zene (1:1) gave a yellow oil which was not further investigated. Further elution with 50 ml of petroleum ether–benzene (1:1) and then with 15 ml of chloroform gave 433 mg of acetoxy ketone XII as pale yellow crystals, mp 57–60°; $\nu_{\max}^{\mathrm{KBr}}$ 1743, 1670, 1652, and 1590 cm^{-1}; $\lambda_{\max}^{\mathrm{EtOH}}$ 247 (log ϵ 3.95) and 280 mμ (shoulder, log ϵ 3.43).

Anal. Calcd for $C_{21}H_{34}O_4$: C, 71.96; H, 9.78. Found: C, 72.07; H, 9.70.

This compound (30 mg) was dissolved in 0.2 *N* alcoholic potassium hydroxide and allowed to stand at room temperature overnight. Then, addition of 20 ml of water gave 16 mg of hydroxy ketone XI as colorless plates, mp 142.5–145°. These crystals were identical with the hydroxy ketone, mp 147–148.5°, which had been previously obtained from hydroperoxide VII by potassium iodide reduction.[3]

Photoinduced Reactions. VII. The Photochemical Formation and the Ground-State Reactions of Bicyclo[2.1.0]pentan-2-one[1]

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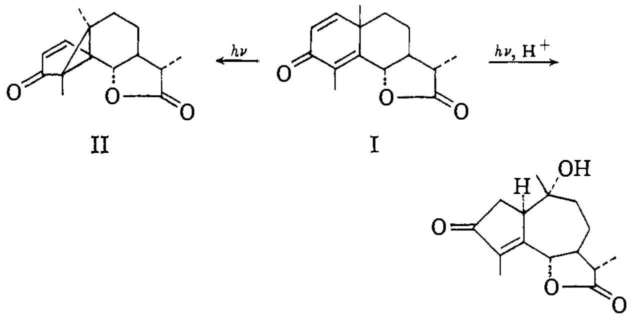
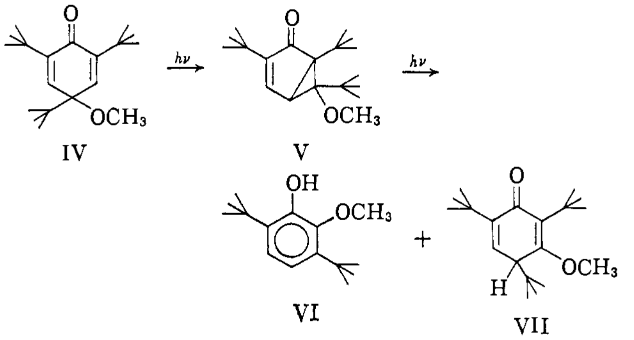
Contribution from the Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto, Japan. *Received February 13, 1967*

Abstract: Photolysis of 2,4,6-tri-*t*-butyl-4-methoxy-2,5-cyclohexadienone (IV) in acetic acid–ethanol–water (2:2:1) afforded two isomeric cyclopentenones, VIII and IX, two isomeric bicyclo[2.1.0]pentan-2-ones, X and XI, and a lactone, XII. Irradiation of VIII and IX in the same media yielded X and XI, respectively, as the major product. On standing at room temperature, X slowly isomerized to give a *ca.* 1:1 mixture of XI and XII. Other ground-state reactions of these two bicyclopentanones leading to several types of products were also investigated. Mechanisms for the formation of these photoproducts are discussed.

The course of many photochemical reactions in solution depends upon the nature of the solvent. One of the earliest examples is the photochemical behavior of santonin (I). On irradiation in neutral media such as dioxane, I undergoes isomerization to lumisantonin (II).[2] However, in aqueous acidic media such as 45% acetic acid, the formation of lumisantonin is supressed, and isophotosantonic lactone (III) is the predominant product.[2] This same hydroxy ketone III can also be nonphotochemically obtained by acid-catalyzed cleavage of lumisantonin (II) with 45% acetic acid.[3] Although the photochemical reactions of cross-conjugated cyclohexadienone with a decalin skeleton related to santonin have received considerable mechanistic studies and discussions,[2,3] relatively little attention has been devoted to the photochemical reactions of monocyclic 2,5-cyclohexadienones in acidic media.[4] We have shown in a previous paper that, in various neutral solvents, 2,4,6-tri-*t*-butyl-4-methoxy-2,5-cyclohexadienone (IV) is photochemially converted to a photophenol VI and a photoketone VII *via* a lumiketone V.[1] In the present paper we report the photochemical reaction of IV in an acidic solution.



II I III



IV V VI VII

Irradiation of IV in acetic acid–ethanol–water (2:2:1) with a high-pressure mercury arc lamp (Pyrex filter) for a short period of time yielded, in addition to unreacted IV (16%), a mixture of products, from which five isomeric compounds, $C_{18}H_{30}O_2$, namely two stereoisomeric cyclopentenones, VIII (17%) and IX (11%), two stereoisomeric bicyclo[2.1.0]pentan-2-ones, X (18%) and XI (4%), and a lactone, XII (4%), were isolated in crystalline forms. Prolonged irradiation of IV afforded X (30%) and XI (24%) in higher yield along with photoketone VII[1] (5%).

Structures VIII and IX for these two cyclopentenones were derived from their spectral and chemical properties and also by considering the fact that 2,6-di-*t*-butyl-4-hydroxy-4-phenyl-2,5-cyclohexadienone is photochemically converted to 2,5-di-*t*-butyl-4-benzoyl-2-cyclopentenone in aqueous media.[5] An ultraviolet maximum at 241 mμ (ϵ 5660) of VIII suggests that VIII

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[1] Part VI; T. Matsuura and K. Ogura, *J. Am. Chem. Soc.*, **89**, 3846 (1967).

[2] For reviews see: (a) H. E. Zimmerman, *Advan. Photochem.*, **1**, 183 (1963); (b) O. L. Chapman, *ibid.*, 1, 323 (1963); (c) K. Schaffner, *ibid.*, 4, 81 (1966); (c) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965, p 162.

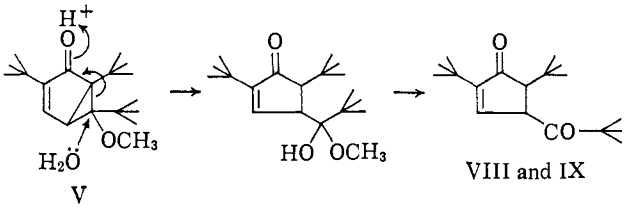
[3] P. J. Kropp, *J. Am. Chem. Soc.*, **87**, 3914 (1965).

[4] H. E. Zimmerman, R. Keese, J. Nasielski, and J. S. Swenton, *ibid.*, **88**, 4895 (1966).

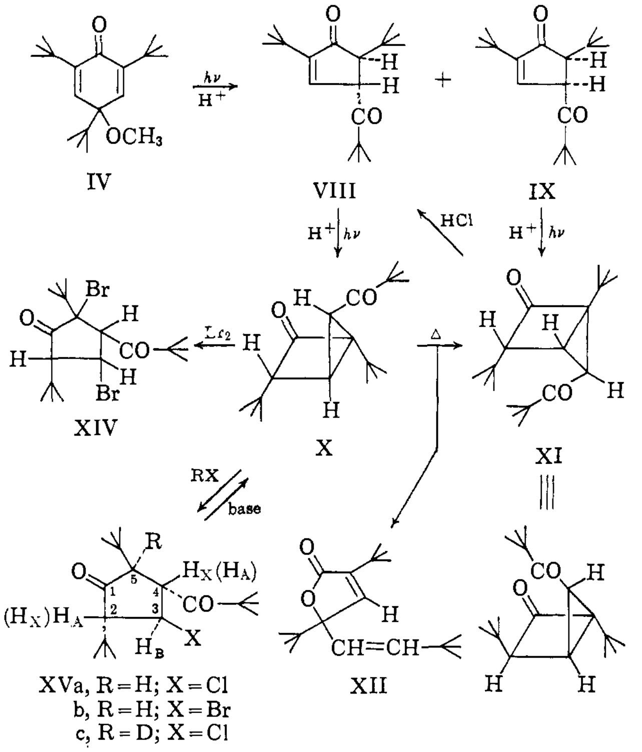
[5] E. R. Altwicker and C. D. Cook, *J. Org. Chem.*, **29**, 3087 (1964). In this paper, they reported that only one stereoisomer of 2,5-di-*t*-butyl-4-benzoyl-2-cyclopentenones was isolated.

