3.04 g of **2** in 100 mL of dry THF and the solution stirred at room temperature for 20 min. The volatiles were removed in vacuo and the residue was dissolved in 100 mL of dichloromethane. The water layer was discarded and the organic layer was dried over anhydrous sodium sulfate. After the solvent was removed in vacuo, the residue was treated in like manner three additional times, with the exception that stirring was continued for 1.5 h for the last two exchanges. The residue was crystallized from benzene to give 1.27 g of **11**. Analysis by NMR showed complete exchange of deuterium for the protons on the carbon adjacent to the carbonyl group.

This deuterated ketone was converted to **12** by a procedure analogous to that described for the preparation of **1**. Using 13.0 g (0.0364 mol) of methyltriphenylphosphonium bromide, 0.0471 mol of *n*-butyllithium, and 2.60 g (0.0107 mol) of **11** gave, after distillation, 1.12 g (46%) of **12**. Analysis by NMR showed no detectable signal at τ 7.6 where the protons on carbon 3 normally appear. We estimate that 10% protons on carbon 3 would have been easily detectable.

Photochemical Apparatus. Preparative irradiations were conducted with a quartz immersion well and a Hanovia 450-W medium-pressure mercury-vapor lamp. In sensitized runs, a Pyrex filter was employed. Water-jacketed vessels of 250 or 500 mL were used and the solutions were purged continuously with a stream of oxygen-free nitrogen.[47]

Analytical irradiations employed the same light source and immersion well combined with a "merry-go-round" type apparatus with quartz or Pyrex photolysis tubes of ca. 15 mL capacity. Solutions (10-15 mL, ca. 10^{-2} M in compound to be studied) were degassed with oxygen-free nitrogen[47] prior to irradiations. Percentages of photoproducts from the various compounds investigated were determined by GLC analysis with internal standards as follows (compound, internal standard, column, and conditions): **1**, benzophenone or biphenyl, column A, temperature programmed from 90 to 220 °C; **14**, naphthalene, column A, temperature programmed from 90 to 160 °C; **15**, acetophenone, column A, temperature programmed from 90 to 190 °C; **6**, biphenyl, column A, temperature programmed from 90 to 220 °C.

Photochemical Solvents. Hexane for photochemical experiments was prepared by stirring practical hexane over concentrated sulfuric acid. After several hours, the hexane was decanted and added to fresh acid. This procedure was continued until the acid layer no longer darkened. The hexane was separated, washed with water, with aqueous sodium bicarbonate solution, and again with water, dried over anhydrous magnesium sulfate, and distilled. *tert*-Butyl alcohol was distilled from calcium hydride. Benzene was stirred overnight over concentrated sulfuric acid, washed twice with water, dried over anhydrous sodium sulfate, and distilled from phosphorus pentoxide under a nitrogen atmosphere.

Identification of the Photoproducts from 1,4-Diphenyl-4-penten-1-ol (1). Tetrahydrofuran derivative **3**, isolated from preparative irradiation of **1** described below, was identified by comparison of its IR and NMR spectra with those of an authentic sample. A solution of 1.96 g of **1** in 500 mL of hexane was irradiated through quartz for 62 h. It was necessary to clean the immersion well every few hours to remove a polymer film that slowed the reaction considerably. The hexane was removed in vacuo and the residue was chromatographed on silica gel using 20% ether in hexane as eluent to give 0.519 g of **3** and 0.459 g of **1**. Compound **3** was identified in a small-scale irradiation of 0.0089 M **1** and 0.1 M dimethoxybenzene in hexane by comparison of its GLC retention time with that of an authentic sample on three different columns (column A at 180 °C; column C at 198 °C; column G at 190 °C). Under these conditions calculations indicate that dimethoxybenzene should absorb greater than 90% of the light.

Acetophenone and α-methylstyrene were identified in a small-scale irradiation in *tert*-butyl alcohol by comparison of their GLC retention times with those of authentic samples on three different columns (column A, temperature programmed run from 89 to 217 °C; column B at 155 °C; and column C at 130 °C). Ketone **6** was identified in a small-scale benzophenone-sensitized irradiation in benzene by comparison of its GLC retention time with that of an authentic sample on three different columns (column A, temperature programmed run from 90 to 200 °C; column D at 184 °C; and column E at 186 °C).

