The Photochemistry of 5,6-Heptadien-2-one

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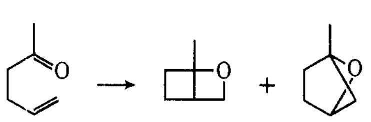
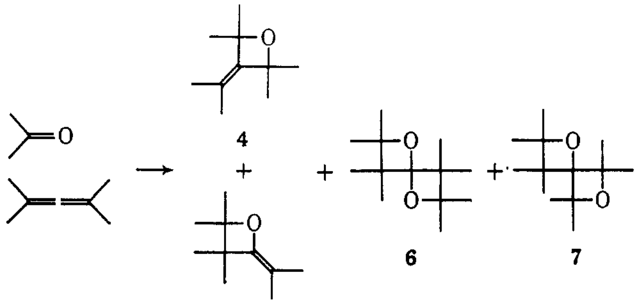
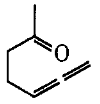
The synthesis and photochemistry of 5,6-heptadien-2-one are described. The major photoproduct is 1-methyl-3-methylene-2-oxabicyclo[2.2.0]hexane. Minor amounts of a second material assigned as isopropenyl 2-butadienyl ether are also observed. Pyrolysis of the bicyclic oxetane yields the minor photoproduct and starting allenic ketone. The first of these thermal products is further rearranged to the second upon standing. The details of these processes are described.

An interesting variation of the Paterno–Büchi[1] reaction (the photochemical 2 + 2 cycloaddition between a ketone and an olefin) is the intramolecular cycloaddition of 5-hexen-2-one (**1**) which yields 1-methyl-2-oxabicyclo[2.2.0]hexane (**2**)[2,3] and 1-methyl-5-oxabicyclo-[2.1.1]hexane (**3**).[3] Several methylated derivatives of **1** have also been found to give analogous products.[3,4]

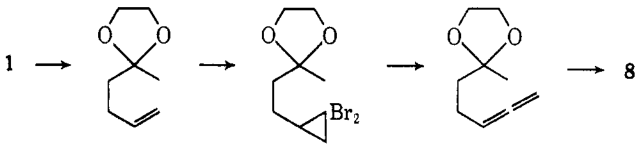

1 **2** **3**

Recent work[5] indicates that allenes can also participate in intermolecular photocycloaddition reactions with carbonyl compounds. For example, Hammond[5a] reports that addition of acetone to tetramethylallene gives monoadducts **4** and **5** and diadducts **6** and **7**. However, in general there appears to be a large preference for carbonyl oxygen to bond to the central carbon of the allene function. In the present study we have examined the photochemistry of 5,6-heptadien-2-one (**8**), an analog of **1** which contains isolated carbonyl and allene functions within the same molecule.


4 **5** **6** **7**

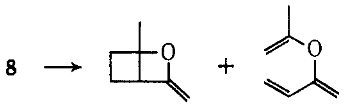

8

5,6-Heptadien-2-one (**8**)[6] was prepared from 5-hexen-2-one (**1**) in a straightforward manner. The ethylene ketal (**9**) of **1** was treated with bromoform and potassium *t*-butoxide in pentane[7] and the resulting adduct **10** was treated with methyllithium to give ketalallene **11**.[8] Careful hydrolysis with 1 *N* sulfuric acid in aqueous tetrahydrofuran gave the desired ketoallene **8**.



9 **10** **11**

A 1% solution of **8** in petroleum ether was irradiated through a Pyrex filter with a 450 W Hanovia lamp. The progress of the reaction was followed by glpc analysis of aliquots taken at intervals. After 46 hr, glpc assay indicated the product to be a 90:6:4 mixture of three materials subsequently identified as 1-methyl-3-methylene-2-oxabicyclo[2.2.0]hexane (**12**), isopropenyl 2-butadienyl ether (**13**), and unreacted starting material. The moderate return of distilled isomeric materials was accompanied by a fair amount of less volatile residue. Volatile fragmentation products were not observed but probably would not have been visible with the glpc analysis utilized. Samples of the isomeric products were obtained for identification by preparative glpc.