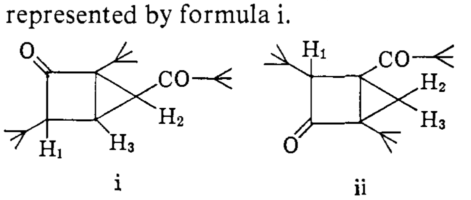
possesses an α,β-unsaturated carbonyl group.[6a] This and an infrared band at 1714 cm^{-1} [6b] of VIII indicate that VIII must have a 2-cyclopentenone skeleton. Its nmr spectrum shows signals of three protons at τ 3.35 (doublet, J = 3.1 cps), 6.17 (quartet, J = 3.1 and 1.5 cps), and 7.66 (doublet, J = 1.5 cps), which are assigned as protons of the type $=CH{-}\overset{|}{C}H{-}\overset{|}{C}H{-}$. Thus, it follows that VIII is a 2,4,5-trisubstituted 2-cyclopentenone. These three substituents were assigned as two *t*-butyl and a pivaloyl group from other spectral data; $\nu_{\max}^{\mathrm{KBr}}$ 1696 cm^{-1} [6b] for the pivaloyl carbonyl and τ 8.77 (9 H, singlet), 8.91 (9 H, singlet), and 9.11 (9 H, singlet) for three *t*-butyl groups. An ultraviolet maximum at 291 mμ (ϵ 580) is characteristic of a homo-conjugated ketone[7] in accordance with structure VIII. The second cyclopentenone IX, which was easily isomerized to VIII by a mild treatment with potassium carbonate in ethanol, showed very similar spectral properties to those of VIII except that in the nmr spectrum the coupling constant between the two aliphatic protons of moiety $=CH{-}\overset{|}{C}H{-}\overset{|}{C}H{-}$ is larger (J = 5.3 cps) than that of VIII. These facts led us to a conclusion that the 4-pivaloyl group and 5-*t*-butyl group are *trans* in VIII and *cis* in IX.[8] Furthermore, that cyclopentenones VIII and IX were also formed by mild acid hydrolysis of lumiketone V supports structures VIII and IX.[4] The hydrolysis of V to VIII and IX may be explained as shown in Scheme I.

Scheme I



Two bicyclopentanones X and XI, which are the main products of the prolonged irradiation of IV, were also obtained as a major product of the photolysis of the isomeric cyclopentenones VIII and IX, respectively, under similar conditions. Therefore, it is followed that X and XI may be formed *via* VIII and IX, respectively, in the photolysis of IV. Molecular formulas, $C_{18}H_{30}O_2$, for X and XI were confirmed by their mass spectrum (parent peak, *m*/*e* 278). The absence of infrared band in the region of 1500–1680 cm^{-1} and of nmr signal in the field lower than τ 5.5 indicates that X and XI must be saturated compounds. This theory was confirmed by the fact that XI was indifferent to catalytic hydrogenation with palladium on charcoal in acetic acid and also to ozonolysis. Infrared bands at 1762, 1701, and 3070 cm^{-1} are considered to be attributed to cyclobutanone, pivaloyl ketone, and cyclopropane[9] absorptions, respectively. A nmr signal at τ 8.77 (9 H, singlet) also supports the presence of the pivaloyl group.[10] On the other hand, by treatment with hydrogen chloride in chloroform, XI was converted into the above-mentioned cyclopentenone VIII in 40% yield along with the formation of a crystalline HCl adduct, $C_{18}H_{31}O_2Cl$ (XIII) (56%). From the above spectral data and the fact that XI was converted into VIII, it follows that the structure of XI can be represented by either of two two-dimensional formulas i or ii. The nmr signals of XI, two doublets at τ 7.45 (1 H, J = 1.5 cps) and 7.55 (1 H, J = 3.2 cps) and a quartet at τ 7.25 (1 H, J = 1.5 and 3.2 cps), can be assigned for protons, H_1, H_2, and H_3, respectively, in formula i or ii, although formula i is more favorable.[11] Formula ii cannot easily explain the fact that XI was smoothly converted into VIII by mild treatment with hydrogen chloride (see mechanism below). Therefore, it is more likely that the structure of XI is represented by formula i.





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(6) (a) That the maximum of VIII occurs at a longer wavelength than the expected (224 mμ), may be caused by the homo-conjugated pivaloyl group. The wavelength of an ultraviolet maximum of a cyclopentenone is much dependent upon its environment, especially upon the unsaturated groups near the enone. For references see: A. I. Scott," Interpretation of the Ultraviolet Spectra of Natural Products," Pergamon Press, New York, N. Y., 1964, pp 231–235. (b) We tentatively assigned the bands at 1714 and 1696 cm^{-1} for the cyclopentenone carbonyl and the pivaloyl carbonyl, respectively.

(7) A. I. Scott, "Interpretation of the Ultraviolet Spectra of Natural Products," Pergamon Press, New York, N. Y., 1964, p 75.

(8) In ref 5, the authors have not mentioned the stereochemistry of the product. From the nmr data given in the literature, it is probable that 2,5-di-*t*-butyl-4-benzoyl-2-cyclopentenone has a 4,5-*trans* configuration as in VIII.

(9) H. Simmons, E. P. Blanchard, and H. D. Hartzler, *J. Org. Chem.*, **31**, 295 (1966).

(10) From the available data on the chemical shift of *t*-butyl protons (for references see below), it may be summarized that *t*-butyl protons appearing in a lower field than τ 8.8 belong to one of the *t*-butyl groups, —C=C-*t*-Bu, O=C-*t*-Bu, and -O-*t*-Bu. Since XI has neither olefinic bond nor ether linkage, the signal at τ 8.77 can be assigned to the *t*-butyl protons of a pivaloyl group. See: (a) H. N. A. Al-Tallo and E. S. Waight, *J. Chem. Soc.*, *B*, 73 (1966); (b) B. Miller and H. Margulies, *Chem. Commun.*, 314 (1965); (c) T. Matsuura, *Bull. Chem. Soc. Japan*, **37**, 564 (1964); (d) H. Musso and D. Maassen, *Ann.*, **689**, 93 (1965).

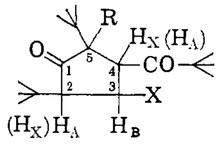
(11) With only a few exceptions, it can be seen that the coupling constant of geminal protons on a cyclopropane ring is higher than 4 cps. [For example see: (a) J. D. Graham and M. T. Rogers, *J. Am. Chem. Soc.*, **84**, 2249 (1962); (b) D. J. Patal, M. H. Howden, and J. D. Roberts, *ibid.*, **85**, 3218 (1963)]. This may also exclude formula ii which has geminal protons on the cyclopropane ring.

The structure of the HCl adduct of XI was tentatively assigned as XIII, which coincides with its spectral data: $\nu_{\mathrm{max}}^{\mathrm{KBr}}$ 1770 (cyclobutanone) and 1717 cm^{-1} (pivaloyl carbonyl); nmr spectrum, τ 5.43 and 6.61 (2 H, AB type, J = 9.3 cps, $\mathrm{Cl{-}\overset{|}{C}H{-}\overset{|}{C}H{-}CO{-}}$), 6.95 and 7.32 (2 H, AB type, J = 18.5 cps, $\geqslant$C–CH$_2$–CO–), 8.84 (18 H, singlet, two *t*-butyl groups), and 8.94 (9 H, singlet, *t*-butyl). The stereochemistry of XIII was derived by considering the stereospecificity of the addition of hydrogen chloride to XI (for detailed discussion see below). This structure XIII also supports formula i for XI.