Identification of the Photoproducts from 4-Phenyl-4-penten-1-ol (14). Tetrahydrofuran derivative **16**, isolated from the preparative irradiation of **14** described below, was identified by comparison of its IR and NMR spectra with those of an authentic sample. A solution of 1.02 g of **14** in 500 mL of benzene was irradiated through quartz for 7 h. The solvent was removed in vacuo and the residue chromatographed on silica gel using ether-hexane as eluent to give 0.199 g of **16** and 0.618 g of **14**.

α-Methylstyrene was identified in a small-scale irradiation in benzene, sensitized with benzophenone, by comparison of its GLC retention time with that of an authentic sample on three different columns (column A, temperature programmed run from 90 to 160 °C; column B at 137 °C; and column F at 120 °C).

Irradiation through Pyrex of a solution of 1.30 g of **14** with 2.05 g of benzophenone as sensitizer in 500 mL of benzene for 58.5 h and chromatograply on silica gel using ether-hexanes as eluent gave tetraphenyl-1,2-ethanediol (benzopinacol; identified by comparison with an authentic sample) and 0.721 g of crystalline oxetane **17** along with 0.367 g of recovered **14**. Recrystallization of **17** from ether-hexane gave an analytical sample: mp 123.5-124.5 °C; NMR $(CDCl_3)$ τ 2.92 (m, 15 H, aromatics), 4.80 (d, J = 6 Hz, 1 H, H of CH_2 in oxetane ring), 5.60 (d, J = 6 Hz, 1 H, H of CH_2 in oxetane ring), 6.65 (t, J = 6 Hz, 2 H, CH_2OH), 7.97 (m, 2 H, CH_2), 8.72 (m, 3 H, CH_2 and OH); addition of D_2O caused the multiplet at 8.72 to decrease in area corresponding to the loss of one H; in Me_2SO-d_6 the OH appeared as a triplet (J = 6 Hz) at τ 5.73 and the methylene group adjacent to the hydroxyl appeared as a quartet (J = 6 Hz) at τ 6.78; λ_{max} (ethanol) 253 nm (ϵ 700), 259 (720), 266 (shoulder, 510); the mass spectrum showed the highest mass peak at m/e 314 (molecular ion minus 30, loss of CH_2O). Anal. $(C_{24}H_{24}O_2)$ C, H.

Identification of the Photoproducts from 1,4-Diphenyl-4-pentene (15). Styrene and α-methylstyrene were identified in a small-scale irradiation of **15** in benzene, sensitized with benzophenone, by comparison of their GLC retention times with those of authentic samples on three different columns (column A, temperature programmed run from 100 to 190 °C; column B at 100 °C; column G at 100 °C).

Identification of the Photoproducts from 1,4-Diphenyl-1-pentanone (6). Acetophenone and α-methylstyrene were identified by comparison of their IR and NMR spectra with those of authentic samples. The products were isolated by preparative GLC on an SE-30 column at 83 °C from a solution of 0.62 g of **6** in 280 mL of benzene that had been irradiated for 45 min.

Preparative Irradiation of 1,4-Diphenyl-1-deuterio-4-penten-1-ol (9). A solution of 1.21 g of **9** and 5.48 g of benzophenone in 500 mL of benzene was irradiated through Pyrex for 24 h. The benzene was removed by distillation and the more volatile components were obtained in a more concentrated form by bulb-to-bulb distillation in vacuo. The distillate was analyzed by gas chromatography-mass spectrometry (Beckman GC-4 gas chromatograph; OV-17 SCOT column, temperature programmed run from 50 to 200 °C; Biemann MS-GC interface; AEI MS-12 mass spectrometer). The GLC peak corresponding to α-methylstyrene showed a molecular ion at m/e 119 and a strong peak at m/e 103.