12 **13**

The infrared spectrum of methyleneoxetane **12** exhibits a strong band at 5.92 μ assigned as the C=C stretch of the enol ether.[9,10] The two olefinic protons are coupled to the bridgehead proton and to each other, giving four-line multiplets centered at δ 3.60 and 3.90.[11] The mass spectrum of **12** is very similar to that of ketoallene **8**, except for a significant peak at *m/e* 68

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[1] (a) E. Paterno and G. Chieffi, *Gazz. Chim. Ital.*, **39b**, 341 (1909); (b) G. Büchi, C. G. Inman, and E. S. Lipinsky, *J. Amer. Chem. Soc.*, **76**, 4327 (1954); (c) G. Büchi, J. T. Kofron, and D. Rosenthal, *ibid.*, **78**, 876 (1956); (d) G. Büchi and N. C. Yang, *ibid.*, **79**, 2318 (1957); (e) N. C. Yang, *Pure Appl. Chem.*, **9**, 591 (1964).

[2] R. Srinivasan, *J. Amer. Chem. Soc.*, **82**, 755 (1960).

[3] N. C. Yang, M. Nussim, and D. R. Coulson, *Tetrahedron Lett.*, 1525 (1965).

[4] H. Morrison, *J. Amer. Chem. Soc.*, **87**, 932 (1965).

[5] (a) H. Gotthardt, R. Steinmetz, and G. S. Hammond, *J. Org. Chem.*, **33**, 2774 (1968); (b) D. R. Arnold and A. H. Glick, *Chem. Commun.*, 813 (1966).

[6] J. W. Wilson, *ibid.*, 143 (1968).

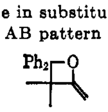
[7] W. Kirmse, "Carbene Chemistry," Academic Press Inc., London, 1964, p 163.

[8] W. R. Moore and H. R. Ward, *J. Org. Chem.*, **27**, 4179 (1962); L. Skattebøl, *Acta Chem. Scand.*, **17**, 1683 (1963).

[9] K. Nakanishi, "Infrared Absorption Spectroscopy—Practical—," Holden-Day Inc., San Francisco, Calif., 1962, p 36.

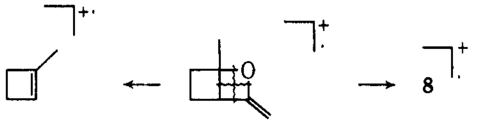
[10] Hammond[5a] observed the corresponding absorption for the monocyclic enol ethers at 5.74–5.79 μ. This difference may be caused by the bicyclic system or the difference in substitution of the double bond.

[11] Hammond[5a] reports an AB pattern centered at δ 3.76 for i.

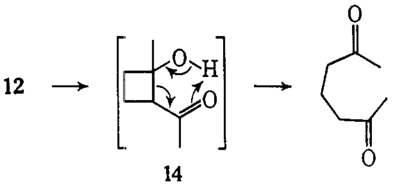


i

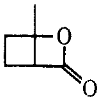
(loss of C_2H_2O). This suggests that the important initial mass-spectrometric processes of the molecular ion are the two possible modes of reverse cycloaddition of the oxetane ring.[12]



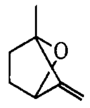
The spectroscopic evidence for structure **12** is bolstered by the following chemical transformations. Hydrolysis in dilute sulfuric acid gave a single product identified as 2,6-heptanedione. This acyclic material undoubtedly forms by hydrolysis of the enol ether to β-hydroxy ketone **14** which spontaneously isomerizes as indicated.[13] Ozonolysis of **12** gave a neutral product



with an intense carbonyl band at 5.49 μ in the infrared[14] consistent with β-lactone structure **15**. The nmr exhibits a one-proton multiplet centered at δ 3.6 appropriate for the bridgehead proton.[14] Further characterization of **15** was not possible because of the tendency for this material to decompose upon glpc purification. The above evidence, however, serves to unambiguously secure structure **15**. Taken together, the above data eliminate **16**, the other possible methyleneoxetane product, as a potential structure for the major photoproduct.