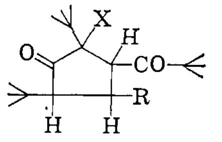
The other bicyclopentanone X showed infrared, ultraviolet, and mass spectra very similar to those of its isomer XI, and it was also indifferent to ozonolysis. Therefore, it follows that the two-dimensional structure of this compound can be also represented by formula i or ii. In its nmr spectrum, however, three ring protons showed a pattern different from that of XI: τ 6.85 (1 H, doublet, J = 7 cps), 7.05 (1 H, doublet, J = 7 cps), and 7.78 (1 H, singlet). This pattern cannot discriminate between formulas i and ii, because it is possible that the spin–spin coupling constant, even between protons of adjacent carbon atoms, is near zero. However, the two-dimensional structure i for X as well as its three-dimensional structure X, was derived from results which had been obtained from the ground-state reactions of X, particularly in the addition reactions of bromine and hydrogen halides.

Bicyclopentanone X absorbed 1 mole of bromine in acetic acid to yield a bromine adduct, $C_{18}H_{30}O_2Br_2$. The infrared spectrum showed bands at 1747 and 1710 cm^{-1} corresponding to cyclopentanone and pivaloyl groups, respectively. The presence of a pivaloyl group and of two additional *t*-butyl groups can be shown by its nmr spectrum which showed three singlets at τ 8.73, 8.83, and 8.87. The remaining three protons appeared as two doublets at τ 6.06 (1 H, J = 7.5 cps) and 6.65 (1 H, J = 6.5 cps) and a quartet at τ 5.46 (1 H, J = 6.5 and 7.5 cps). These signals may be attributed to protons of $\mathrm{-\overset{|}{C}H{-}\overset{|}{C}H{-}\overset{|}{C}H{-}}$. From the above spectral data and by assuming that a bond of the cyclopropane ring of X was cleaved by a bromine molecule, the bromine adduct may be formulated as XIV. It follows that the two-dimensional structure of X must be represented by formula i but not by formula ii.

Treatment of bicyclopentanone X with hydrogen chloride in carbon tetrachloride yielded an HCl adduct XVa, $C_{18}H_{31}O_2Cl$, whose infrared and nmr spectra were quite similar to those of an HBr adduct XVb obtained from X by the treatment with hydrogen bromide in acetic acid. This indicates that both adducts may have the same structure except that a chlorine atom is replaced by a bromine atom in XVb. In contrast to the HCl adduct XIII, which was obtained from the isomeric bicyclopentanone XI, these adducts XVa and XVb showed an infrared band around 1740 cm^{-1} indicating the presence of a cyclopentanone moiety. Furthermore, both adducts showed an infrared band around 1690 cm^{-1} corresponding to a pivaloyl carbonyl group and three *t*-butyl signals in their nmr spectrum. By considering cleavage of a bond of the cyclopropane ring of X with hydrogen halide analogous to cleavage with bromine, the adducts XVa and XVb may be formulated by either iii or iv. The nmr spectral pattern of the remaining four protons of the adducts was not simple enough to make first-order analysis (Figure 1).



iii



iv

R = H or D
X = Cl or Br

Similar treatment of X with deuterium chloride afforded a DCl adduct XVc, whose spectral data were almost same as those of the HCl adduct XVa except that the pattern of the nmr signals of the ring protons was simplified (Figure 1). Of two possible structures (iii and iv) for the DCl adduct, the latter was eliminated by nmr analysis. The nmr signals of the three ring protons of the DCl adduct were analyzed as an ABX pattern: H_A, τ 5.74; H_B, τ 5.83; H_X, τ 7.56; J_{AB} = J_{BX} = 6.8 cps; J_{AX} = 1.7 cps.[12] The calculated pattern[13] showed an excellent agreement with the observed one (Figure 1). Structure iv is not consistent with the fact that the diffuse doublet at τ 8.05 (J = *ca.* 5 cps) in the nmr spectrum of the HCl adduct XVa disappears in the spectrum of the DCl adduct XVc.[14] Thus it is concluded that the HCl, HBr, and DCl adducts are represented by formula iii.

We shall now discuss the stereochemistry of the bicyclopentanone X and its hydrogen halide adduct XV. By treatment with alcoholic alkali, both XVa and XVb were easily reverted into the parent bicyclopentanone X. This indicates that the hydrogen atom at the 5 position and the halogen atom at the 3 position may be *trans* so that *trans* dehydrohalogenation proceeds easily. Furthermore, the *cis* relationship between the halogen atom and the adjacent hydrogen atoms at the 2 and 4 positions can be suggested by the stability of XVb to triethylamine in boiling benzene. The three-dimensional structure XV thus assigned for the hydrogen halide adducts is consistent with the nmr spectral data of the DCl adduct XVc. In its nmr spectrum, there is observed a considerably strong long-range coupling (J_{AX} = 1.7 cps) between the protons H_A and H_X, which also couple with H_B with the equal coupling constant (J_{AB} = J_{BX} = 6.8 cps). Only the *cis* relationship between the protons H_A and H_X permits such a long-range coupling,[15] and J_{AB} and J_{BX} must be equal in the case where the configuration of H_A is the same as that of H_X with respect to H_B.

All of the available examples in the literature[16] indicate that the acid cleavage of the cyclopropane ring in

(12) 1-H, H_A or H_X; 2-H, H_B; 3-H, H_X or H_A.

(13) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co. Inc., New York, N. Y., 1959, p 132.

(14) In formula iv, the doublet at τ 8.05 must appear with a coupling constant near 20 cps. The coupling constant of geminal protons on a cyclopentane ring is usually around 20 cps. For example see: (a) T. Matsuura and K. Ogura, *J. Am. Chem. Soc.*, **88**, 2602 (1966); (b) T. Takabayashi, *Tetrahedron Letters*, 565 (1964).

(15) For the long-range coupling between W type of protons, see A. Rassat, C. W. Jefford, J. M. Lehn, and B. Waegell, *ibid.*, 233 (1964).

(16) (a) P. D. Gardner, W. W. Kwie, and B. A. Shoulders, *J. Am. Chem. Soc.*, **84**, 2268 (1962); (b) L. F. Fieser and M. Fieser, "Steroids," Reinhold Publishing Corp., New York, N. Y., 1959, p 315; (c) H. O. House, S. G. Boots, and V. K. Jones, *J. Org. Chem.*, 30, 2519 (1965).

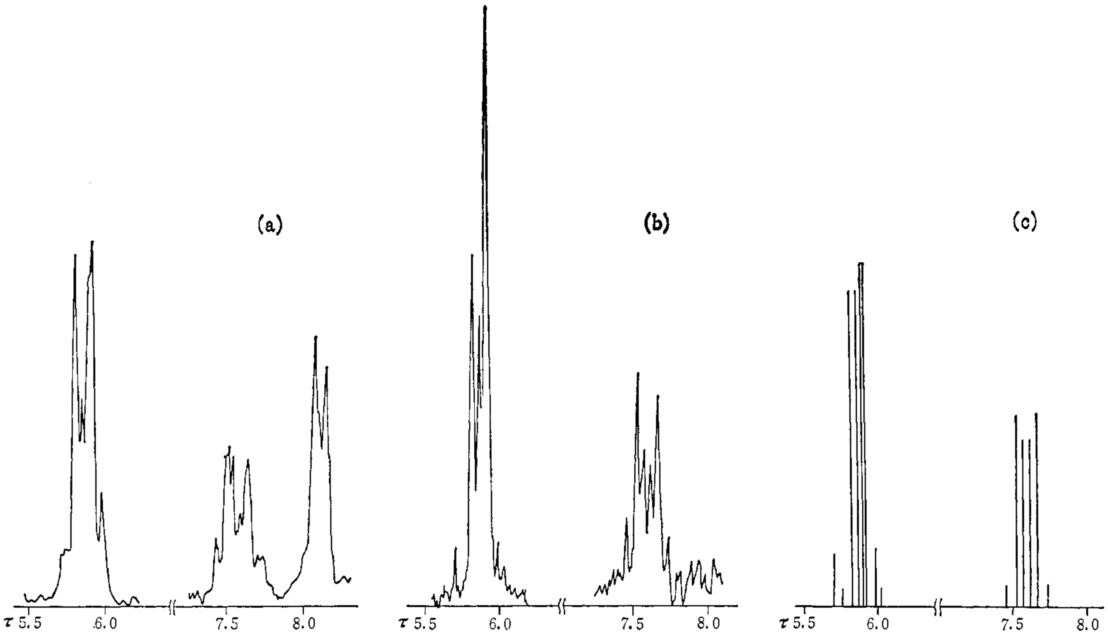
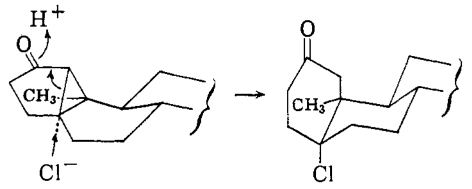
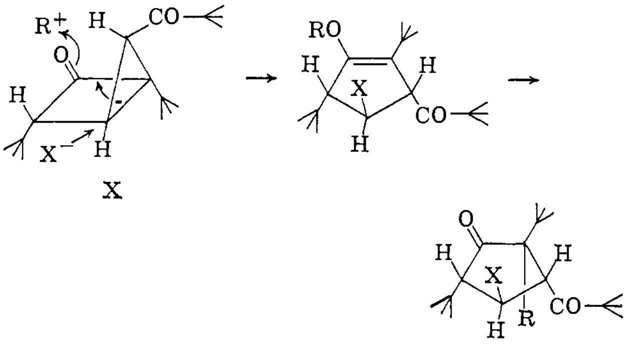


