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Intramolecular Photoaddition of Ketenes to Conjugated Cycloalkenones

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Diazo ketones linked to cycloalkenones by a hydrocarbon chain were irradiated with UV light. The photochemically generated ketene is shown to add the enone forming 1,4-diketones in moderate yield. The scope and limitation of the cycloaddition for this process are discussed, and a mechanism is proposed.

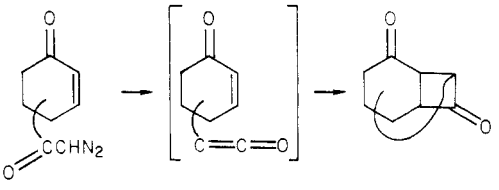
Ketenes can be generated from α-diazo ketones by means of thermolysis, photolysis, and catalytic decomposition via the Wolff rearrangement.[1] Agreement has not yet been achieved as to the mechanism, the excited state(s),[2,3] and the participating intermediates[4-6] despite theoretical and experimental efforts.[7,8]

[2 + 2] thermal cycloadditions of ketenes to olefins are well known and have been used for the synthesis of four-membered rings.[9] To the best of our knowledge, no thermal [2 + 2] cycloaddition of ketene to cycloalkenone is known in the literature,[10] although a 1,4-cycloaddition has been recently[11] reported. On the other hand, intramolecular photoadditions do take place as we have reported.[12,13] Recently, Agosta[14] has described a similar intramolecular cyclization of an acyclic system.

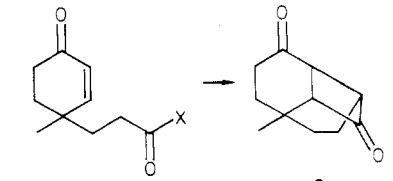
Intramolecular additions of ketenes to olefins are well known. The ketenes were formed from α-diazo ketones by pyrolysis or irradiation, by reaction of acyl chlorides with base,[15,16] or by irradiation of ketoenones.[17] The intermolecular photocycloaddition of unsymmetrical olefins to conjugated cycloalkenones is still being studied intensively since it is of theoretical and practical interest.[18,19]

This report describes the first examples of intramolecular photocycloaddition of ketenes to conjugated cycloalkenones. The results can be interpreted in light of Corey's mechanism[20] for [2 + 2] photocycloadditions.

Scheme I

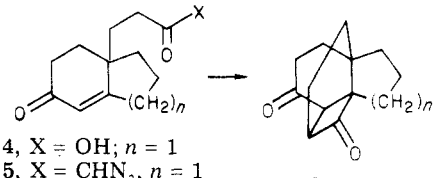


Scheme II



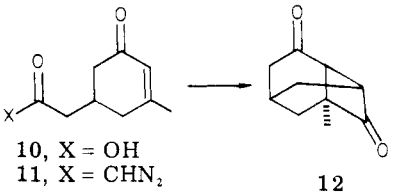
1, X = OH
2, X = CHN_2

3



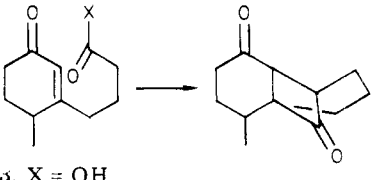
4, X = OH; n = 1
5, X = CHN_2, n = 1
7, X = OH; n = 2
8, X = CHN_2; n = 2

6, n = 1
9, n = 2



10, X = OH
11, X = CHN_2

12



13, X = OH
14, X = CHN_2

15

Results and Discussion

It was found that a [2 + 2] photoadduct was formed upon irradiation of systems containing both an α-diazo ketone and a cyclohexenone according to Scheme I.

The diazo ketones were prepared from the corresponding acids via the acid chlorides which were treated with excess diazomethane and irradiated with UV light, λ > 300 nm. Only 1,4-diketones were isolated (20–40% yield) from the

(1) H. Meier and K. P. Zeller, *Angew. Chem., Int. Ed. Engl.*, **14**, 32 (1975).
(2) E. Bothe, H. Meier, D. Schulte-Frohlinde, and C. von Sonntag, *Angew. Chem., Int. Ed. Engl.*, **15**, 380 (1976).
(3) H. D. Roth and M. L. Monion, *J. Am. Chem. Soc.*, **98**, 3392 (1976).
(4) S. A. Matlin and P. G. Sammes, *J. Chem. Soc., Perkin Trans. 1*, 2623 (1972).
(5) J. Fenwic, G. Frater, K. Ogi, and O. P. Strausz, *J. Am. Chem. Soc.*, **95**, 124 (1973).
(6) K. P. Zeller, *Angew. Chem., Int. Ed. Engl.*, **16**, 780 (1977).
(7) A. C. Hopkinson, *J. Chem. Soc., Perkin Trans. 2*, 794 (1973).
(8) I. G. Csizmadia, H. E. Gunning, R. K. Gosavi, and O. P. Strausz, *J. Am. Chem. Soc.*, **95**, 133 (1973).
(9) E. J. Corey, Z. Arnold, and J. Hutton, *Tetrahedron Lett.*, 307 (1970).
(10) L. Ghosez and M. J. O'Donnell, "Pericyclic Reactions", Vol. II, H. D. Marchand and R. E. Lehr, Eds., Academic Press, New York, 1977, p 79.
(11) R. Bonjouklian and R. A. Ruden, *J. Org. Chem.*, **42**, 4095 (1977).
(12) D. Becker, M. Nagler, and D. Birnbaum, *J. Am. Chem. Soc.*, **94**, 4771 (1972).
(13) D. Becker, Z. Harel, and D. Birnbaum, *J. Chem. Soc., Chem. Commun.*, 377 (1975).
(14) S. Ayral-Kaloustian, S. Wolff, and W. C. Agosta, *J. Org. Chem.*, **43**, 3314 (1978).
(15) S. W. Baldwin and E. H. Page, J., *J. Chem. Soc., Chem. Commun.*, 1337 (1972).
(16) P. Yates and A. G. Fallis, *Tetrahedron Lett.*, 2493 (1968).
(17) H. Hart and G. M. Love, *J. Am. Chem. Soc.*, **93**, 6266 (1971).
(18) P. de Mayo, *Acc. Chem. Res.*, **4**, 41 (1971).
(19) A. J. Wexler, J. A. Hyatt, P. W. Raynold, C. Cottrell, and J. S. Swenton, *J. Am. Chem. Soc.*, **100**, 512 (1978).
(20) E. J. Corey, J. D. Bass, R. le Mahieu, and R. B. Mitra, *J. Am. Chem. Soc.*, **86**, 5570 (1964).

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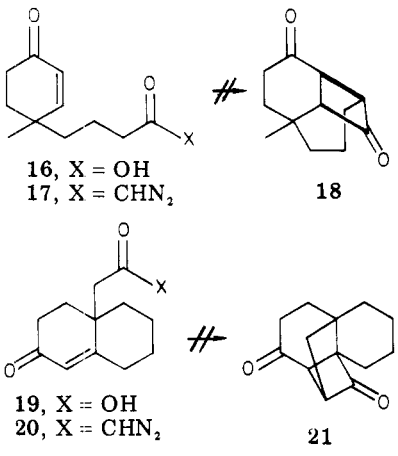
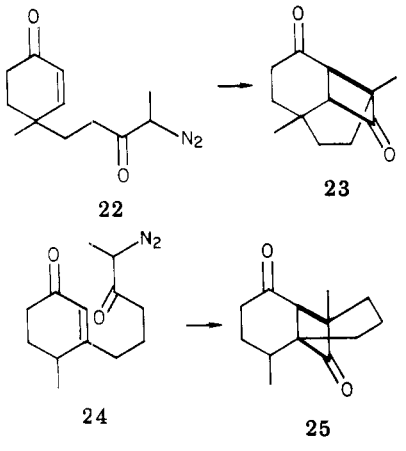
Scheme III



Scheme IV



reaction mixtures. The alternate 1,3-diketone structures could be excluded on the basis of the stability of the products to base.

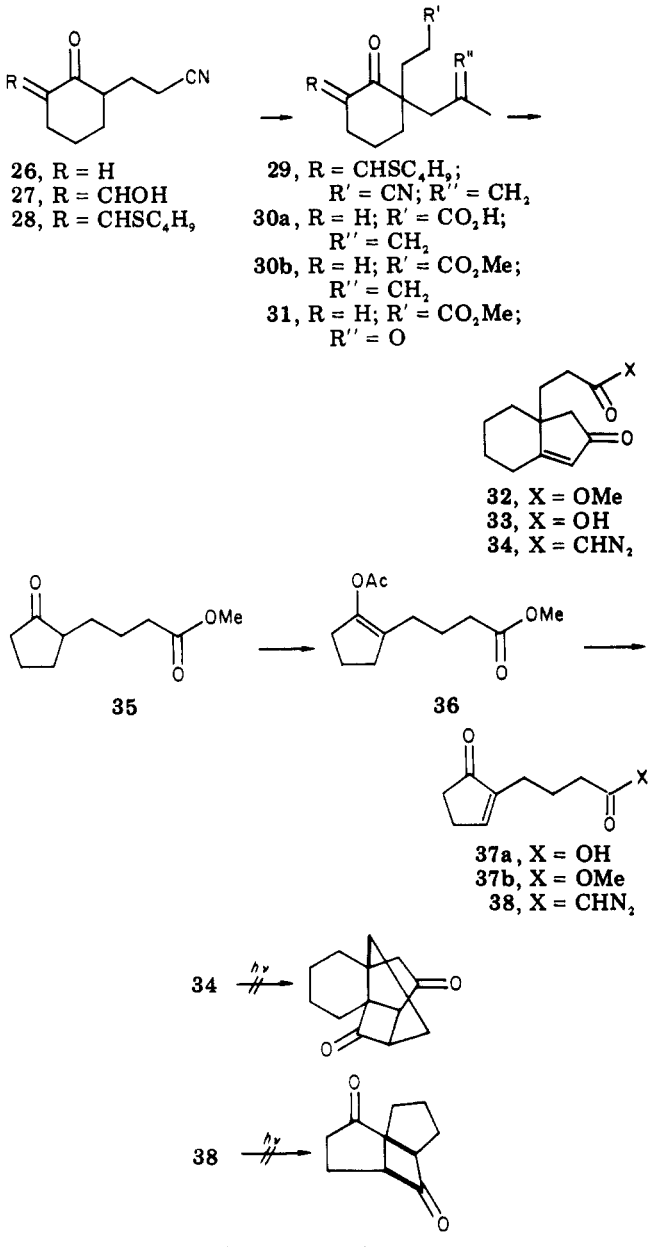
It was found that in order to obtain cyclobutanone systems the structure of the starting material must be designed carefully to minimize side reactions. The discussion will be divided into three topics: the structural requirements for successful cycloaddition, the factors that influence the yield, and the mechanism. Typical examples of molecules which yielded the adduct upon irradiation are presented in Scheme II.