15



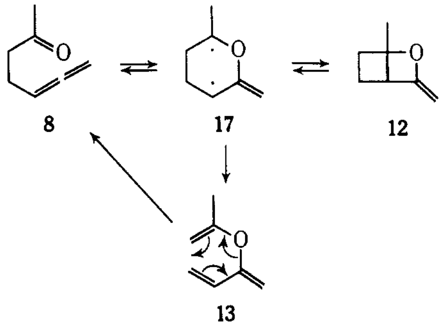
16

The infrared spectrum of minor photoproduct **13** displays medium-intensity bands at 6.00, 6.12, and 6.29 μ which are assigned to double-bond stretching modes, in addition to strong C–O bands.[9] The only nonolefinic protons in the nmr are those of a methyl group on a double bond (δ 1.84). Absorptions typical for an isolated vinyl group appear at δ 6.14, 5.40, and 5.02 (one proton each), while the four remaining protons appear at δ 4.56 (2), 4.30 (1), and 4.18 (1), positions appropriate for β protons of enol ethers.[15] Insufficient quantities of **13** were isolated for further characterization, but its spectral data, its appearance as a pyrolysis product of methyleneoxetane **12**, and its ready conversion into ketoallene **8** substantiate the proposed structure (*vide infra*).

Vapor phase pyrolysis of methyleneoxetane **12** at 400° gave a mixture of ketoallene **8** and enol ether **13**, whose ratios varied from 7:1 to 3:1 in different runs. When a pyrolysis sample containing an internal standard was allowed to stand at room temperature, **13** decreased by $^1/_2$ in 6 days and disappeared completely within 12 days. However, the total quantity of **8** plus **13** remained unchanged during this period, thus indicating that enol ether **13** rearranges to ketoallene **8** under rather mild conditions. Pyrolysis of **8** resulted in no change.

Discussion

Photocycloadditions of carbonyls to olefins[1] are thought to be initiated by attack of the electrophilic oxygen of the carbonyl n-π^* triplet[16] on the double bond. The resulting biradical species then leads to oxetane by spin inversion and bond formation.[17] In the present instance a similar mechanism is probably operative. Thus, the excited ketone is transformed to biradical **17** which subsequently collapses to bicyclic oxetane **12** by coupling of the transannular radical sites. Alternatively, **17** can fragment to enol ether **13**. Interestingly, no products attributable to oxygen attack at either of the terminal allenic carbons were observed from the photolysis of **8** (*e.g.*, **15**).



Predominance of oxetane products resulting from oxygen bonding to the central carbon of allenes was noted in the earlier work[5] on intermolecular cycloadditions. The most likely explanation for this strong preference is that it reflects the relative stabilities of the intermediate biradicals which result from the different modes of addition.[18] An alternate but less probable rationale is that attack at the terminal allenic carbons occurs competitively with central attack, but that the intermediate from this mode of reaction is not effective in product formation, since its activation energy for reversion to starting material is appreciably less than that for product formation.[19] Superimposed upon this in-

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[12] The base peak of the mass spectrum of oxetane results from this type of cleavage: J. H. Beynon in "Advances in Mass Spectrometry," J. D. Waldron, Ed., Pergamon Press, London, 1959, pp 328–354. Cyclobutanones also cleave to olefins and ketenes: H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day Inc., San Francisco, Calif., 1967, pp 145–146.

[13] P. de Mayo, H. Takeshita, and A. B. M. A. Sattar, *Proc. Chem. Soc.*, 119 (1962); P. de Mayo and H. Takeshita, *Can. J. Chem.*, **41**, 440 (1963).

[14] E. J. Corey and J. Streith, *J. Amer. Chem. Soc.*, **86**, 950 (1964).

[15] R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1968, p 139.

[16] H. E. Zimmerman, *Advan. Photochem.*, **1**, 183 (1963).

[17] Evidence has been presented which indicates that excited singlet states of ketones also undergo cycloaddition, but orientational features appear to be unchanged. N. J. Turro and P. A. Wriede, *J. Amer. Chem. Soc.*, **90**, 6863 (1968); N. J. Turro, P. A. Wriede, and J. C. Dalton, *ibid.*, **90**, 3274 (1968); N. J. Turro, P. A. Wriede, J. C. Dalton, D. Arnold, and A. Glick, *ibid.*, **89**, 3950 (1967).

[18] Estimates on the energetics for the possible positions of carbonyl oxygen attack on allenes suggest that formation of a vinyl radical by terminal carbon attack should be appreciably less favorable than generation of the radical from central attack, even if significant allylic stabilization is not developed in the transition state for the latter process: B. E. Knox and H. B. Palmer, *Chem. Rev.*, **61**, 247 (1961); T. L. Cottrell, "The Strength of Chemical Bonds," 2nd ed, Butterworths Scientific Publications, London, 1958, pp 173–183; C. Walling, "Free Radicals in Solution," John Wiley & Sons, Inc., New York, N. Y., 1957, pp 50–53.