Figure 1. Nmr spectra of the HCl adduct XVa and the DCl adduct XVc: (a) observed spectrum of XVa; (b) observed spectrum of XVc; (c) calculated spectrum of XVc.

certain bicyclo systems bearing a cyclopropyl ketone moiety takes place with a high stereospecificity. For example, a compound with a bicyclo[3.1.0]hexan-2-one group (as formula v) is converted into a 4-chlorocyclohexanone (as formula vi) by treatment with hydrogen chloride.[16a] Thus, one can predict the stereochemistry of such a product, at least formally, by the mechanism that the anion approaches along the extension line of the bond to be cleaved from the opposite side of the protonated carbonyl group, as v → vi. Such a mechanism can easily rationalize the formation of XV from bicyclopentanone X as shown below, and it follows that the three-dimensional structure of the bicyclopentanone is represented as X in accordance with all of its chemical and spectral properties.[17]



v vi



X

XV, R = H or D
X = Cl or Br

Application of this mechanism to the conversion of bicyclopentanone XI with hydrogen chloride into cyclopentenone VIII leads to two possible three-dimensional structures, XI and XVII. As shown in Scheme II, both XI and XVII can form the *trans*-cyclopentenone VIII by the attack of hydrogen chloride followed by *trans*-dehydrochlorination of an unstable HCl adduct, XVIa or XVIb. The formation of the HCl adduct XIII,[18] which was obtained from XI as described before, is also rationalized by a similar mechanism in which the pivaloyl carbonyl of either formula XI or XVII is predominantly protonated (Scheme II).

Of these two formulas, XI and XVII, the former was finally assigned for bicyclopentanone XI on the basis of the results obtained in the thermal reaction of X. Bicyclopentanone X was thermally unstable and, on standing at room temperature, it was slowly converted into a 1:1 mixture of its stereoisomer XI and an isomeric lactone. The latter was identified as lactone XII, *i.e.*, the fifth product obtained in the photolysis of IV. This thermal isomerization is explained by assuming that a homolytic cleavage occurs at the 1,4 bond of X leading to a diradical intermediate XVIII which then recombines internally to form the more stable isomer XI (Scheme III). Under such mild conditions it does not appear that epimerization of the pivaloyl group takes place simultaneously to form XVII. The thermal instability of X is probably due to steric hindrance between *cis*-*t*-butyl groups on the cyclobutanone ring and also between *t*-butyl and pivaloyl groups in *cis* relation on the cyclopropane ring.

Pyrolysis of bicyclopentanone XI at 220° yielded lactone XII (14%) and a new isomeric lactone XIX (61%). Lactone XII exhibits an infrared band at 1748 cm^{-1} and an ultraviolet maximum at 218 mμ (ε 7250) which suggest the presence of a Δ^1-butenolide moiety.

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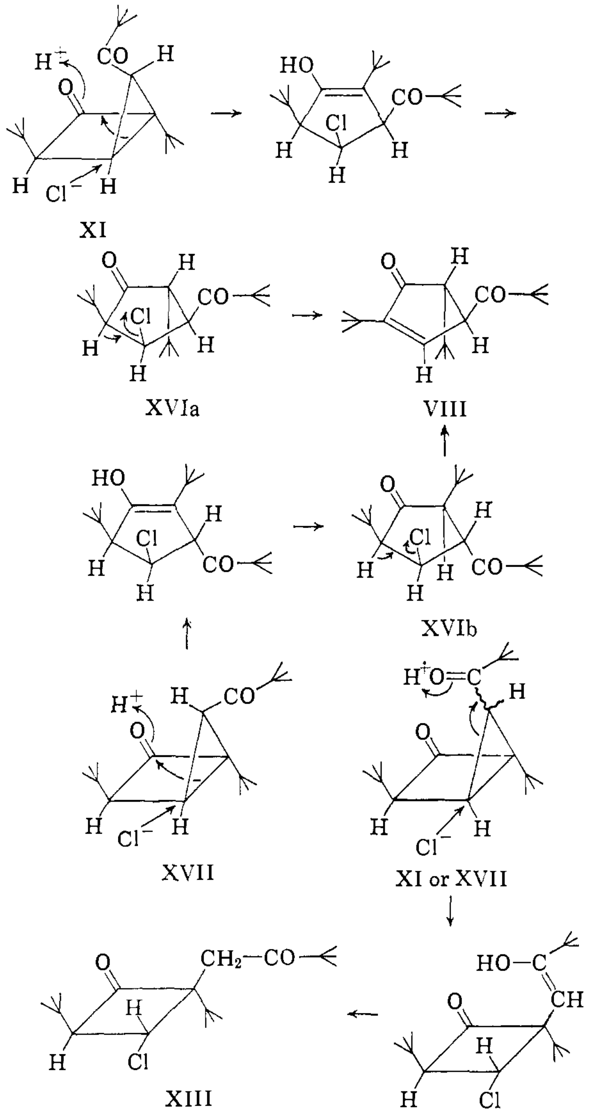
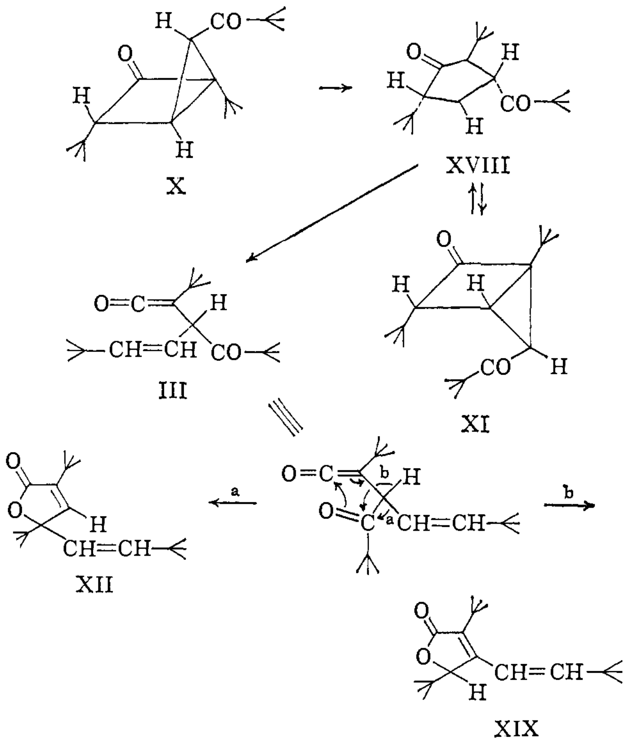
[17] A scale model for X demonstrates that the dihedral angle between two hydrogen atoms on the cyclobutanone ring is near 90°. This coincides with the fact that no spin–spin coupling was observed for these two protons. *Cf.* M. Karplus, *J. Chem. Phys.*, 30, 11 (1959).