In all of these examples three carbon atoms separate the diazo ketone and the enone moieties. Cyclobutanones were not detected in the reaction mixtures from irradiation of **17** (two carbon atoms between diazoketene and enone) or from **20** (four carbon atoms between diazoketene and the enone). In these cases a mixture of many compounds was obtained which did not contain a single major component (by TLC analysis). By examination of Dreiding models, it is obvious that a three-carbon chain provides the best interaction between the ketene and the enone. On the other hand, a shorter or longer chain makes the approach very difficult. Since it is reasonable to assume that ketocarbenes and ketenes are intermediates in the course of the photoaddition, alternative reactions, such as insertion or dimerization, could compete successfully with the [2 + 2] photoaddition. It is known that aldoketenes are unstable and tend to dimerize easily.[21]

All of the cases described above involve intermediate aldoketenes. In order to investigate the possibility that

(21) D. E. Thornton, R. K. Gosavi, and O. P. Strausz, *J. Am. Chem. Soc.*, **92**, 1768 (1970).

Scheme V



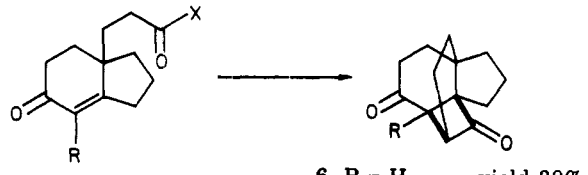
side reactions would be lessened with ketoketenes, compounds **22** and **24** were prepared (by reaction of acid chlorides with diazoethane) and irradiated. However, yields of cyclobutanones (**23** and **25**) were very low, probably because the methyl group, which was intended to reduce side reactions, actually hindered the approach of the ketene to the enone and slowed down the cyclization.

Another approach to improving the yield was based on the assumption that the half-life of the excited enone triplet should be as long as possible. Since it was known[18] that the half-life of a cyclopentenone triplet is longer than that of a cyclohexenone triplet, the systems in Scheme V were prepared.

Compound **33** was prepared in the usual way[22] via condensation of **28** with methallyl chloride, ozonolysis, and alkaline cyclization. Compound **37** was prepared according to three known procedures,[23-26] and it was found that the

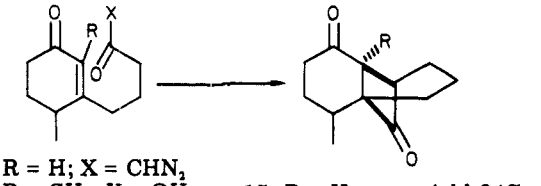
(22) E. Piers, W. De Waal, and W. Britton, *Can. J. Chem.*, **47**, 4303 (1969).
(23) D. P. Wyman, P. R. Kaufman, and W. R. Freeman, *J. Org. Chem.*, **29**, 2706 (1964).
(24) H. O. House and H. W. Thompson, *J. Org. Chem.*, **26**, 3729 (1961).
(25) H. O. House, M. Gall, and H. D. Olmstead, *J. Org. Chem.*, **36**, 2361 (1971).

Scheme VI



5, R = H; X = CHN_2
39, R = CH_3; X = OH
40, R = CH_3; X = CHN_2

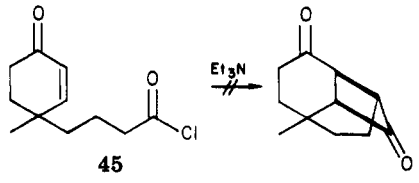
6, R = H yield 30%
41, R = CH_3 yield 30%



14, R = H; X = CHN_2
42, R = CH_3; X = OH
43, R = CH_3; X = CHN_2

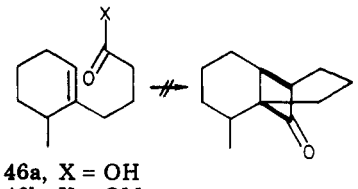
15, R = H yield 34%
44, R = CH_3 yield 30%

Scheme VII

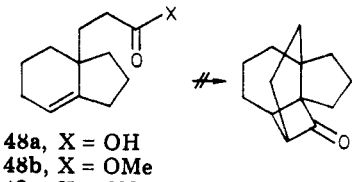


45 3

Scheme VIII

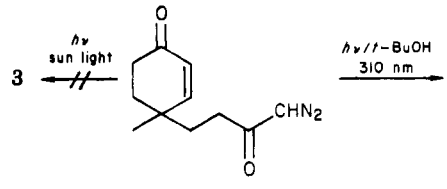


46a, X = OH
46b, X = OMe
47, X = CHN_2

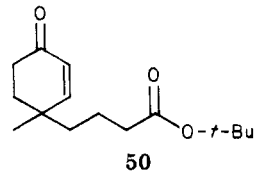


48a, X = OH
48b, X = OMe
49, X = CN_2

Scheme IX



2



50

best yield was obtained via bromination and dehydrobromination. The corresponding diazo ketones, **34** and **38**, were prepared in the usual way and irradiated, but to our surprise no cyclobutanone whatsoever was detected in the reaction mixture (IR). It is well known that cyclopentenones rearrange or abstract hydrogen atoms upon irradiation.[27-29] In a preliminary experiment, it was found that when the corresponding ester **32** was irradiated, the enone chromophore disappeared quickly. Thus, it is reasonable to assume that highly efficient side reactions are competing successfully, and hence the use of cyclopentenones to improve the yield of the cycloaddition failed. Other approaches to improve product yield, such as irradiation at low temperature (−50 °C) or high dilution, also failed.

2-Substituted cycloalkenones are known to react in [2 + 2] intermolecular photocycloadditions more slowly than the unsubstituted systems and yield complicated mixtures.[20,30] We found that the substituted systems **40** and **43**, which were prepared from the corresponding acids **39** and **42**, cyclized upon irradiation to **41** and **44** in similar yield to those obtained with the unsubstituted systems **5** and **14**.

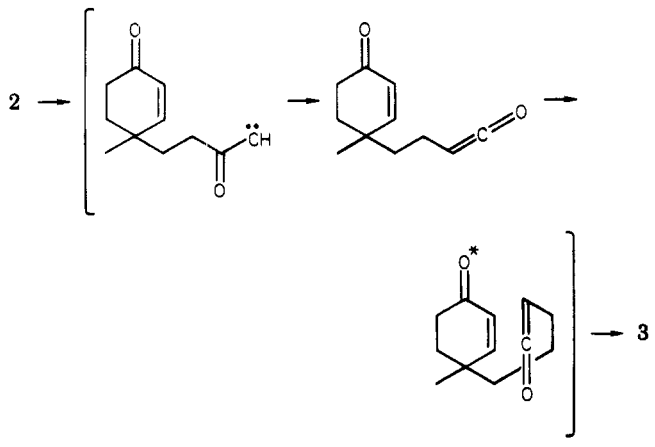
It is generally agreed that [2 + 2] photocycloaddition occurs by addition of an olefin to an excited enone to form a diradical which cyclizes to a cyclobutane.[18,20] We would like to present some experimental results before adopting this mechanism for our systems. The following experiments were aimed at producing the carbene and the ketene in the ground state and determining whether they would undergo cyclization. Use of known procedures such as decomposition of diazo ketones **2** or **14** by pyrolysis or Ag^+, or dehydrohalogenation[31] of the acid chloride **45**, did not lead to any cyclobutanone such as **3**. The fact that [2 + 2] cycloaddition did not occur in the ground state is not surprising, considering the well-documented[31] fact that olefins conjugated to electron-withdrawing groups do not react even with the highly electrophilic halogenated ketenes.

In order to support the assumption that the excited enone is essential to the cycloaddition, the carbonyl function was removed from compounds **5** and **14**. As expected, irradiation of the corresponding diazo ketones, **49** and **47**, gave no cyclobutanone product, as shown by IR spectra. Since the ground state double bonds of **47** and **49** did not add to the ketene, it is reasonable to assume that the same double bond conjugated to a carbonyl function, which makes them less active as nucleophiles, would have to react via the excited state in order to obtain products **6** and **15**. It is worth noting that in all cases described in the literature[15,16] the addition of the ketenes to double bonds occurred when the double bond was located in a five-membered ring or a chain, while in **47** and **49** the double bond is located in a six-membered ring.