[19] A similar explanation has been advanced to account for orientation effects in simple free-radical additions to allenes: D. R. Taylor, *Chem. Rev.*, **67**, 317 (1966).

herent orientational preference in the instance of an intramolecular example such as **8** is the effect of the methylene chain which links the interacting functions. An accurate assessment of this feature is difficult, owing to a paucity of information about the geometry and electron distribution of the excited carbonyl function.[20] However, the present results indicate that the intramolecular reaction is, if anything, more selective than its intermolecular counterpart.

The thermal isomerization of oxetane **12** is also of some interest and appears to proceed by initial bond fission to the familiar biradical **17**. This species is capable of reverting to ketoallene **8** or undergoing bond reorganization to produce **13**. Evidently, thermal equilibrium is not achieved in the flow pyrolysis experiment, since **13** would be expected to isomerize completely to **8** by a thermal Cope rearrangement.[23] Indeed, such was found to occur under relatively mild conditions. Pyrolysis of ketoallene **8** does not yield **12**, in consonance with this explanation.

Experimental Section

Infrared spectra were obtained with Perkin-Elmer Infracord Model 137 and 137-G spectrophotometers as neat films unless otherwise noted. Nuclear magnetic resonance (nmr) spectra were recorded on a Varian A-60 spectrometer in carbon tetrachloride with tetramethylsilane as internal standard. Mass spectra were determined using an AEI MS9 spectrometer at 70 eV. Gas-liquid partition chromatography (glpc) was carried out on a Varian-Aerograph Series 1200 chromatograph (analytical, flame ionization detector) using a 10 ft × $^1/_8$ in. 15% Carbowax 20M on 60-80 Chromosorb W column and on an Aerograph Model A700 chromatograph (preparative) using a 5 ft × $^3/_8$ in. 15% Carbowax 20M on 60-80 Chromosorb W column. Percentage composition data were measured using a Disc Model 224 integrator and are not corrected for detector response. Analyses were performed by Midwest Microlab, Inc. All solvents were Fisher reagent grade unless otherwise noted.

5,6-Heptadien-2-one (8).[6]—A stirred mixture of 68 g of 5-hexen-2-one (1) (Aldrich Chemical Co.), 50 g of ethylene glycol, 100 ml of benzene, and 53 mg of *p*-toluenesulfonic acid was heated to reflux for 17 hr with removal of 16.5 ml of water by a Dean-Stark trap. The solution was allowed to cool to room temperature and washed with three 75-ml portions of saturated sodium bicarbonate solution and 75 ml of water. The benzene and water were removed at atmospheric pressure. The residue was distilled at reduced pressure to give 84 g (85%) of ethylene ketal (**9**): bp 80-82° (43 mm); glpc purity, 98%; ir 3.22, 6.08, 10.0, and 11.0 μ ($CH{=}CH_2$), and 8.0, 8.2, 8.9, and 9.5 μ (COCOC); nmr δ 5.80 (m, 1, $CH{=}CH_2$), 4.9 (m, 2 $CH{=}CH_2$), 3.82 (s, 4, OCH_2), 2.1 (m, 2), 1.7 (m, 2), and 1.22 ppm (s, 3).

To a stirred slurry of 50 g of potassium *t*-butoxide (MSA Research Corp.) in 50 ml of pentane and 63.5 g of **9** at 0° was added dropwise 113 g of bromoform. Pentane (350 ml total) was added to the reaction mixture as required to keep the slurry thin enough to stir. Stirring was continued for 30 min after the addition time. Water (200 ml) was added and the mixture was suction filtered to remove a brown solid. To the two-phase filtrate was added 100 ml of saturated salt solution, the mixture was shaken, and the layers were separated. The organic layer was washed with two 100-ml portions of saturated salt solution and dried (Na_2SO_4). The solvent was removed at reduced pressure. Most of the unreacted ketal **9** and bromoform were distilled from the mixture at reduced pressure (84 g, bp 76-82°, 40 mm). Nmr analysis shows a 1.4:1.0 mole ratio of **9** to bromoform in this mixture which could be used as starting material for additional **10**.