[18] Cyclobutane 1,2-proton coupling constants are reported to be *ca.* 4 cps in the *cis* and *ca.* 8 cps in the *trans* [P. E. Eaton, *J. Am. Chem. Soc.*, **84**, 2344 (1962)]. This is in accordance with the structures for the HCl adduct XIII (*trans*-1,2-protons, J = 9.3 cps) and also for cyclobutanone XXI (*cis*-1,2-protons, J = 4.5 cps).

Scheme II



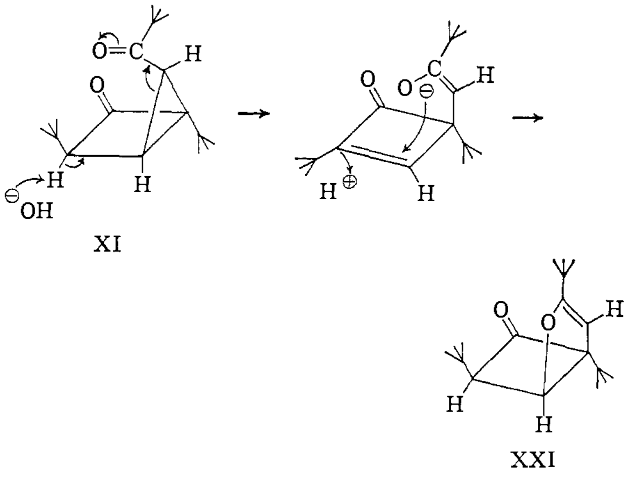
Scheme III



This was supported by the fact that, on treatment with potassium hydroxide in boiling 1-butanol, XII formed a carboxylate anion which was characterized by infrared analysis and was reverted into XII by acidification. The nmr spectrum showed an AB-type quartet at τ 4.32 and 4.35 (J_{AB} = 15.5 cps), a singlet at τ 2.98 (1 H), and three singlets at 8.73, 8.98, and 9.06, which were assigned as protons of —CH=CH—, $-CH=\overset{|}{C}-\overset{|}{C}=O$, and three *t*-butyl groups, respectively. These data coincide with structure XII assigned for this lactone.

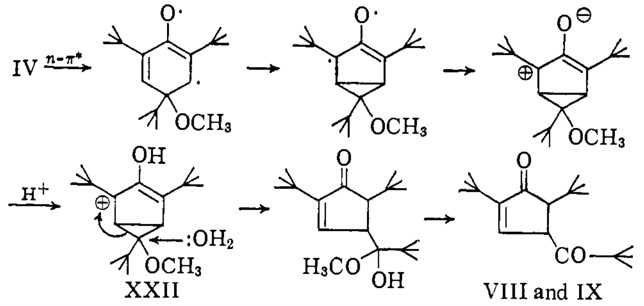
Structure XIX for the isomeric lactone was tentatively given on the basis of its spectral properties. This compound showed an infrared band at 1740 cm^{-1} and an ultraviolet maximum at 215 mμ (ϵ 8430) which indicate that XIX is also a Δ^1-butenolide. The nmr spectrum showed three singlets of three *t*-butyl groups at τ 8.70, 8.93, and 9.03, a doublet at 5.49 (1 H, J = *ca.* 1 cps $-O-\overset{|}{C}H-\overset{|}{C}=\overset{|}{C}-$), a doublet at 4.59 (1 H, J = 13.5 cps), and a quartet at 4.07 (1 H, J = 13.5 and *ca.* 1 cps). The latter two signals were assigned for an AB-type of olefinic protons in which the low-field proton has a long-range coupling with the allylic proton. In spite of an extended conjugation of the butenolide in the assigned structure XIX, this compound exhibits a normal ultraviolet maximum for a Δ^1-butenolide. This is probably due to the nonplanarity between the butenolide group and the extended double bond. A possible mechanism for the thermal reactions of X and XI leading to butenolides XII and XIX is illustrated in Scheme III. In this mechanism the formation of a common ketene intermediate XX *via* the diradical XVIII is proposed.

We note an additional ground-state reaction of bicyclopentanone XI. While X is stable to alcoholic alkali at room temperature, XI is readily isomerized under the same conditions to yield a cyclobutanone, for which we proposed structure XXI. This compound showed an infrared band at 1762 cm^{-1} corresponding to a four-membered ketone and ultraviolet maxima at 260 mμ (ϵ 2260) and 322 mμ (ϵ 825) characteristic of a β,α-unsaturated ketone.[7] The nmr spectrum showed a singlet at τ 5.38 (1 H, $-O-\overset{|}{C}=CH-$), an AB-type quartet at 5.24 and 6.84 (2 H, J = 4.5 cps), and three singlets at 8.88, 8.99, and 9.08 (three *t*-butyl groups). These spectral data are in accord with structure XXI.[18] A possible mechanism for the formation of XXI is illustrated below.

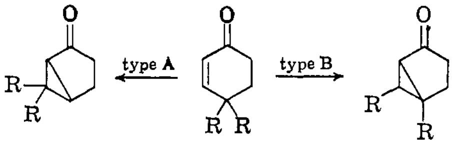


Finally, we wish to discuss mechanisms for the formation of the products obtained by irradiation of 2,4,6-tri-*t*-butyl-4-methoxy-2,5-cyclohexadienone (IV) in acidic media. First, we envision two possible routes from IV to cyclopentenones VIII and IX, involving either a nucleophilic attack of a water molecule to an intermediate XXII analogous to that proposed for the photolysis of some 2,5-cyclohexadienones[2] in acidic media, or an acid hydrolysis of lumiketone V by nonphotochemical process (Schemes IV and I). The latter possibility, however, seems to be less likely on the basis of the facts that lumiketone V is rapidly converted into photophenol VI and photoketone VII by irradiation,[1] and that V is slowly hydrolyzed with dilute acetic acid to a mixture of VIII and IX.

Scheme IV



Second, bicyclopentanones X and XI are certainly formed by the photolysis of cyclopentenones VIII and IX, respectively, as already mentioned. However, the photolysis of cyclopentenone VIII in ether afforded a complex mixture of products containing only a trace of bicyclopentanone X. This indicates that an acidic solvent may promote the photochemical isomerization of VIII to X. Rearrangements to bicyclo[2.1.0]pentan-2-ones X and XI are similar to the photochemical transformation of 2-cyclohexenones to bicyclo[3.1.0]hexan-2-ones in neutral media. For this transformation two types of reaction have been reported, type A[19] and type B[20] as shown below.



On the above standpoint, we now propose two possible mechanisms, namely, (a) skeletal rearrangement analogous to type A isomerization (type A′), and (b) migration of the pivaloyl group similar to the type B phenyl migration of 4-phenyl-substituted cyclohexenones (type B′). Although the latter mechanism has an analogy in which a β,γ-unsaturated ketone XXIII is photochemically isomerized to a cyclopropyl ketone XXIV by benzoyl migration,[21] we cannot distinguish these two mechanisms from our experimental results.