Further evidence that an excited state of the enone is involved in the cycloaddition was provided by observation of wavelength dependence. When diazo ketone **2** (ϵ_{380} 10) was irradiated at $\lambda > 380$ nm, slow decomposition of **2** was observed without formation of any cyclobutanone. As noted earlier, formation of cyclobutanones did occur at $\lambda > 300$ nm (Pyrex). At $\lambda > 260$ nm (Vycor), cyclobutanone was formed but underwent photodecomposition. There-

(26) T. Shono, M. Okawa, and I. Nishiguchi, *J. Am. Chem. Soc.*, **97**, 6144 (1975).
(27) S. Wolff and W. C. Agosta, *J. Chem. Soc., Chem. Commun.*, 226 (1972).
(28) H. E. Zimmerman and D. Little, *J. Am. Chem. Soc.*, **96**, 4623 (1974).
(29) S. Ayral-Kaloustian, S. Wolff, and W. C. Agosta, *J. Am. Chem. Soc.*, **99**, 5984 (1977).
(30) R. M. Bowman, C. Colvo, J. J. McCullough, P. W. Rasmussen, and F. F. Snyder, *J. Org. Chem.*, **37**, 2084 (1972).
(31) W. T. Brady and O. H. Waters, *J. Org. Chem.*, **32**, 3703 (1967).

Scheme X



fore, we can conclude that the enone system must be excited by light in order to enable the [2 + 2] cycloaddition to occur.

The presence of a ketene as an intermediate in photochemical reactions can be shown directly by a low-temperature IR spectrum[32] or indirectly by trapping experiments with alcohols. We found that irradiating diazo ketone **2** in *tert*-butyl alcohol led to the formation of the homologous keto ester **50**, and the photocycloaddition was quenched completely. This result can be explained if we assume that the alcohol competes very efficiently with the enone and traps the ketene.

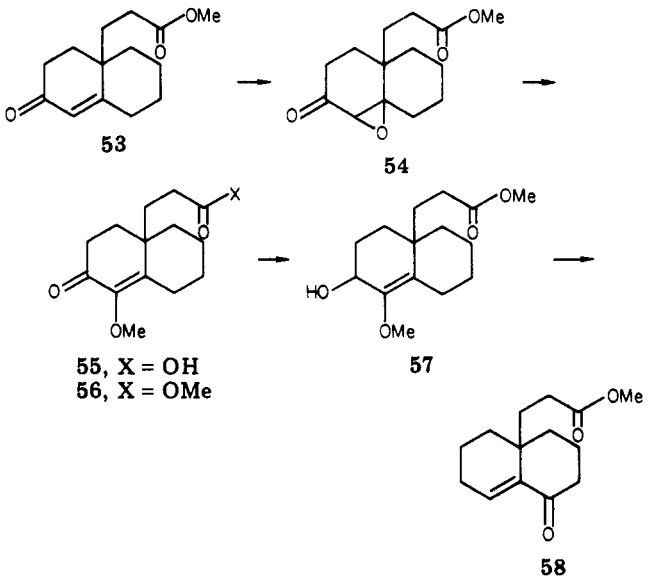
Our experimental results lead to the conclusion that in order for the cyclization to take place the system must (a) contain a conjugated enone, (b) contain a diazo ketone group from which a ketene will be formed, and (c) have chromophores that both reach excited states. All of the products isolated were 1,4-diketones whose formation may be explained by preorientation of the ketene and the excited enone before any bond formation, as described in Scheme X.

However, there are two additional possibilities which should be considered since they are not ruled out by the experimental results: (a) a one photon reaction which involves energy transfer from the excited ketene to the enone and (b) the ketene in the ground state is excited by the enone and only then will the addition take place.

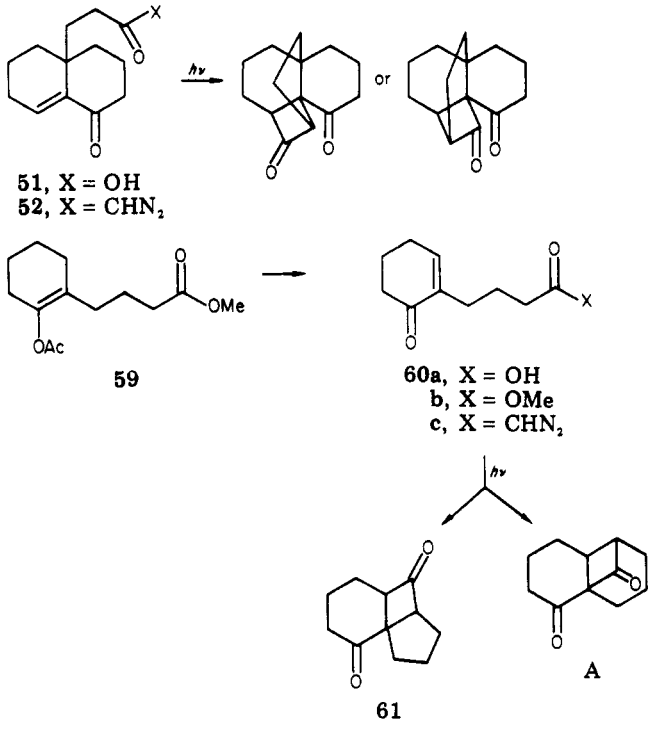
According to Corey's mechanism, the formation of 1,4-diketones can be explained by the polarity of the interacting excited and ground states. The polarization of the double bond of a specific enone system can be reversed by transposition of the carbonyl group from one side of the double bond to the other side. Two examples of such reversal of polarization are the pairs of compounds **8**, **52** and **14**, **60c**. If the Corey hypothesis is correct, 1,4-diketones will be formed in all cases even though different approaches of the ketene side chain to the enone will be required.

Syntheses of **52** and **60c** are described in Schemes XI and XII. Irradiation of **52** produced a complex mixture which did not contain any cyclobutanone.[33] However, irradiation of **60c** produced only one cyclobutanone, **61**, in 39% yield. As mentioned earlier, the possibility that

Scheme XI



Scheme XII



61 might be the isomeric 1,3-diketone A could be ruled out by the fact that the compound was recovered unchanged after 2 h of boiling in 10% methanol potassium hydroxide; a 1,3-diketone would not survive under such conditions.[13] An additional conclusion which can be drawn from the fact that the compound was stable under these conditions is that **61** has a cis[35] junction of both the six- and the five-membered rings fused to the cyclobutanone. Comparing the structure of 1,4-diketone **61** vs. that of the 1,3-diketone, it is obvious that the chain was forced to fold in the direction opposite to that of compound **14**, in accordance with the polarity of the system.

Upon irradiation of steroids containing conjugated dienones, intramolecular cycloaddition occurred mainly on

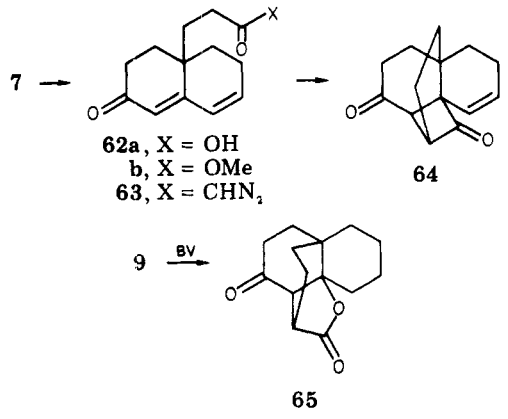
(32) G. Quinkert, *Pure Appl. Chem.*, **33**, 285 (1973).

(33) It should be mentioned that two factors were changed in system **52**. The chain bearing the ketene was attached to the α position of the enone system and the enone has an s-cis configuration. Weisbuch describes in *Tetrahedron Lett.*, 3441 (1973), the behavior of s-cis cycloenones and concludes that they do not tend to undergo intramolecular [2 + 2] photocycloaddition with olefins. Postpactum these results may explain the failure of our experiment.

(34) Von W. Eisele, C. A. Grob, E. Renk, and H. von Tochammer, *Helv. Chim. Acta*, **51**, 816 (1968).

(35) Y. Tamura, H. Ishibashi, M. Hirai, Y. Kita, and M. Ikeda, *J. Org. Chem.*, **40**, 2702 (1975).

Scheme XIII



the α,β double bond.[36,37] Similarly, we found that upon irradiation of compound **63** photoadduct **64** could be isolated in 29% yield.

In order to examine the synthetic potential of these adducts, compound **9** was exposed to Baeyer–Villager oxidation, and the corresponding lactone **65** was formed selectively and isolated in good yield.

In summary we can conclude, based on the facts described herein, that intramolecular photocycloaddition of ketene to cyclohexenone will occur if the distance between the two reactive sites is three carbon atoms, and the product that can be obtained in moderate yield will be a 1,4-diketone.

Experimental Section

1-Methyl-4-oxo-2-cyclohex-2-ene-1-propionic Acid (1). The keto ester[38] (3.2 g, 16.5 mmol) was hydrolyzed by boiling it with a 60 mL 1:4 solution of acetic acid and 20% hydrochloric acid for 3 h under a nitrogen atmosphere. The solvents were removed, and the oil received was purified on a silica gel column (30 g, Woelm Activity I), eluting with methylene chloride. The keto acid **1** was crystallized from petroleum–ether: 60–70 °C; mp 73–74 °C; IR ($CHCl_3$) 1725 (–C(O)–), 1685 (–C=CC(O)–), 1620 cm^{-1} (–C=C–); NMR ($CDCl_3$) δ 6.35 (2 H), 2.1 (8 H), 1.2 (s, 3 H). Anal. Calcd for $C_{10}H_{14}O_3$: C, 65.91; H, 7.74. Found: C, 65.75; H, 8.05.