Preparative Irradiation of 1,4-Diphenyl-3,3-dideuterio-4-penten-1-ol (12). A solution of 1.12 g of **12** and 5.71 g of benzophenone in 500 mL of benzene was irradiated through Pyrex for 12 h. The benzene was removed by distillation and the more volatile components (benzene, α-methylstyrene, acetophenone, and a small amount of benzophenone) were collected by bulb-to-bulb distillation in vacuo. The pot residue was dissolved in benzene and the irradiation and collection procedures were repeated twice. The combined distillates were concentrated to a volume of 1 mL. This resulted in a solution of α-methylstyrene, acetophenone, and benzophenone in benzene. However, none of these latter three compounds has signals in the NMR that overlap with those of α-methylstyrene and it was possible to analyze this mixture directly by NMR for the location of the deuterium in the α-methylstyrene. The spectrum showed no detectable signals at τ 4.69 and 5.03, where the vinyl protons of α-methylstyrene appear in benzene solution (we estimate that 10% proton incorporation would have been easily detectable); in addition the singlet at τ 8.02 for the methyl group of α-methylstyrene was sharper than the corresponding signal in a nondeuterated sample.

Comparative Irradiation of 1,4-Diphenyl-4-penten-1-ol (1) and 1,4-Diphenyl-1-deuterio-4-penten-1-ol (9). Deuterium Isotope Effect. Two photolysis tubes were prepared. Both tubes contained 10.0 mL of a benzene solution which contained 0.400 M benzophenone. In addition, the first tube contained 0.0200 M undeuterated alkene **1** and the second tube contained 0.0203 M deuterated alkene **9**. The tubes were irradiated in parallel, through Pyrex, for 4.2 h. Analysis by GLC (column C, temperature programmed run from 80 to 120 °C) using naphthalene as internal standard showed the first tube to contain 6.59 $\times 10^{-4}$ M acetophenone and the second to contain 1.48×10^{-4} M acetophenone. From this data, the deuterium isotope effect is calculated to be $\Phi_H/\Phi_D = 4.4$. A duplicate run gave $\Phi_H/\Phi_D = 5.6$. The average is $\Phi_H/\Phi_D = 5.0 \pm 0.6$.

Relative Efficiencies of the Photoreaction of 1,4-Diphenyl-4-penten-1-ol (1), 4-Phenyl-4-penten-1-ol (14), and 1,4-Diphenyl-4-pentene (15). Three photolysis tubes, each containing 10.0 mL of a 0.402 M benzophenone in benzene solution, were irradiated, through Pyrex, in parallel for 15.5 h. The first tube also contained 0.0529 M **1**, the second contained 0.0580 M **14**, and the third contained 0.0523 M **15**. Analysis by GLC (column A, temperature programmed run from 60 to 225 °C) using m-methylanisole as internal standard showed the first tube to contain 1.54×10^{-3} M α-methylstyrene, the second tube to contain 5.39×10^{-5} M α-methylstyrene, and the third to contain 6.64×10^{-4} M α-methylstyrene.

A similar experiment with 0.400 M benzophenone in each tube and 0.0534 M **1** in the first tube, 0.0549 M **14** in the second, and 0.0500 M **15** in the third gave 2.11×10^{-3} M α-methylstyrene in the first tube, 1.14×10^{-4} M α-methylstyrene in the second, and 7.67×10^{-4} M α-methylstyrene in the third, after 16 h of irradiation.

Quantum Yield for 1,4-Diphenyl-4-penten-1-ol (1). The quantum yield was measured using an apparatus patterned after the "Wisconsin Black Box"[48] with 2 cm each of 2.0 M $NiSO_4$ in 5% H_2SO_4, 0.38 M $CoSO_4$ in 5% H_2SO_4, and 0.0199 M $SnCl_2$ in 40% HCl as filter solutions[48] to isolate a window from 300 to 350 nm. A solution (700 mL) of 0.0301 M benzophenone and 0.002 94 M **1** in benzene was irradiated. Calculations indicate that the benzophenone should absorb greater than 99% of the light under these conditions. Potassium ferrioxalate actinometry[49] showed that 23.7 mEinsteins of light was absorbed and GLC analysis (column C at 88 °C) using naphthalene as internal standard showed that 5.2×10^{-6} mol of acetophenone was produced. Using these data, the quantum yield is 2×10^{-4}. A similar experiment gave a quantum yield of 8×10^{-4}. The average quantum yield is $5 \pm 3 \times 10^{-4}$.