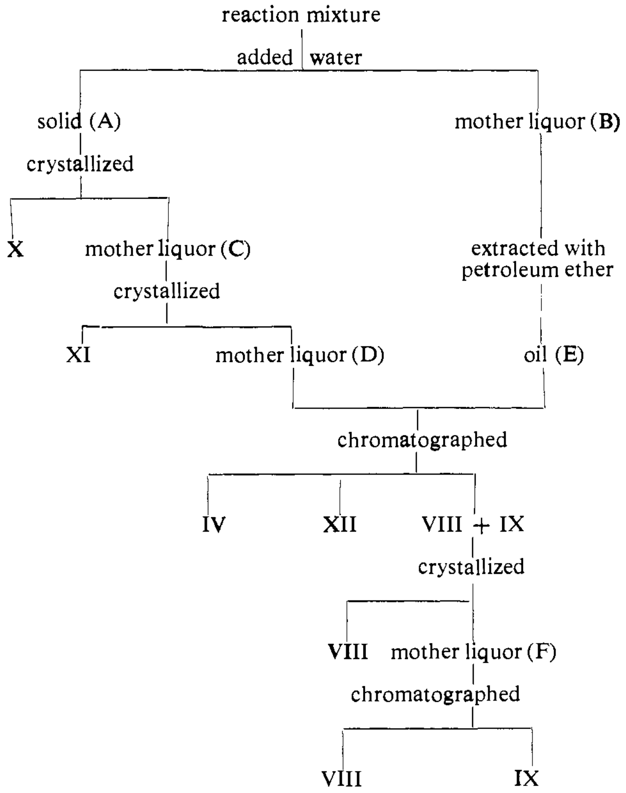
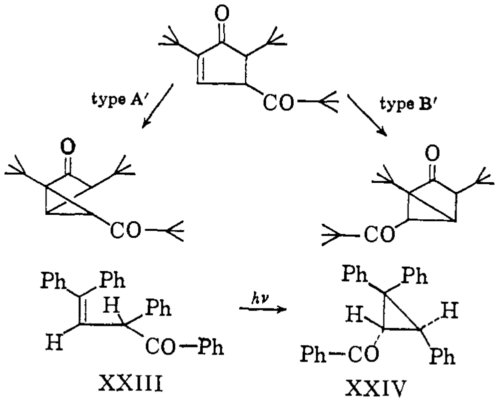


Figure 2. Flow sheet for the fractionation of the reaction mixture from the short-time irradiation of IV.



Since bicyclopentanones X and XI are considerably stable to irradiation, it is certain that lactone XII and also some of bicyclopentanone XI were formed from bicyclopentanone X by thermal reaction as discussed previously.

Experimental Section[22]

Photolysis of 2,4,6-Tri-*t*-butyl-4-methoxy-2,5-cyclohexadienone (IV) in Acidic Media. a. Short-Time Irradiation. A solution of 6.0 g of IV[1] in 850 ml of a mixture of acetic acid, ethanol, and water (2:2:1) was irradiated under bubbling nitrogen using a 450-w high-pressure mercury arc lamp (Ushio UM 450) with a water-cooled Pyrex jacket for 20 min. The reaction mixture was fractionated as shown in the flow sheet in Figure 2. After the addition of 800 ml of water, the resulting solid (A, 4.15 g) was collected

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[19] (a) H. E. Zimmerman, R. G. Lewis, J. J. McCullough, A. Padwa, S. W. Stanley, and M. Semmelhack, *J. Am. Chem. Soc.*, **88**, 159, 1965 (1966); (b) O. L. Chapman, J. A. Rettig, A. A. Griswold, A. Z. Dutton, and P. Fitton, *Tetrahedron Letters*, 2049 (1963); (c) W. W. Kwie, B. A. Shoulders, and P. D. Gardner, *J. Am. Chem. Soc.*, **84**, 2286 (1962); (d) B. Nann, D. Gravel, R. Schorta, H. Wehrli, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, 46, 2473 (1963).

[20] (a) H. E. Zimmerman and J. W. Wilson, *J. Am. Chem. Soc.*, **86**, 4036 (1964); (b) T. Matsuura and K. Ogura, *ibid.*, **88**, 2602 (1966).

[21] L. P. Tenney, D. W. Boykin, Jr., and R. E. Lutz, *ibid.*, **88**, 1835 (1966).

[22] Melting points were determined in capillary tubes and are uncorrected. The infrared spectra were measured with a Japan Spectroscopic Co. recording spectrophotometer, Model DS-402 G. All ultraviolet spectra were measured in ethanol with a Shimazu recording spectrophotometer, Model SV-50, and with a JASCO recording spectrophotometer, Model ORD/UV-5. The nmr spectra were taken with a Varian A-60 spectrometer and with a Japan Electron Optical Laboratory spectrometer, Model 3H-60.

by filtration. Crystallization from methanol gave 1.03 g (18%) of bicyclopentanone X as colorless needles. Two recrystallization from methanol gave needles, mp 101–102°; $\nu_{\max}^{\mathrm{KBr}}$ 3075, 1765 (sh), 1752, and 1699 cm^{-1}; $\gamma_{\max}^{\mathrm{CHCl_3}}$ 3075, 1760, and 1702 cm^{-1}; $\lambda_{\max}^{\mathrm{EtOH}}$ 282 mμ (ε 83) and ϵ_{210} 2680; nmr spectrum: τ (CDCl$_3$) 6.85 (1 H, doublet, J = 7 cps), 7.05 (1 H, doublet, J = 7 cps), 7.78 (1 H, singlet), 8.76 (9 H, singlet), 8.97 (9 H, singlet), and 9.00 (9 H, singlet); τ (C$_6$H$_6$) 7.00 (1 H, doublet, J = 7 cps), 7.26 (1 H, doublet, J = 7 cps), 7.84 (1 H, singlet), 8.91 (9 H, singlet), 8.99 (9 H, singlet), and 9.01 (9 H, singlet); mass spectrum (direct inlet); m/e 278 (parent peak), 222 (67), 207 (49), 57 (100, base peak), 41 (72), and 29 (49).

Anal. Calcd for $C_{18}H_{30}O_2$: C, 77.65; H, 10.86. Found: C, 77.29; H, 10.83.

The mother liquor (C), on standing in a refrigerator, deposited 245 mg (4%) of bicyclopentanone XI as crystals. Recrystallization from petroleum ether (bp 30–60°) gave colorless plates, mp 141–141.5°; $\nu_{\max}^{\mathrm{KBr}}$ 3070, 1762, and 1701 cm^{-1}; $\lambda_{\max}^{\mathrm{EtOH}}$ 274 mμ (ε 239) and ϵ_{210} 3190; nmr spectrum: τ (CDCl$_3$) 7.00–7.17 (3 H, multiplet), 8.77 (9 H, singlet), 9.00 (9 H, singlet), and 9.13 (9 H, singlet); τ (benzene) 7.25 (1 H, quartet, J = 1.5 and 3.2 cps), 7.45 (1 H, doublet, J = 1.5 cps), 7.55 (1 H, doublet, J = 3.2 cps), 8.97 (9 H, singlet), 9.06 (9 H, singlet), and 9.08 (9 H, singlet); mass spectrum: m/e 278 (parent peak), 222 (41), 207 (29), 57 (100, base peak), 41 (66), and 29 (47).

Anal. Calcd for $C_{18}H_{30}O_2$: C, 77.65; H, 10.86. Found: C, 77.50; H, 10.87.

The mother liquor (B) was extracted with petroleum ether (two 750-ml portions), and the organic layer was evaporated to give 1.32 g of a yellow oil (E). The oil (E) and the mother liquor (D) were combined and chromatographed on 40 g of silica gel. Elution with 250 ml of petroleum ether–benzene (1:1) yielded 951 mg (16%) of yellow crystals, which were identified as the starting material IV (by infrared spectroscopy). Further elution with 400 ml of the same solvent yielded 230 mg (4%) of a yellow solid, mp 81–85°. Recrystallization from methanol gave lactone XII as colorless needles, mp 91.5–92.5°; $\nu_{\max}^{\mathrm{KBr}}$ 3080, 3040, 1748, 1660, and 1640 cm^{-1}; $\lambda_{\max}^{\mathrm{EtOH}}$ 218 mμ (ε 7250); nmr spectrum: τ (CDCl$_3$) 2.98 (1 H, singlet), 4.32 (1 H, doublet, J = 15.5 cps), 4.35 (1 H, doublet, J = 15.5 cps), 8.73 (9 H, singlet), 8.98 (9 H, singlet), and 9.06 (9 H, singlet).

Anal. Calcd for $C_{18}H_{30}O_2$: C, 77.65; H, 10.86. Found: C, 77.62; H, 11.08.