Further distillation gave 37 g (26%) of the dibromocarbene adduct **10**: bp 101-105° (0.25 mm); ir 8.0, 8.2, 8.6, 9.0, 9.5, and 9.6 μ (COCOC); nmr δ 3.89 (s, 4, OCH_2), 1.26 (s, 3), and 1.2 and 1.7 ppm (m, 7).

A solution of 57 g of methyl iodide in 50 ml of ether was added slowly to a stirred suspension of 8.5 g of lithium wire in 100 ml of ether under nitrogen. The mixture was kept at reflux for 1 hr after addition of the methyl iodide. The mixture was cooled to 25°, the excess lithium was removed with a spatula, and the methyllithium solution was transferred to an addition funnel under a nitrogen atmosphere. This mixture was added slowly to a stirred solution of 32 g of dibromocyclopropane **10** in 150 ml of ether at 0°. The solution was stirred for 30 min after the addition was completed; then 100 ml of water was added. The layers were separated and the organic layer was washed with two 100-ml portions of water. The water solutions were combined and washed with 50 ml of ether. The ether solutions were combined and dried (Na_2SO_4), and the ether was removed to give crude **11**. Distillation afforded 14.0 g (84%) of **11**: bp 96-99° (20 mm); glpc purity, 95%; ir 5.10 and 11.8 μ ($C{=}C{=}CH_2$), and 8.0, 8.2, 8.8, 9.1, and 9.5 μ (COCOC); nmr δ 5.0 (m, 1, $C{=}C{=}CH$), 4.6 (m, 2, $CH_2{=}C{=}C$), 3.82 (s, 4, CH_2O), 1.8 (m, 4), and 1.22 ppm (s, 3).

To a mixture of 25 ml of 6 *N* sulfuric acid and 125 ml of tetrahydrofuran was added 14.0 g of **11** and the homogeneous solution was stirred at 25° for 4 hr. The solution was diluted with 250 ml of water and extracted with three 100-ml portions of pentane. The pentane extract was washed with two 100-ml portions of saturated sodium bicarbonate solution and 100 ml of saturated salt solution. The pentane and most of the tetrahydrofuran were removed. Another 50 ml of pentane was added and the solution was dried (Na_2SO_4). The pentane was removed and the residue was distilled to yield 6.73 g (66%) of 5,6-heptadien-2-one (**8**): bp 64-67° (15 mm); glpc purity, 95%; ir 5.10 and 11.8 μ ($C{=}C{=}CH_2$), and 5.82 μ ($C{=}O$); nmr δ 5.1 (m, 1, $C{=}C{=}CH$), 4.6 (m, 2, $CH_2{=}C{=}C$), 2.3 (m, 4), and 2.07 ppm (s, 3); mass spectrum *m/e* (rel intensity) 110 (4), 95 (9), 67 (15), 58 (10), 53 (12), 43 (100), and 15 (6).

Photolysis of 5,6-Heptadien-2-one (8).—Irradiations were carried out using a Pyrex-filtered 450 W Hanovia Type L medium-pressure mercury arc with a water-cooled quartz immersion well. The solutions were degassed prior to irradiation by bubbling prepurified nitrogen through them for 1 min using a glass tube with a fritted-glass tip, immediately inserting the immersion well, and maintaining a slight positive nitrogen pressure throughout the photolysis. Aliquots were removed by syringe through a serum cap for periodic glpc assay.

Irradiation of a stirred solution of 4.32 g of 98% pure **8** in 410 ml of redistilled 30-60° petroleum ether for 46 hr gave a mixture which glpc analysis indicated to be 91% 1-methyl-2-oxa-3-methylenebicyclo[2.2.0]hexane (**12**), 6% isopropenyl 2-butadienyl ether (**13**), and 4% **8**. Most of the solvent was removed at reduced pressure and the residue was transferred to a Dry Ice-acetone trap at 25° (0.35 mm). A yellow, nonvolatile (0.9 g) remained. After removal of the remaining solvent, the residual 2 ml of colorless liquid was separated by preparative glpc to give 0.38 g of **12**: glpc purity, 98%; ir 5.92 μ ($C{=}C{-}O$); nmr δ 3.9 and 3.6 (m, 2, $O{-}C{=}CH_2$), 3.3 (m, 1, $CH{-}C{=}CH_2$), 2.3 (m, 4), and 1.42 ppm (s, 3); mass spectrum *m/e* (rel intensity) 110 (13), 95 (13), 68 (12), 67 (24), 58 (13), 53 (16), 43 (100), and 15 (5). Re-collection gave an analytical sample.