1-Methyltricyclo[4.2.2.0^{5,8}]deca-4,7-dione (3). Acid **1** (0.8 g) was dissolved in dry benzene, and to the stirred solution were added 1.5 mL of oxalyl chloride and 2–3 drops of pyridine diluted with benzene. After 2 h at room temperature, the solvents were removed under pressure. The acyl chloride was transferred by 10 mL of benzene to an ethereal solution of diazomethane (prepared from 5 g of nitrosomethylurea and dried over potassium hydroxide for 2 h in the refrigerator). After 15 min, the solvents were removed, yielding the diazo ketone **2**: IR ($CHCl_3$) 2115 (C=N$^+$=N$^-$), 1685 (C=CC=O), 1650 cm^{-1} ($N_2HCC(O)$). It was dissolved in 50 mL of dry dioxane, added to 800 mL of cyclohexane, and irradiated for 1.5 h. The solution was flushed with dry nitrogen for 0.5 h before irradiation and maintained under nitrogen for the duration of the reaction. Removal of the solvents gave an oil which was purified on a florisil column (30 g), eluted with 1:2 petroleum–ether (60–70 °C)–methylene chloride, and yielded 260 mg (32%) of the diketone **3**, mp 77–78 °C, after crystallization from petroleum–ether (60–70 °C). **3** could also be distilled at 120 °C (0.2 mm): IR ($CHCl_3$) 1790 ($\overline{CH_2CH_2CH_2C}$=O), 1715 cm^{-1} (–C(O)–); NMR ($CDCl_3$) δ 3.42 (1 H); MS for $C_{11}H_{14}O_2$ at 178.0988 (theory 178.0993).

5,6,7,8-Tetrahydro-5-oxoindan-8-propionic Acid (4). A 1 N solution of sodium methoxide was prepared from 7 g (0.3 mol) of sodium in 300 mL of absolute methanol. To the stirred solution were added dropwise 25 g (0.18 mol) of 2-oxocyclopenta-β-propionitrile[39] during 0.5 h under nitrogen. The solution was then cooled to –5 °C, and 16 g (0.23 mol) of methyl vinyl ketone diluted with 50 mL of absolute methanol were added. The addition continued for 4 h, and the mixture was stirred overnight. Water (100 mL) was added and the methanol removed. The aqueous solution was extracted four times with 50 mL of methylene chloride then dried over magnesium sulfate. Removal of the solvent yielded 36 g of keto nitrite. The starting material was removed by distillation, and the residue of the neutral material was dissolved in 210 mL of a 1:1:1 mixture of water, acetic acid, and concentrated hydrochloric acid and refluxed under nitrogen for 24 h. The solvents were removed, and the solution was extracted six times with 50 mL of methylene chloride. The combined organic solution was washed with five portions of 50 mL each of a dilute solution of potassium carbonate then acidified with concentrated hydrochloric acid. After extraction with methylene chloride, drying over anhydrous magnesium sulfate, and filtration, the solvents were removded, yielding 28 g of keto acid **4**. Crude **4** (3.3 g) was chromatographed on a column of silica gel (60 g, 10% deactivated). A clean keto acid **4**, which crystallized on standing, was received with methylene chloride–chloroform 1:1 as an eluent. **4** (2.7 g, 82%) was collected: mp 93–94 °C; IR ($CHCl_3$) 3000–3500 (acid), 1720 (—C(O)—), 1665 cm^{-1} (—C=C(O)C—); NMR ($CDCl_3$) δ 5.87 (m, 1 H), 8.60 (broad s, 1 H). The keto ester of **4** was prepared by treating the acid with an excess of diazomethane in an ethereal solution for 10 min. It was distilled at 110 °C (0.1 mm): IR (CCl_4) 1734 (C(O)OMe), 1663 cm^{-1} (–C=CC(O)–); UV (MeOH) λ_{max} 238 (ϵ 15 080), 293 nm (ϵ = 100); NMR ($CDCl_3$) δ 3.76 (s, 3 H), 5.87 (t, 3 H); MS for $C_{13}H_{18}O_3$ at 222 (theory 222). Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 70.13; H, 8.13.

Tetracyclo[5.4.2.0^{1,5}.0^{5,8}]trideca-6,9-dione (6). Diazo ketone **5** was prepared as usual from 2 g of **4**: IR ($CHCl_3$) 2113 (C=N$^+$=N$^-$), 1658 (–C=CC(O)–), 1643 cm^{-1} ($N_2HCC(O)C$). It was chromatographed on a florisil column (60–80 mesh). A clean diazo ketone **5** was eluted with chloroform–methylene chloride, yielding 1.2 g (60%) of pure compound according to TLC with silica gel and IR. **5** (100 mg) was dissolved in 5 mL of dry dioxane and added to 130 mL of cyclohexane (thiophene free) in an irradiation flask with a stream of nitrogen bubbling for 0.5 h before irradiating. The irradiation continued for 0.5 h, affording after removal of the solvents 70 mg of an oil which was purified by chromatography on a silica gel preparative plate, yielding 19 mg (31%) of diketone **6**, mp 80–81 °C. **6** could be distilled at 75 °C (0.1 mm) and its purity was demonstrated by GC: IR ($CHCl_3$) 1783 ($\overline{CH_2CH_2CH_2C}$=O), 1707 cm^{-1} (–C(O)–); NMR ($CDCl_3$) δ 3.42 (1 H); MS for $C_{14}H_{20}O_3$ at 204.1150 (theory 204.1146).

2,3,4,5,6,7,8,10-Octahydro-2-oxonaphthalene-10-propionic Acid (7). A sodium methoxide solution was obtained from 4.6 g (0.2 mol) of sodium and 100 mL of absolute methanol. To the ice-cooled solution was added 7.5 g (56 mmol) of **26**.[39] To the mixture were added dropwise 3.5 g (50 mmol) of methyl vinyl ketone diluted, 1:3, with absolute methanol over 2 h. The reaction mixture was stirred another 1 h at 0 °C, then 100 mL of water was added and the methanol evacuated. The aqueous solution was extracted with 4 × 50 mL of methylene chloride, dried, and filtered. The solvent was removed under reduced pressure to yield 7.5 g of a neutral product, which was hydrolyzed by dissolving it in 15 mL of methanol, 50 mL of concentrated hydrochloric acid, 50 mL of acetic acid, and 50 mL of water. The mixture was refluxed overnight under nitrogen. The solvents were removed, and the aqueous solution was extracted with 6 × 50 mL of methylene chloride. The organic layer was washed with 5 × 50 mL of a dilute solution of potassium bicarbonate, acidified with concentrated hydrochloric acid, and the keto acid **7** extracted with methylene chloride affording 7 g of an oily acid which was crystallized from isopropyl ether: mp 81–83 °C; IR ($CHCl_3$) 1715 (–C(O)–), 1670 (–C=C(O)–), 1620 cm^{-1} (–C=C–); NMR ($CDCl_3$) δ 11.2 (broad s, 1 H), 5.88 (s, 1 H). The dinitrophenylhydrazone with a deep red color was prepared and crystallized from methanol: mp 120 °C; mass spectrum peak at 402 (theory 402). The methyl ester of acid **7** was prepared by treating a solution of the acid with

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an excess of ethereal diazomethane for 10 min. The keto ester was distilled at 120 °C (0.2 mm): IR (CCl_4) 1730 (C(O)OMe), 1665 (-C=CC(O)), 1620 cm^{-1} (-C=C-); UV (methanol) λ_{max} 240 nm (ϵ 11 000); NMR ($CDCl_3$) δ 5.86 (s, 1 H), 3.68 (s, 3 H); MS for $C_{14}H_{20}O_3$ at 236 (theory 236). Anal. Calcd for $C_{14}H_{20}O_3$: C, 71.16; H, 8.53. Found: C, 69.94; H, 8.37.

Tetracyclo[6.4.2.0^{1,6}.0^{6,9}]tetradeca-7,10-dione (9). The diazo ketone **8** was prepared as usual. Half a gram was irradiated in dry THF or dry cyclohexane (thiophene free) for 2 h. The oil obtained was purified on a florisil column (70 g), yielding 0.2 g (40%) of diketone **9**: mp 78 °C after crystallization from isopropyl ether; IR ($CHCl_3$) 1785 ($CH_2CH_2CH_2C$=O), 1705 cm^{-1} (-C(O)-); NMR ($CDCl_3$) δ 3.39 (1 H); MS for $C_{14}H_{18}O_2$ at 218.1311 (theory 218.1307).

Methyl (5-Methyl-3-oxo-4-cyclohexen-1-yl)acetate (10). The corresponding diazo ketone of the known[40] keto acid was prepared in the usual way: IR ($CHCl_3$) 1640 (N_2HCC=O), 1670 (-C=CC(O)-), 2110 cm^{-1} (C=N$^+$=N$^-$). The crude diazo ketone was dissolved in absolute methanol and refluxed under an atmosphere of nitrogen. To the stirred mixture were added in three portions a solution of silver oxide (3 g of Ag_2O freshly prepared). The addition took 0.5 h and the reflux continued another 2.5 h. The cooled mixture was filtered through Celite, the methanol evacuated, 35 mL of methyl acetate added, and the solution boiled for 10 min. The solution was filtered again through a column of florisil, and distillation of the solvent afforded 0.8 g (70%) of the keto ester **10**: bp 80 °C (0.05 mm); IR ($CHCl_3$) 1735 (ester), 1665 (-C=CC(O)-), 1629 cm^{-1} (-C=C-); NMR ($CDCl_3$) δ 1.97 (s, 3 H), 3.70 (s, 3 H), 5.93 (broad s, 1 H); UV (methanol λ_{max} 234 (ϵ 11 530), 305 nm (ϵ 56.6); MS for $C_{10}H_{14}O_3$ at 182 (theory 182). Anal. Calcd for $C_{10}H_{14}O_3$: C, 65.91; H, 7.74. Found: C, 65.84; H, 7.75.