Further elution with 940 ml of chloroform yielded 1.90 g of a pale yellow solid, which, on several recrystallizations from methanol, gave 93 mg of cyclopentenone VIII as colorless prisms, mp 80–81°; $\nu_{\max}^{\mathrm{KBr}}$ 1714, 1696, and 1624 cm^{-1}; $\lambda_{\max}^{\mathrm{EtOH}}$ 241 mμ (ε 5660) and 291 mμ (shoulder, ε 580); nmr spectrum, τ (CCl$_4$) 3.35 (1 H, doublet, J = 3.1 cps), 6.17 (1 H, quartet, J = 3.1 and 1.5 cps), 7.66 (1 H, doublet, J = 1.5 cps), 8.77 (9 H, singlet), 8.91 (9 H, singlet), and 9.11 (9 H, singlet).

Anal. Calcd for $C_{18}H_{30}O_2$: C, 77.65; H, 10.86. Found: C, 77.99; H, 11.03.

The mother liquor (F) was evaporated to give 1.80 g of a yellow solid, which was shown by tlc and infrared to be a mixture of cyclopentenones VIII and IX. Part (1.02 g) of the solid was chromatographed on 150 g of silica gel. Elution with 800 ml of petroleum ether–benzene (1:1) yielded 364 mg of crystals, which were shown by tlc and infrared to consist of IX contaminated with a trace of VIII. Two recrystallizations gave cyclopentenone IX as colorless prisms, mp 79.5–80.5°; $\nu_{\max}^{\mathrm{KBr}}$ 1712, 1700, and 1620 cm^{-1}; $\lambda_{\max}^{\mathrm{EtOH}}$ 233 mμ (ε 6600) and 300 mμ (ε 627); nmr spectrum: τ (CCl$_4$) 3.45 (1 H, doublet, J = 2.7 cps), 5.90 (1 H, quartet, J = 2.7 and 5.3 cps), 7.80 (1 H, doublet, J = 5.3 cps), 8.77 (9 H, singlet), 8.91 (9 H, singlet), and 9.08 (9 H, singlet).

Anal. Calcd for $C_{18}H_{30}O_2$: C, 77.65; H, 10.86. Found: C, 77.92; H, 11.25.

Further elution with petroleum ether–benzene (1:1) and then with 300 ml of chloroform yielded 501 mg of pale yellow crystals, which were identified as cyclopentenone VIII (by infrared and tlc). The total yields of VIII and IX amounted to 17 and 11%, respectively.

b. **Prolonged Irradiation.** A solution of 3.00 g of IV in 425 ml of acetic acid–ethanol–water (2:2:1) was irradiated under similar conditions to those described above for 80 min. After the addition of 500 ml of water, the resulting solid was collected by filtration. Recrystallization from petroleum ether gave 1.52 g (54%) of a semicrystalline solid, which was shown to be a mixture of cyclopentenones VIII and IX (6.5:5.2) (by nmr). Evaporation of the mother liquor followed by recrystallization from methanol afforded 150 mg (5%) of photoketone VII,[1] which was identified by infrared spectroscopy.

Isomerization of Cyclopentenone IX to Cyclopentenone VIII. A solution containing 10 mg of IX and 30 mg of potassium carbonate in 2 ml of ethanol was allowed to stand at room temperature overnight. After dilution with 2 ml of water followed by standing in a refrigerator for a day, colorless needles, 7 mg, mp 80–81°, were obtained, which were identical with cyclopentenone VIII (by infrared and mixture melting point).

Hydrolysis of Lumiketone V to Cyclopentenones VIII and IX. a. **With Hydrobromic Acid.** Three drops of hydrobromic acid (specific gravity 1.48) was added to a solution of 4 mg of lumiketone V[1] in 1 ml of acetic acid. After 5 min, 1 ml of water was added, and the mixture was allowed to stand in a refrigerator for 2 days to deposit a colorless semicrystalline solid, mp 68–74°. This solid was shown to consist of cyclopentenone IX contaminated with a trace of cyclopentenone VII, by tlc, by a direct comparison of its infrared spectrum with that of an authentic specimen, and by a mixture melting point determination.

b. **With Aqueous Acetic Acid.** A solution of 4 mg of lumiketone V in 1 ml of acetic acid containing three drops of water was allowed to stand at room temperature overnight. After the addition of 1 ml of water followed by standing in a freezer for 2 days, colorless crystals deposited and were collected by filtration, mp 57–64°. The crystals were shown to be a mixture of three compounds, two of which were identified as cyclopentenones VIII and IX, by tlc. The melting point was raised to 59–75° on admixture with cyclopentenone VIII, mp 80–81°.

c. **With Silica Gel.** A solution of 14 mg of lumiketone V in petroleum ether was adsorbed on 5 g of silica gel and was allowed to stand for 3 days. Elution with 50 ml of ether yielded a yellow oil which was shown to be a mixture of three compounds, two of which were identified as cyclopentenones VIII and IX, by mixed thin layer chromatography.

Photolysis of Cyclopentenone VIII. a. In Acidic Media. A solution of 60 mg of cyclopentenone VIII in 70 ml of acetic acid–ethanol–water (2:2:1) was irradiated with a 100-w, high-pressure mercury lamp (Pyrex filter) for 30 min. After the addition of 80 ml of water followed by standing in a refrigerator, a crystalline solid was deposited (33 mg, 55%) and was identified as bicyclopentanone X (by infrared spectroscopy). Extraction of the filtrate with ether (three 150-ml portions) yielded 27 mg of a yellow oil which was shown by tlc to consist of X and a small amount of XI.

b. **In Neutral Media.** A solution of 75 mg of VIII in 100 ml of ether was irradiated under similar conditions (section a) for 80 min. Evaporation of the solvent yielded an oil which was shown by tlc to be a complex mixture of products containing a trace of X and was not further investigated.

Photolysis of Cyclopentenone IX in Acidic Media. A solution of 45 mg of cyclopentenone IX in 70 ml of acetic acid–ethanol–water (2:2:1) was irradiated under similar conditions to those described in irradiation of VIII in the same solvent. After the addition of 100 ml of water followed by standing in a refrigerator for 5 days, a crystalline solid deposited which was collected by filtration. This solid was shown by infrared and tlc analyses to be a mixture of bicyclopentanone XI and the starting material IX. Extraction of the filtrate with ether (three 100-ml portions) yielded 29 mg of a yellow oil, which was shown by mixed tlc analyses to consist mainly of IX and XI contaminated with a trace of VIII and X.

HCl Adduct XVa of Bicyclopentanone X. Dry hydrogen chloride was passed through a solution of 552 mg of bicyclopentanone X in 100 ml of carbon tetrachloride for 3 hr. After the evaporation of the mixture under reduced pressure, the resulting pale yellow crystals were recrystallized from petroleum ether to afford 195 mg (31%) of the HCl adduct XVa as colorless needles, mp 164–166°. Further recrystallization from the same solvent gave crystals, mp 167–167.2°; $\nu_{\max}^{\mathrm{KBr}}$ 1742 and 1695 cm^{-1}; ultraviolet spectrum, no maximum above 210 mμ; nmr spectrum: τ (CDCl$_3$) 5.73–5.93 (2 H, multiplet), 7.40–7.63 (1 H, multiplet), 7.98–8.12 (1 H, diffused doublet, $J \cong 5$ cps), 8.71 (9 H, singlet), 8.96 (9 H, singlet), and 9.00 (9 H, singlet).

Anal. Calcd for $C_{18}H_{31}O_2Cl$: C, 68.66; H, 9.92. Found: C, 68.24; H, 10.07.

DCl Adduct XVc of Bicyclopentanone X. Dry deuterium chloride, which was prepared from deuterium oxide and distilled phosphorus trichloride, was passed through a solution of 240 mg of bicyclopentanone X in 100 ml of pure chloroform for 4 hr, and the mixture was allowed to stand at room temperature overnight. After the evaporation of the solvent under reduced pressure, the resulting crystals were recrystallized from dry benzene to give the

DCl adduct as colorless needles, mp 166–167°. The melting point did not depress on admixture with the HCl adduct XVa.