Anal. Calcd for $C_7H_{10}O$: C, 76.33; H, 9.15. Found: C, 76.04; H, 9.37.

A small amount of **13** was also collected: ir (CCl_4) 6.00, 6.12, 6.29, 8.0, and 9.6 μ ($C{=}C{-}O$ and $C{=}C{-}C{=}C$); nmr δ 6.1 (m, 1, $CH{=}CH_2$), 5.4 and 5.0 (m, 2, $CH{=}CH_2$), 4.56 (m, 2, $C{=}CH_2$), 4.3 and 4.18 (m, 2, $CH_3{-}C{=}CH_2$), and 1.84 ppm (d, 3, J = 1 Hz, CH_3).

Vapor Phase Pyrolysis of 12.—The apparatus consisted of a 10 mm i.d. Pyrex tube packed with 0.25 in. o.d. Pyrex helices inserted through a 170 mm E. H. Sargent and Co. tube furnace. The sample was placed in a flask attached at one end of the tube and the vapors were condensed in a Dry Ice-acetone trap at the other end. The pressure in the system was reduced to less than 1 mm by a vacuum pump attached at the trap, and the samples

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[20] One reasonable model would utilize the carbonyl group in its ground-state geometry with attack by the half-filled oxygen p orbital in the plane of the carbonyl.[21] However, rehybridization to a nonplanar geometry is also a reasonable possibility.[22]

[21] N. J. Turro and D. S. Weiss, *J. Amer. Chem. Soc.*, **90**, 2185 (1968).

[22] D. E. Freeman and W. Klemperer, *J. Chem. Phys.*, **45**, 52 (1966); J. C. D. Brand and D. G. Wilkinson, *Advan. Phys. Org. Chem.*, **1**, 365 (1963); E. W. Abrahamson, J. G. F. Littler, and K. P. Vo, *J. Chem. Phys.*, **44**, 4082 (1966).

[23] A. C. Cope and E. M. Hardy, *J. Amer. Chem. Soc.*, **62**, 441 (1940); A. C. Cope, K. E. Hoyle, and D. Heyl, *ibid.*, **63**, 1843 (1941); W. von E. Doering and W. R. Roth, *Angew. Chem. Intern. Ed. Engl.*, **2**, 115 (1963).

were allowed to vaporize and pass through the tube. About 40 mg of methyleneoxetane **12** was pyrolyzed at 400°. Less than 5 min was required for passage, and longer pumping reduced the amount of trapped dienol ether **13**. Glpc assay revealed a ratio of 72:28 for **8**:**13**. The nmr of this mixture exhibited the absorptions of **13** at δ 6.14, 5.4, 4.3, 4.18, and 1.84 ppm, the remaining peaks being hidden by the spectrum of **8**. To *ca.* 0.1 ml of a mixture (47% **8**, 47% **12**, and 6% **13**) from photolysis of a 1% solution of **8** in redistilled 30–60° petroleum ether was added ~1 μl of the above pyrolysis mixture. Glpc analysis of this sample on three different columns (10 ft 10% DEGS, 10 ft 15% Carbowax 20M, 5 ft 10% SE-30; all $^1/_8$ in. o.d.) showed only the three peaks originally present in the photolysis mixture.

Another 55-mg sample of **12** was pyrolyzed in the same manner as above. The trapped product mixture was transferred to an nmr capillary microtube and 1 drop of *p*-xylene was added. Integration of the nmr revealed an initial ratio of 6:1 for **8**:**13**. After 6 days at 25°, the corresponding ratio was 12:1; after 12 days, no **13** remained. Standardization against the added *p*-xylene demonstrated that the (**8** + **13**)/*p*-xylene ratio remained constant, thus indicating the conversion of **13** into **8**.

A sample of ketoallene **8** was recovered unchanged from pyrolysis at 400°.