1-Methyltricyclo[3.3.1.0^{2,7}]nona-3,8-dione (12). Diazo ketone **11** was prepared as usual from 100 mg of keto acid **10** which was dissolved in 5 mL of dry dioxane and irradiated in cyclohexane (120 mL/for 0.5 h) with magnetic stirring and bubbling of dry nitrogen through the solution. The solvents were removed, and the oil was chromatographed on a florisil column with methylene chloride–hexane 1:1 as an eluent. Clean diketone **11** (24 mg, 28%) was collected, mp 74–74.5 °C, and crystallized from hexane: bp 90 °C (0.2 mm); IR ($CHCl_3$) 1782 ($CH_2CH_2CH_2C$=O), 1710 cm^{-1} (C=O); NMR δ 1.20 (s, 3 H), 2.50 (s, 1 H), 2.60 (s, 1 H), 3.35 (t, 1 H); MS for $C_{10}H_{12}O_3$ at 164.0854 (theory 164.0837). Anal. Calcd for $C_{10}H_{12}O_3$: C, 73.14; H, 7.37. Found: C, 73.60; H, 7.51.

2-Methyltetracyclo[5.3.1.0^{1,6}]undeca-5,11-dione (15). Diazo ketone **14** was prepared from 3 g of keto acid **13**[41] in the usual way. It was purified on a water-cooled florisil column and eluted with 1:1 methylene chloride–hexane, yielding 2.1 g of purified diazo ketone **14** as shown by TLC: IR ($CHCl_3$) 2104 (C=N$^+$=N$^-$), 1660 (-C=CC(O)-), 1635 cm^{-1} (N_2HCC(O)). **14** (1 g) was dissolved in 10 mL of dry dioxane and added to 3 L of cyclohexane and irradiated for 1.3 h. Yellow oil (1 g) was obtained after removal of the solvents. The yield (100 mg) was purified on a preparative silica gel plate with 1:1 hexane–acetone: 30 mg (34%) of diketone **15** were obtained; mp 58.5–59 °C; bp 55 °C (0.1 mm); IR ($CHCl_3$) 1780 ($CH_2CH_2CH_2C$=O), 1715 cm^{-1} (-C(O)-); NMR ($CDCl_3$) δ 1.07 (d, 3 H), 3.37 (m, 1 H); mass spectrum peak for $C_{12}H_{16}O_2$ at 192.1150 (theory 192.1166).

Keto ester 16 was synthesized according to Becker.[42]

Keto ester 19 was synthesized according to Becker.[43]

2-Oxo-3-hydrindene-8-propionic Acid (33). Sodium (3 g, 0.13 mol) was added to 40 mL of absolute methanol in a 250-mL three-necked flask equipped with a magnetic stirrer, an addition funnel, and a condenser. Excess methanol was removed under reduced pressure (25 mm). The residue, solid sodium methoxide, was dried by high vacuum. It was crushed, and 9.52 g (0.13 mol) of ethyl formate diluted with 80 mL of dry benzene was added. To the ice-cooled solution were added dropwise 10 g (0.66 mol) of keto nitrile **26**. The mixture was left to stand at 0 °C for 4–5 h, then cold water was added and the organic phase washed with 10% sodium hydroxide. The washings were collected, washed with ether, acidified with 10% hydrochloric acid, extracted with ether, and dried over anhydrous magnesium sulfate. The solvent was removed, yielding 9.8 g of **27** which was pure according to TLC: IR ($CHCl_3$) 3400–3700 (C=COH), 2240 (CN), 1710 (-C(O)-), 1660 cm^{-1} (C=CC(O)).

To a 50-mL flask fitted with a Dean–Stark trap and a condenser were added 20 mL of dry benzene, 4 g (23 mmol) of **27**, 2.25 g (25 mmol) of *n*-butylmercaptan, and 5 mg of *p*-toluenesulfonic acid monohydrate. The solution was refluxed for 5 h, and 0.4 mL of water was separated. The mixture was cooled and washed with a saturated solution of potassium carbonate and then with water. After the benzene was dried over anhydrous magnesium sulfate, the solvent was removed, yielding 4.6 g of **28**: IR ($CHCl_3$) 2250 (CN), 1670 cm^{-1} (-C=CC(O)-).

To 2.4 g (0.1 mol) of sodium hydride (50% powder in oil) in a 250-mL three-necked flask equipped with a magnetic stirrer, an addition funnel, and a condenser was added during 10 min 10 g (45 mmol) of **28**. After the solution was stirred for 0.5 h at room temperature, there was added 15 g (0.166 mol) of methallyl chloride during 10 min, and the mixture was refluxed at 80 °C for 3.5 h. The flask was cooled to 0 °C and acidified with 10% hydrochloric acid. The product was extracted with methylene chloride, washed with a dilute solution of sodium carbonate, dried, and filtered. Removal of the solvent yielded 11 g of **29**: IR ($CHCl_3$) 2240 (CN), 1670 (-C=CC(O)-), 900 cm^{-1} (>CH_2).

To a 250-mL flask fitted with a magnetic stirrer were added 30 g of **29**, 75 mL of 25% potassium hydroxide solution, and 75 mL of ethylene glycol. The mixture was refluxed overnight under nitrogen, cooled, and washed three times with ether. The aqueous solution was acidified with 10% hydrochloric acid, extracted with methylene chloride, dried, and filtered. Removal of solvent yielded 23 g of acid **30a**: IR ($CHCl_3$) 2500–3500 (acid), 1715 (-C(O)-), 905 cm^{-1} (=CH_2); NMR ($CDCl_3$) δ 1.66 (s, 3 H), 4.70 (1 H), 4.86 (1 H), 8.39 (1 H).

Acid **30a** (2 g, 9 mmol) was dissolved in 8.1 mL of 1,2-dichloroethane, and to the solution were added 3.3 mL of methanol and 0.08 mL of concentrated sulfuric acid. After 24 h of reflux, the solution was washed with water, with 10% sodium carbonate, and again with water. The organic solution was dried over anhydrous magnesium sulfate and filtered. The solvent was removed, yielding 1.64 g of **30b**: bp 100 °C (0.04 mm), pure according to GC; IR ($CHCl_3$) 1730 (C(O)OMe), 1705 (-C(O)-), 905 cm^{-1} (>CH_2); NMR ($CDCl_3$) δ 1.66 (s, 3 H), 3.67 (s, 3 H), 4.70 (1 H), 4.86 (1 H); MS for $C_{14}H_{22}O_3$ at 238 (theory 238). Anal. Calcd for $C_{14}H_{22}O_3$: C, 70.55; H, 9.31. Found: C, 70.51; H, 9.31.

30b (5 g, 21 mmol) was ozonolyzed in 350 mL of methylene chloride and 7 mL of absolute methanol at −78 °C. The excess ozone was removed by a stream of nitrogen, and the solvents were removed at 0 °C under reduced pressure. To the oily ozonide, 30 mL of acetone and 12 mL of Jones' reagent were added at 0 °C with vigorous stirring. The excess oxidizing reagent was decomposed by isopropyl alcohol, and the solvents were removed under reduced pressure. The product was extracted with methylene chloride, which was washed with saturated sodium bicarbonate solution and brine. The solvent was removed, yielding 4.55 g (90%) of **31**: bp 110 °C (0.03 mm); IR ($CHCl_3$) 1731 (C(O)OMe), 1708 cm^{-1} (-C(O)-); NMR ($CDCl_3$) δ 2.16 (s, 3 H), 3.70 (s, 3 H); MS for $C_{13}H_{20}O_4$ at 240 (theory 240). Anal. Calcd for $C_{13}H_{20}O_4$: C, 64.98; H, 8.39. Found: C, 65.23; H, 8.75.

To a 1-L flask were added 450 mL of *tert*-butyl alcohol and 10 g of potassium *tert*-butoxide (sublimed) under nitrogen. To the stirred solution was added 6.25 g of **31**, and the mixture was left to stand at room temperature for 2 h. Water was added, and acidification was performed with 20% hydrochloric acid. The organic solvents were removed under reduced pressure, and the aqueous solution was extracted with methylene chloride. Removal of the solvent yielded 6 g of crude keto acid **33**: IR ($CHCl_3$) 2500–3600 (acid), 1710 (-C(O)-), 1625 cm^{-1} (-C=C-); NMR ($CDCl_3$) δ 5.90 (broad s, 1 H), 8.02 (1 H). The keto acid was treated with an excess of ethereal diazomethane solution for 10 min, affording keto ester **32**: bp 125 °C (0.3 mm); IR ($CHCl_3$) 1735 (C(O)OMe), 1688 (-C(O)-), 1625 cm^{-1} (-C=C-); UV (MeOH) λ_{max} 228.4 (ϵ 12 000), 298 nm (ϵ 45); NMR ($CDCl_3$) δ 3.67 (s, 3 H), 5.86 (1 H); MS for $C_{13}H_{18}O_3$ at 222 (theory 222). Anal. Calcd for

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$C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 70.30; H, 8.54.