Efficiency of Energy Transfer. A solution containing 0.100 M benzophenone and 0.100 M benzhydrol in benzene and a solution containing 0.100 M benzophenone, 0.100 M benzhydrol, and 5.38×10^{-3} M **1** in benzene were irradiated through Pyrex in the "merry-go-round" apparatus until ca. 25% of the benzophenone in the first solution had reacted. The amount of benzophenone remaining in each tube was then determined by UV spectroscopic analysis of diluted samples. The average of two experiments indicated that energy transfer was 98 ± 2% efficient.

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Cyclobutene Derivatives as Isoprene Equivalents in Terpene Synthesis. 3. Bicyclo[2.2.0]hexanes[1]

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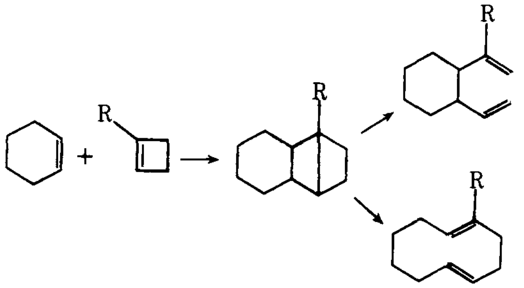
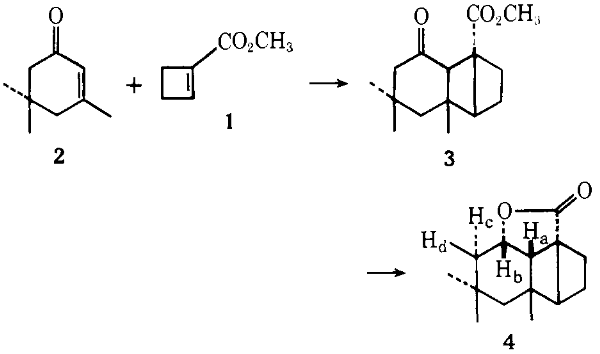
Abstract: Two new syntheses of cyclobutene esters and the use of 1-cyanocyclobutene as potential isoprene synthons are described. Photocycloaddition of methyl cyclobut-1-enecarboxylate and 1-cyanocyclobutene to piperitone, followed by reduction and lactonization, gives photodihydroaristolactone **15**. Single-crystal X-ray analysis of **15** and related **4** reveals interesting structural features in the strained bicyclo[2.2.0]hexane system. Thermolysis of lactones **15** and **4** yields 1,5-cyclodecadienes related to germacrene sesquiterpenes.

As part of a continuing program of terpene synthesis, we have for several years been attempting to utilize cyclobutenes as reactive isoprene synthons.[2a,b] Ring opening of suitable cyclobutenes may be induced to occur in either of two directions yielding "terminal"[2a,2c] or "internal"[2b] isoprene residues. Cycloaddition reactions of cyclobutene derivatives (eq 1) leads to strained bicyclo[2.2.0]hexanes capable of thermolysis to either 1,5-cyclodecadienes or divinylcyclohexanes. The photocycloaddition of cyclobutenes is the best route to strained bicyclo[2.2.0]hexane derivatives,[3] and ample evidence has accumulated that the cycloreversion of bicyclo[2.2.0]hexanes proceeds with some stereospecificity.[4]



(1)

The importance of medium-ring carbocycles such as germacradienes[5] has prompted a number of recent elegant approaches to these molecules[6] including several using the strategy outlined in eq 1.[7] For example, photocycloaddition[7b] of methyl cyclobutenecarboxylate (**1**) and isophorone (**2**) (eq 2) gave derivative **3** which was converted to lactone **4**. Lactone **4** can by pyrolyzed at 185 °C yielding **5** and **6**. Since germacrene-type sesquiterpenes undergo Cope rearrangement to elemanes,[8] the bicyclo[2.2.0]hexane approach possesses general features which are attractive in terpene syntheses. We report herein our efforts in this area.[9]



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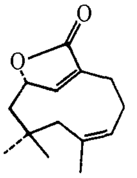

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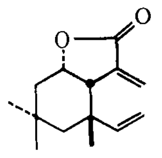

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Synthesis of Cyclobutene Derivatives. It was clear from the outset that, for a cyclobutene-based methodology to be generally applicable, efficient routes to the reactive precursors must be available. In our experience the lengthy[12] synthesis of **1** gave low overall yields. Consequently, two new routes to cyclobutene esters were developed (eq 3 and 4). Both sulfen-

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