Hydrolysis of 12.—A solution of 100 mg of methyleneoxetane **12** in 1 ml of ether was shaken with 5 ml of 1 *M* sulfuric acid for 5 min. To this was added 20 ml of ether, the mixture was shaken, and the layers were separated. The water layer was washed with two 15-ml portions of ether. The combined ether solutions were washed with 5 ml of saturated sodium bicarbonate solution and dried (Na_2SO_4). Removal of the ether gave 0.13 g of a colorless liquid which was collected by glpc to yield 48 mg (41%) of 2,6-heptanedione: glpc pure; mp 29–32° (lit.[24] mp 30–33°); ir (CCl_4) 5.83 μ (C=O); nmr δ 2.40 (m, 4, CH_2CO), 2.05 (s, 6, CH_3CO), and 1.76 ppm (m, 2, $CH_2CH_2CH_2$).

Ozonolysis of 12.—A solution of 1.00 g of vacuum transferred product mixture from photolysis of **8** (~45% **12** by glpc analysis) in 50 ml of methylene chloride containing 2 ml of pyridine was cooled to −80°. The output of a Welsbach Model T-408 ozonator was bubbled through the solution for 2 hr. The solution was flushed with oxygen for 30 min, allowed to warm to room temperature, and washed with three 25-ml portions of 10% hydrochloric acid. The combined aqueous washings were back extracted with 20 ml of methylene chloride. The combined methylene chloride solutions were shaken vigorously with four 15-ml portions of saturated sodium bicarbonate solution (an unidentified carboxylic acid was removed only with much effort) and dried (Na_2SO_4). The solvent was removed to give 0.24 g (~50%) of 1-methyl-2-oxa-3-oxobicyclo[2.2.0]hexane (**15**): ir 5.49 μ (vs, β-lactone); nmr δ 3.6 (m, 1, CHCO), 2.3 (m, 4), and 1.58 ppm (s, 3). Attempts at glpc analysis or purification of neat samples of **15** gave two peaks with very short elution times and only a relatively small peak with an elution time appropriate for β-lactone **15**. Presumably, decomposition of **15** to carbon dioxide and olefinic products is occurring on the glpc column.

Photolysis of 8 in Methanol.—Irradiation of 1% solutions of ketoallene **8** in methanol on several occasions revealed the presence of methyleneoxetane **12** after a few per cent conversion. However, further irradiation led to disappearance of **12** and formation of several unidentified products with glpc elution times longer than that of **8**. A buffered methanol–water mixture was prepared by adding 5 ml of saturated sodium bicarbonate solution to 105 ml of methanol. The mixture was stirred for 6 hr at 25° to allow equilibration, and the undissolved sodium bicarbonate was removed by gravity filtration. Irradiation of 1.00 g of **8** in this solvent for 28 hr gave 42% conversion (glpc assay) to **12** with only traces of other products. A sample of **12** isolated by preparative glpc gave infrared and nmr spectral data identical with those reported previously for **12**.

Registry No.—**8**, 20449-20-1; **9**, 20449-21-2; **10**, 20449-22-3; **11**, 20449-23-4; **12**, 20500-56-5; **13**, 20449-24-5; **15**, 20455-51-0; 2,6-heptanedione, 13505-34-5.

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Nuclear Magnetic Resonance Studies of Enol–Enol and Keto–Enol Equilibria in Substituted Benzoylacetones[1a,b]

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Nmr investigation of a series of *para*-substituted benzoylacetones has established that they exist largely (75–98%) as chelated *cis*-enols. Long-range coupling constants suggest that the benzoyl carbonyl group enolizes, forming the cinnamoyl chromophore, and that little benzoylethylene enol is present. Substituent effects on the keto–enol equilibrium are discussed. It has been found that the rule that electron-releasing groups stabilize adjacent carbonyl groups is valid in these systems.

The tautomerism of benzoylacetone and its derivatives has been investigated by a number of physical methods[2-6] and treated briefly by simple Hückel molecular orbital calculations.[7] Although it is generally accepted that the phenyl group increases the enol content, there is disagreement over the question of whether the stabilization derives from mesomeric electron delocalization[7,8] or inductive electron withdrawal.[9] In an attempt to shed some light on this question, we have undertaken a nuclear magnetic resonance study of substituent effects on the tautomeric equilibria in a series of six *para*-substituted benzoylacetones in chloroform-*d*. Study of the long-range couplings provides evidence for the direction of enolization, and consideration of the concentration and substituent dependence of the hydroxyl resonance position allows us to discuss the probable importance of *trans*-enols.[4,10]

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