5-Oxo-1-cyclopentene-1-butyric Acid (37a). **35**[44] (4 g, 21.6 mmol) was dissolved in 80 mL of carbon tetrachloride. To the stirred solution were added 10 g (116 mmol) of acetic anhydride and a few drops of 70% perchloric acid. After 1 h at room temperature, the solution was poured into 100 mL of a cold mixture of pentane–10% sodium bicarbonate solution. Sodium carbonate (3 g) was added to neutralize the acetic acid. The phases were separated, and the aqueous layer was extracted with pentane, which was dried and filtered. Removal of the solvent yielded 4.94 g of oil, which after distillation yielded 4.4 g of **36**: by 70 °C (0.08 mm); IR ($CHCl_3$) 1745 cm^{-1} (OAc, C(O)OMe); NMR ($CDCl_3$) δ 2.10 (s, 3 H), 3.63 (s, 3 H); MS for $C_{12}H_{18}O_4$ at 226.1205 (theory 226.1218). Anal. Calcd for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02. Found: C, 63.90; H, 8.14.

To a solution containing 1.6 g of **36**, 4.5 mL of chloroform, 6 mL of water, and 0.55 g of calcium carbonate were added, dropwise during 0.5 h, 1.57 g of bromine diluted with 1.5 mL of chloroform. The mixture was stirred for 1 h at room temperature, the phases were separated, and the organic layer was washed with 10% sodium thiosulfate and brine. The solvent was removed, and the residue was dissolved in 5 mL of dry DMF to which 1.3 g of lithium bromide and 1.3 g of lithium carbonate were added. The mixture was refluxed for 45 min. To the cooled mixture was added 50 mL of cold water, and the red solution was neutralized with 20% hydrochloric acid and extracted with ether. The ethereal solution was washed with brine, dried, and filtered. Distillation of the crude product afforded 1.1 g (85%) of **37b**: bp 55 °C (0.01 mm); IR ($CHCl_3$) 1734 (C(O)OMe), 1695 cm^{-1} (cyclopentenone); NMR ($CDCl_3$) δ 3.63 (s, 3 H), 7.30 (broad s, 1 H); UV (MeOH) λ_{max} 236 nm (ϵ 17 430); MS for $C_{10}H_{14}O_3$ at 182.0943 (theory 182.0847). Anal. Calcd for $C_{10}H_{14}O_3$: C, 65.91; H, 7.74. Found: C, 65.68; H, 7.78.

37b (1 g) was dissolved in 15 mL of methanol, and 150 mL of 10% sodium hydroxide was added. The solution was refluxed for 3 h and the methanol removed under reduced pressure. The aqueous solution was extracted with methylene chloride, cooled, acidified with 10% hydrochloric acid, and extracted with chloroform. Removal of the solvent yielded 910 mg of keto acid **37a**: IR ($CHCl_3$) 1704 (–C(O)–), 1686 cm^{-1} (cyclopentenone).

5,6,7,8-Tetrahydro-4-methyl-5-oxoindene-8-propionic Acid (39). A sodium methoxide solution was prepared from 2.2 g (95 mmol) of sodium and 100 mL of absolute methanol. To the stirred solution were added dropwise 8 g of the keto nitrile[39] over 0.5 h. The solution was ice cooled (–5 °C) and 15 g of ethyl vinyl ketone, diluted with 50 mL of methanol, were added dropwise over 4 h. The solution stood overnight under nitrogen. Water (100 mL) was added and the methanol removed. The aqueous phase was extracted with 3 × 30 mL of methylene chloride, dried, and filtered. Removal of the solvent yielded 4.79 g of neutral keto nitrile. The starting material was distilled, and the residue was hydrolyzed with 30 mL of 1:1:1 water–acetic acid–concentrated hydrochloric acid. The mixture was refluxed overnight under nitrogen. The organic solvents were removed, and the aqueous solution extracted with 5 × 40 mL of methylene chloride and washed with 4 × 50 mL of 10% potassium bicarbonate. The basic washing was acidified with concentrated hydrochloric acid and extracted well with methylene chloride, yielding 3.5 g of keto acid **39**, which was crystallized from ether: mp 135–136 °C; IR ($CHCl_3$) 2500–3500 (acid), 1718 (–C(O)–), 1648 cm^{-1} (–C=CC(O)–); NMR ($CDCl_3$) δ 1.73 (s, 3 H), 8.97 (1 H). The keto ester of acid **39** was prepared by treatment with an excess of ethereal diazomethane for 10 min. It was distilled at 100 °C (0.1 mm): IR ($CHCl_3$) 1735 (C(O)OMe), 1648 cm^{-1} (–C=CC(O)–); UV (MeOH) λ_{max} 242 nm (ϵ 10 760); NMR ($CDCl_3$) δ 1.73 (s, 34), 3.67 (s, 3 H); MS for $C_{14}H_{20}O_3$ at 236 (theory 236). Anal. Calcd for $C_{14}H_{20}O_3$: C, 71.16; H, 8.53. Found: C, 71.58; H, 8.18.

Irradiation of Diazo Ketone 40. Diazo ketone **40** was prepared in the usual way from 0.8 g of keto acid **39**: IR ($CHCl_3$) 2100 (C=N^+=N^-), 1660 (–C=CC(O)–), 1645 cm^{-1} ($N_2HCC(O)$). It was dissolved in 5 mL of dry dioxane, added to 700 mL of cyclohexane, and irradiated for 2 h under a stream of dry nitrogen, followed successively by infrared. The solvents were removed under pressure, and the crude product was purified on a florisil column (60 g) eluted with methylene chloride–hexane 1:2; 250 mg (30%) of **41** was collected: bp 95 °C (0.2 mm); IR ($CHCl_3$) 1778 ($\overline{CH_2CH_2CH_2C}$=O), 1698 cm^{-1} (–C(O)–); NMR ($CDCl_3$) δ 1.16 (d, 3 H), 2.57 (m, 3 H), 2.94 (m, 1 H); MS for $C_{14}H_{18}O_2$ at 218 (theory 218). Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 77.06; H, 8.15.

Irradiation of Diazo Ketone 43. Diazo ketone **43** was prepared as usual from acid **42**:[45,41] IR ($CHCl_3$) 2100 (C=N^+=N^-), 1660 (–C(O)C=C–), 1635 cm^{-1} ($N_2HCC(O)$). **43** (100 mg) was dissolved in 5 mL of dry dioxane, added to 150 mL of cyclohexane, and irradiated for 1 h. The oil obtained after removal of the solvents was distilled at 60 °C (0.3 mm), yielding 34 mg (34%) of diketone **44**: IR ($CHCl_3$) 1774 ($\overline{CH_2CH_2CH_2C}$=O), 1725 cm^{-1} (–C(O)–); MS for $C_{13}H_{18}O_2$ 206.1308 (theory 206.1307).

Methyl 6-Methyl-1-Cyclohexene-1-butyrate (46b). The keto ester (5.0 g) of acid **13** was dissolved in 150 mL of chloroform. To the cooled solution (0 °C) were added 7 mL of boron trifluoride etherate and 7 mL of 1,2-ethanedithiol. After the usual workup there was obtained 6.5 g of the corresponding thioketal: IR ($CHCl_3$) 1730 (C(O)OMe); NMR ($CDCl_3$) δ 0.97 (d, 3 H), 3.30 (s, 4 H), 3.63 (s, 3 H), 5.33 (s, 1 H). The thioketal without further purification was dissolved in 200 mL of absolute methanol. To the stirred solution was added 5 cups of Raney Nickel W2, and the mixture was refluxed for 4.5 h. Filtration through Celite and removal of the solvent yielded 4.7 g of **46b**: bp 60 °C (0.8 mm); IR ($CHCl_3$) 1734 (C(O)OMe), 1602 cm^{-1} (–C=C–); NMR ($CDCl_3$) δ 1.07 (d, 3 H), 3.70 (s, 3 H), 5.50 (broad s, 1 H); MS for $C_{12}H_{20}O_2$ at 196.1476 (theory 196.1463). Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.48; H, 10.31.

Methyl 5,6,7,8-Tetrahydroindan-8-propionate (48b). To a solution of 5.7 g (22.5 mmol) of the keto ester of acid **4** in 150 mL of chloroform were added 7.5 mL of boron trifluoride etherate and 7.5 mL of 1,2-ethanedithiol in a 250 mL ice-cooled flask. After 24 h, 30 mL of 10% potassium hydroxide was added, and workup was performed as usual, affording 9.3 g of the corresponding thioketal: IR ($CHCl_3$) 1740 cm^{-1} (C(O)OMe); NMR ($CDCl_3$) δ 3.36 (s, 4 H), 3.70 (s, 3 H), 5.33 (s, 1 H). The thioketal without further purification was reduced with Raney Nickel W2 as described for **46a**. **48b** (4 g) was obtained after distillation: bp 60 °C (0.1 mm); IR (CCl_4) 1725 cm^{-1} (C(O)OMe); NMR ($CDCl_3$) δ 3.70 (s, 3 H), 5.40 (s, 1 H); MS for $C_{13}H_{20}O_2$ at 208 (theory 208). Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.46; H, 9.80.