The nmr spectrum showed 12 lines at 241.8, 244.8, 249.2, 251.6, 254.6, 261.5, 138.0, 142.0, 145.0, 147.6, 150.4, and 154.6 cps (from tetramethylsilane), in addition to signals of three *t*-butyl groups. The lines were calculated as an ABX system (ν_A 255.7 ν_B 251.5, ν_X 146.2; $J_{AB} = J_{AX} = 6.8$ cps, $J_{BX} = 1.7$ cps): 241.9 (relative intensity, 0.03), 244.8 (0.29), 248.7 (1.97), 248.9 (1.97), 251.6 (1.71), 254.4 (1.71), 255.7 (0.03), 261.2 (0.29), 137.9 (0.07), 142.0 (1.00), 144.9 (0.93), 147.5 (0.93), 150.4 (1.00), and 154.6 cps (0.07).

HBr Adduct XVb of Bicyclopentanone X. To a solution of 277 mg of bicyclopentanone X in 5 ml of acetic acid was added six drops of hydrobromic acid (specific gravity 1.48), and the mixture was allowed to stand at room temperature for 1 hr. Addition of 3 ml of water deposited 134 mg (38%) of crystals, which were recrystallized from methanol to give the HBr adduct XVb as colorless needles, mp 171–172°; ν_{max}^{KBr} 1740 and 1691 cm^{-1}; nmr spectrum: τ ($CDCl_3$) 5.64–5.97 (2 H, multiplet), 7.27–7.65 (1 H, multiplet), 8.03 (1 H, diffused doublet, $J \cong 5$ cps), 8.71 (9 H, singlet), 8.97 (9 H, singlet), and 9.03 (9 H, singlet).

Anal. Calcd for $C_{18}H_{31}O_2Br$: C, 60.16; H, 8.69. Found: C, 60.01; H, 8.76.

Alkali Treatment of the HCl Adduct XVa. To a solution of 61 mg of the HCl adduct XVa in 10 ml of ethanol was added five drops of 4 *N* aqueous potassium hydroxide, and the mixture was allowed to stand at room temperature overnight. After the addition of 5 ml of water, the crystals (28 mg, 52%) which deposited were collected by filtration and then dried. The product was identified as bicyclopentanone X (by infrared spectroscopy).

Treatment of the HBr Adduct XVb with Base. A solution of 45 mg of the HBr adduct XVb in 5 ml of ethanol was mixed with 15 drops of 4 *N* aqueous potassium hydroxide, and the mixture was allowed to stand at room temperature overnight. After the addition of 5 ml of water followed by standing in a freezer for 3 hr, the colorless crystals (28 mg) which were deposited were collected by filtration and identified as bicyclopentanone X (by infrared spectroscopy).

A solution of 14 mg of XVb and 115 mg of triethylamine in 10 ml of benzene was heated at reflux for 10 hr. The mixture was worked up as usual to yield a colorless solid, mp 160–168°, which was identified as the starting material XVb (by infrared spectroscopy).

Bromine Adduct XIV of Bicyclopentanone X. A solution containing 275 mg of bicyclopentanone X and 200 mg of bromine in 10 ml of acetic acid was stirred at room temperature for 1 hr, then was diluted with 10 ml of water. A colorless solid was deposited (385 mg, mp 108–114°) and was collected by filtration and chromatographed on 15 g of silica gel. Elution with petroleum ether–benzene (7:3) yielded 58 mg of a colorless solid, which on recrystallization from methanol gave colorless needles, ν_{max}^{KBr} 1750 and 1697 cm^{-1}; nmr spectrum: τ 5.10 (1 H, quartet, $J = 6$ and 10.5 cps), 5.69 (1 H, doublet, $J = 6$ cps), 7.14 (1 H, doublet, $J = 10.5$ cps), 8.72 (9 H, singlet), 8.84 (9 H, singlet), and 8.87 (9 H, singlet). This compound was not further investigated.

Elution with 25 ml of petroleum ether–benzene (7:3) yielded 27 mg of a mixture of the above compound and an unidentified compound. Further elution with the same solvent mixture, then with 1:1 petroleum ether–benzene, yielded a colorless solid, mp 124–125° (229 mg, 73%). Recrystallization from petroleum ether gave the bromine adduct XIV as colorless needles, mp 126.5–127°; ν_{max}^{KBr} 1747 and 1710 cm^{-1}.

Anal. Calcd for $C_{18}H_{30}O_2Br_2$: C, 49.33; H, 6.90. Found: C, 49.02; H, 7.03.

Treatment of Bicyclopentanone XI with Hydrogen Chloride. Dry hydrogen chloride was bubbled through a solution of 140 mg of bicyclopentanone XI in 100 ml of chloroform for 4 hr. After the evaporation of the mixture under reduced pressure, the residue was chromatographed on 5 g of silica gel. Elution with 25 ml of petroleum ether yielded 89 mg (56%) of colorless crystals, mp 77–85°. Recrystallization from methanol gave the HCl adduct XIII as colorless needles, mp 93–93.5°.

Anal. Calcd for $C_{18}H_{31}O_2Cl$: C, 68.66; H, 9.92. Found: C, 68.18; H, 10.41.

Further elution with petroleum ether yielded 56 mg (40%) of crystals, which on recrystallization from methanol gave 33 mg of colorless crystals, mp 74–76°. This compound was identical with cyclopentenone VIII (by infrared and mixture melting point).

Thermal Reaction of Bicyclopentanone X. The nmr spectrum of bicyclopentanone X, which was allowed to stand in the crystalline state at room temperature for several weeks, showed that it was converted to a mixture of bicyclopentanone XI and lactone XII (*ca.* 1:1) containing some of the starting material X.

Pyrolysis of Bicyclopentanone XI. Bicyclopentanone XI (200 mg) was distilled at bath temperature 220–270° (760 mm). Crystallization of the distillate from methanol gave 90 mg of colorless plates, mp 84–89°. Further recrystallization from methanol gave pure lactone XIX as colorless needles, mp 91–92.5°; ν_{max}^{KBr} 1740, 1669, and 1613 cm^{-1}.

Anal. Calcd for $C_{18}H_{30}O_2$: C, 77.65; H, 10.86. Found: C, 77.61; H, 10.79.

The mother liquor was evaporated to give 104 mg of an oil, 50 mg of which was chromatographed on 5 g of silica gel. Elution with petroleum ether–benzene (7:3) yielded 14 mg of colorless crystals, mp 87–89°, which were identical with lactone XII (by infrared and mixture melting point). Further elution with the same solvent mixture yielded 16 mg of lactone XIX. The total yields of XII and XIX amounted to 14 and 61%, respectively.

Alkaline Hydrolysis of Lactone XII. A solution of 50 mg of lactone XII and 250 mg of potassium hydroxide in 10 ml of 1-butanol was heated at reflux for 10 hr. The solvent was evaporated under reduced pressure to leave a brownish residue whose infrared spectrum showed a broad band at 1600–1560 cm^{-1} but no band near 1750 cm^{-1}. Acidification of the residue with 2 *N* hydrochloric acid gave 34 mg of a pale yellow solid, which was identified as the starting material XII (by infrared spectroscopy).

Alkali Treatment with Bicyclopentanone XI. To a solution of 165 mg of bicyclopentanone XI in 25 ml of ethanol was added under cooling with an ice–salt mixture 2 ml of 1 *N* alcoholic potassium hydroxide, and the mixture was stirred at 0° for 1 hr, then at room temperature for 2.5 hr. After the addition of 100 ml of water, the mixture was extracted with petroleum ether (three 100-ml portions). The organic layer was evaporated under reduced pressure, and the residue was chromatographed on 15 g of silica gel. Elution with petroleum ether yielded 37 mg of cyclobutanone XXI as colorless needles, mp 63–64°; ν_{max}^{KBr} 1762 cm^{-1} with a shoulder at 1770 and 1635 cm^{-1}.

Anal. Calcd for $C_{18}H_{30}O_2$: C, 77.65; H, 10.86. Found: C, 77.90; H, 10.77.