2,3,4,5,6,7,8,10-Octahydro-8-oxonaphthalene-10-propionic Acid (51). To a cooled (15 °C) and stirred solution of 1.7 g (7 mmol) of keto ester **53**[43] were added dropwise 3 mL of 30% hydrogen peroxide and 2 mL of 6 N sodium hydroxide during 0.5 h. The temperature was kept below 25 °C, and the solution was stirred for an additional 4 h, poured into 100 mL of water, and extracted with chloroform. The aqueous solution was cooled and acidified to pH 6.25. Extraction with chloroform yielded the crude acid of **54**, which was crystallized from isopropyl ether: mp 141–143 °C; total yield 1.2 g; IR ($CHCl_3$) 2500–3400 (acid), 1710 cm^{-1} (–C(O)–); NMR ($CDCl_3$) δ 2.95 (s, 1 H), 10.40 (1 H). The methyl ester **54** was prepared as usual: IR ($CHCl_3$) 1724 cm^{-1} (C(O)OMe); NMR ($CDCl_3$) δ 2.93 (s, 1 H), 3.73 (s, 3 H); MS for $C_{14}H_{20}O_4$ at 252.1361 (theory 252.1365). Anal. of acid calcd for $C_{13}H_{18}O_4$: C, 65.53; H, 7.61. Found: C, 65.38; H, 7.65.

To 1.2 g (4.5 mmol) of the keto acid of ester **54** dissolved in 300 mL of methanol was added, under nitrogen and with magnetic stirring, 60 mL of 4 N sodium hydroxide, and the mixture was boiled for 2.5 h. Water (100 mL) was added and the methanol removed. The cooled solution was acidified with 10% hydrochloric acid until pH 6.2 with a total yield 1.1 g of **55**: IR ($CHCl_3$) 2350–3500 (acid), 1714 (–C(O)–), 1674 (–C=CC(O)–), 1614 cm^{-1} (–C=C–). The methyl ester **56** was prepared with an excess of diazomethane, bp 100 °C (0.1 mm). The crude keto ester **56** (2.5 g) was purified on a florisil column eluted with methylene chloride–hexane 1:1: 1.3 g was collected; IR ($CHCl_3$) 1730 (C(O)OMe), 1624 (–C=CC(O)–), 1610 cm^{-1} (–C=C–); NMR ($CDCl_3$) δ 3.73

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(s, 3 H), 3.63 (s, 3 H); UV (MeOH) λ_{max} 254 nm (ϵ 3320); MS for $C_{13}H_{22}O_4$ at 266.1498 (theory 266.1518). Anal. Calcd for $C_{15}H_{22}O_4$: C, 67.64; H, 8.33. Found: C, 67.35; H, 8.24.

56 (290 mg) was dissolved in 35 mL of dry THF, to the stirred solution was added 900 mg of sodium borohydride, and the mixture was refluxed for 2.5 h. Water (150 mL) was added and the organic solvent removed. The aqueous phase was extracted with methylene chloride, yielding 284 mg of **57**: IR ($CHCl_3$) 3300–3500 (OH), 1734 cm^{-1} (C(O)OMe); NMR ($CDCl_3$) δ 3.53 (s, 3 H), 3.62 (s, 3 H), 4.27 (1 H); mass spectrum peak for $C_{15}H_{24}O_4$ at 268.1674 (theory 268.1676).

To a stirred solution of 100 mg of **57** in 6 mL of methylene chloride was added 2–3 drops of 70% perchloric acid.[46] The mixture stood at room temperature for 1 h, and a saturated solution of sodium bicarbonate was added until the solution was basic. The organic phase was separated and dried over anhydrous magnesium sulfate. After removal of the solvents, 95 mg of crude **58** was obtained. The yield (90 mg) was purified on a silica gel preparative plate, yielding 57 mg (65%) of pure **58**: bp 85 °C (0.01 mm); IR ($CHCl_3$) 1730 (C(O)OMe), 1680 (-C=CC(O)-), 1620 cm^{-1} (-C=C-); NMR ($CDCl_3$) δ 3.63 (s, 3 H), 6.40 (t, 1 H); MS for $C_{14}H_{20}O_3$ at 236.1412 (theory 236.1412); UV (MeOH) λ_{max} 243 nm (ϵ 8100). Anal. Calcd for $C_{14}H_{20}O_3$: C, 71.16; H, 8.53. Found: C, 71.16; H, 8.51.

Keto ester **58** (120 mg) was hydrolyzed with 10 mL of 10% sodium hydroxide in a mixture of 1:1 methanol–water. After 2 h of reflux under nitrogen, 15 mL of water was added and the methanol removed. The aqueous solution was extracted with chloroform which was dried, filtered, and evacuated, yielding 86 mg of acid **51**, mp 102.5–103.5 °C, crystallized from isopropyl ether: IR ($CHCl_3$) 2300–3500 (acid), 1705 (-C(O)-), 1660 (-C(O)C=C-), 1618 cm^{-1} (-C=C-).

Diazo ketone **52** was prepared as usual from 400 mg of **51** and purified on a water-cooled florisil column, affording 230 mg of purified **52**: IR ($CHCl_3$) 1634, 2109 ($C(O)CHN_2$), 1674 cm^{-1} (-C(O)C=C-); NMR ($CDCl_3$) δ 5.30 (s, 1 H), 6.50 (t, 1 H).

Methyl 2-Acetoxy-1-Cyclohexene-1-butyrate (59). To a stirred solution of 2.0 g (10 mmol) of the known[47] keto ester in 10 mL of carbon tetrachloride were added 4.6 g of anhydrous acetic acid and 0.01 mL of 70% perchloric acid. Stirring was continued for 1 h, and workup was performed as for **36**. Distillation of the crude product yielded 1.9 g (80%) of **59**: bp 95 °C (0.1 mm); IR ($CHCl_3$) 1734 (ester); NMR (CCl_4) δ 2.67 (s, 3 H), 3.64 (s, 3 H); MS for $C_{12}H_{20}O_4$ at 240.1372 (theory 240.1361). Anal. Calcd for $C_{13}H_{20}O_4$: C, 64.98; H, 8.39. Found: C, 65.23; H, 8.35.

Methyl 6-Oxo-1-cyclohexene-1-butyrate (60b). To a stirred solution of 4.54 g (2.2 mmol) of keto ester[47] in 20 mL of carbon tetrachloride was added dropwise 9.0 g (66 mmol) of sulfuryl chloride diluted to twice its volume with carbon tetrachloride. After 4 h at room temperature, the solution was washed with 200 mL of water, 10 mL of saturated sodium bicarbonate, and brine. The solution was dried and filtered and the solvent evaporated, yielding 6.0 g of yellow oil which without further purification was dehydrochlorinated with 10 mL of collidrine at 145 °C for 0.5 h under nitrogen. The solution was diluted with 100 mL of petroleum ether (60–70 °C), the collidine hydrochloride was filtered, and the organic layer was washed with water, sodium bicarbonate solution, and brine. Crude **60b** (3.8 g) was obtained and purified on a silica gel column eluting with methylene chloride–hexane 1:2: total yield 2.1 g (55%); IR ($CHCl_3$) 1734 (C(O)OMe), 1670 (-C(O)CC-), 1618 cm^{-1} (-C=C-); NMR ($CDCl_3$) δ 3.62 (s, 3 H), 6.70 (t, 1 H); MS for $C_{10}H_{16}O_3$ at 196 (theory 196).

Alternative Route to 60b.[26] **59** (1 g) was dissolved in 50 mL of glacial acetic acid in an electrochemical cell fitted with two graphite electrodes and a magnetic stirrer. *tetra*-Ethylammonium tosylate (1 g) was added, and a current of 100 mA was set for 26 h. The mixture was poured into 300 mL of ether and washed with a saturated solution of sodium bicarbonate until all the acetic acid was neutralized. The ethereal layer was washed with water, and brine and dried. Removal of the solvent yielded 880 mg of crude **60b**, which was purified on silica gel preparative plates with a total yield 560 mg (70%).

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6-Oxo-1-cyclohexene-1-butyric Acid (60a). 60b (100 mg) was hydrolyzed with 50 mL of a 1:1 mixture of methanol–water and 0.5 g of potassium hydroxide overnight under nitrogen at room temperature. The methanol was removed, and the aqueous phase was extracted with chloroform, yielding 95 mg of the expected acid **60a**, which was crystallized from isopropyl ether: mp 57.5–58 °C; IR ($CHCl_3$) 2350–3400 (acid), 1712 (-C(O)-), 1670 (-C=C-C(O)-), 1620 cm^{-1} (-C=C-).

Irradiation of Diazo Ketone 60c. Diazoketene **60c** was prepared in the usual way. It was purified on a florisil column eluting with 1:1 methylene chloride–hexane: yield 60%; IR ($CHCl_3$) 2109 (N≡N), 1664 (-C(O)C=C-), 1640 cm^{-1} ($C(O)CHN_2$). Purified diazo ketone (130 mg) was dissolved in 5 mL of dry dioxane, added to 150 mL of dry cyclohexane, and irradiated for 25 min (the peak of the diazo ketone disappeared in IR). Removal of the solvents yielded an oil which was purified on a silica gel preparative plate. Pure **61** (47 mg, 39%) was collected and recrystallized from petroleum ether–hexane: mp 46–47 °C; IR ($CHCl_3$) 1784 ($\overline{CH_2CH_2CH_2C=O}$), 1694 cm^{-1} (-C(O)-); NMR ($CDCl_3$) δ 3.53 (1 H), 3.13 (1 H); MS for $C_{11}H_{14}O_2$ at 178.0993 (theory 178.0885). Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.25; H, 8.03.

Basic Cleavage of 61. Diketone **61** (30 mg) was dissolved in 5 mL of a 1:1 solution of methanol–water under a nitrogen atmosphere. The mixture was stirred, and a 10% solution of potassium hydroxide was added at room temperature. After 24 h, the methanol was removed, and the aqueous phase was acidified with dilute hydrochloric acid and extracted twice with 25 mL of chloroform. The organic solution was dried over magnesium sulfate and filtered. The product isolated was identified as the starting diketone **61**. The same experiment was conducted but with refluxing for 2 h. After isolation of the organic material, it was found by TLC and IR that no cleavage had occurred.

Methyl 2,3,4,5,6,10-Hexahydro-2-oxonaphthalene-10-propionate (62b). The keto ester of acid **7** (560 mg) was dissolved in 70 mL of dry *tert*-butyl alcohol. Chloranil (3 g) was added, and the solution was refluxed under nitrogen for 3 h. The reaction mixture was filtered through Celite and the solvent removed under reduced pressure. The yellow oil which was obtained was dissolved in chloroform and washed twice with 40 mL of water, twice with 20 mL of 5% sodium hydroxide, and again with water. The organic layer was dried over anhydrous sodium sulfate and the solvent removed, yielding 500 mg (90%) of keto ester **62b**: bp 105 °C (0.04 mm); IR ($CHCl_3$) 1732 (C(O)OMe), 1654 (-C(O)-C=C-), 1627 cm^{-1} (-C=C-); NMR ($CDCl_3$) δ 3.70 (s, 3 H), 5.76 (1 H), 6.23 (2 H); UV (MeOH) λ_{max} 279 nm (ϵ 19350); MS for $C_{14}H_{18}O_3$ at 234 (theory 234). The dinitrophenylhydrazone was prepared, mp 175–175.5 °C, after crystallization from methanol–methylene chloride: MS for $C_{20}H_{22}O_6N_4$ at 414 (theory 414). Anal. Calcd for $C_{20}H_{22}O_6N_4$: C, 57.96; H, 5.35; N, 13.52. Found: C, 57.85; H, 5.41; N, 13.61.

Keto ester **62b** (270 mg) was hydrolyzed as for **60b**, yielding 230 mg (85%) of crude acid **62a**: IR ($CHCl_3$) 2500–3500 (acid), 1720 (-C(O)-), 1657 (-C(O)C=C-), 1625 cm^{-1} (-C=C-).

Irradiation of Diazo Ketone 63. Diazo ketone **63** was prepared from 540 mg of **62a**: IR ($CHCl_3$) 2107 ($C(=N^+=N^-)$), 1654 cm^{-1} (-C(O)C=C-, $N_2HCC(O)$). It was dissolved in 10 mL of dry dioxane, added to 800 mL of cyclohexane, and irradiated for 20 min, yielding 540 mg of crude product which was purified on a florisil column (80 g) eluted with 1:1 methylene chloride–chloroform: 160 mg (29%) of purified **64** were collected; IR ($CHCl_3$) 1783 ($\overline{CH_2CH_2CH_2C=O}$), 1707 (-C(O)), 1623 cm^{-1} (-C=C-); NMR ($CDCl_3$) δ 3.40 (m, 1 H), 5.37 (1 H), 6.0 (1 H); MS for $C_{14}H_{18}O_2$ at 216.1150 (theory 216.1166).

Baeyer–Villiger Reaction on 9. **9** (45 mg) was dissolved in 1 mL of 90% aqueous acetic acid, and to the cooled solution was added 65 mg of 30% hydrogen peroxide diluted in 1 mL of 90% aqueous acetic acid. The mixture was stirred for 24 h at 0 °C and then extracted with ether, which was mixed with 10% sodium bisulfite and sodium bicarbonate solution. A crystalline product was isolated after removal of the solvent and crystallized from isopropyl ether: mp 137 °C; yield 70%; IR ($CHCl_3$) 1784 (five-membered lactone); 1720 cm^{-1} (-C(O)-); NMR ($CDCl_3$) δ 2.93 (s, 2 H), 1.40–2.00 (16 H); MS for $C_{14}H_{18}O_3$ 234.1255 (theory 234.1257).

Registry No. 1, 33948-32-2; 2, 38431-97-9; 3, 38432-00-7; 4, 71988-25-5; 4 methyl ester, 71988-26-6; 4 methyl ester, thio ketal, 71988-27-7; 5, 71988-28-8; 6, 71988-29-9; 7, 71988-30-2; 7 dinitrophenylhydrazone, 71988-31-3; 8, 38431-96-8; 9, 38431-99-1; 10, 71988-32-4; 11, 38431-98-0; 12, 38432-01-8; 13, 7499-70-9; 13 methyl ester, 57234-61-4; 13 methyl ester, thio ketal, 71988-33-5; 14, 57234-59-0; 15, 57234-63-6; 26, 4594-78-9; 27, 71988-34-6; 28, 71988-35-7; 29, 71988-36-8; 30a, 71988-37-9; 30b, 71988-38-0; 31, 71988-39-1; 32, 71988-40-4; 33, 71988-41-5; 35, 13672-62-3; 36, 71988-42-6; 37a, 54996-34-8; 37b, 57155-71-2; 39, 71988-43-7; 39 methyl ester, 71988-44-8; 40, 71988-45-9; 41, 71988-46-0; 42, 71988-47-1; 43, 71988-48-2; 44, 71988-49-3; 46b, 71988-50-6; 48b, 71988-51-7; 51, 71988-52-8; 52, 71988-53-9; 53, 15070-50-5; 54, 71988-54-0; 54 acid, 71988-55-1; 55, 71988-56-2; 56, 71988-57-3; 57, 71988-58-4; 58, 71988-59-5; 59, 71988-60-8; 60a, 19214-14-3; 60b, 71988-61-9; 60c, 71988-62-0; 61, 71988-63-1; 62a, 71988-64-2; 62b, 71988-65-3; 62b dinitrophenylhydrazone, 71988-66-4; 63, 71988-67-5; 64, 71988-68-6; 65, 71988-69-7; 2-oxocyclopenta-β-propionitrile, 4594-77-8; methyl vinyl ketone, 78-94-4; butylmercaptan, 109-79-5; methallyl chloride, 563-47-3; ethyl vinyl ketone, 1629-58-9; 1,2-ethanedithiol, 540-63-6.

Photocycloaddition Reactions of Norbornadiene and Quadricyclane with *p*-Benzoquinone

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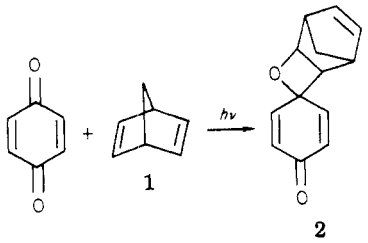
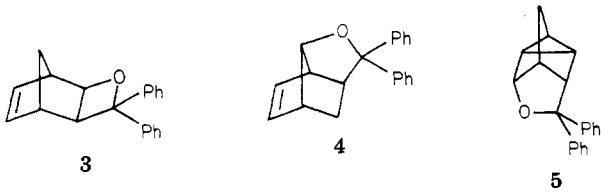
The photocycloaddition reactions of norbornadiene and its valence isomer quadricyclane with *p*-benzoquinone have been studied and compared. Irradiation of a solution of norbornadiene and *p*-benzoquinone in benzene yielded a mixture of the four isomeric 1:1 adducts **7**, **8**, **9**, and **10** in a ratio of ~48:16:21:15, respectively. Irradiation of a solution of quadricyclane and *p*-benzoquinone in benzene under similar conditions yielded a product mixture which consisted almost exclusively of the two exo adducts **7** and **8** in a ratio of ~56:44, along with traces of the endo adducts **9** and **10**. Chemical and spectroscopic evidence for the structures of the products is presented, and reaction pathways are proposed to account for their formation and for the different product distributions obtained from norbornadiene and quadricyclane.

Although photocycloaddition reactions of alkenes with carbonyl compounds have been extensively investigated,[1] only a few examples of reactions involving the photocycloaddition of a carbonyl compound to norbornadiene (**1**) have been described in the literature. In 1967 Bryce-Smith, Gilbert, and Johnson reported that the photoaddition of *p*-benzoquinone to norbornadiene gave the spirooxetane **2** in 22% yield as the only isolable product.[2] A

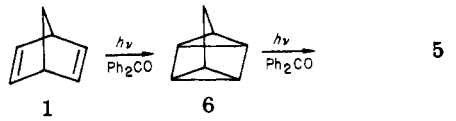


1 2

few years later, Kubota, Shima, and Sakurai reported that irradiation of a solution of benzophenone and norbornadiene in benzene led to the formation of the adducts **3**, **4**, and **5** in yields of 32, 15, and 3%, respectively.[3] A kinetic study of the latter reaction subsequently revealed that these adducts actually resulted not from the addition of benzophenone to norbornadiene but from addition of the excited ketone to quadricyclane (**6**), generated in situ by benzophenone-sensitized photoisomerization of **1**.[4]



3 4 5



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Consequently, the same cycloaddition products and the same product-distribution ratios were obtained when either norbornadiene or quadricyclane was irradiated in the presence of benzophenone under similar conditions.

Since efficient photosensitized isomerization of **1** to **6** requires sensitizers with triplet energies of at least 65–70 kcal mol^{-1} (e.g., benzophenone, $E_T \approx 69$ kcal mol^{-1}, and acetophenone, $E_T \approx 74$ kcal mol^{-1}),[5] *p*-benzoquinone ($E_T \approx 50$ kcal mol^{-1}) cannot serve effectively as a sensitizer for this photoisomerization. It seems likely, therefore, that adducts such as **2** formed in the irradiation of *p*-benzoquinone–norbornadiene mixtures result from the direct attack of quinone triplets on ground-state norbornadiene.[6] If this is true, it would be anticipated that different

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