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Photochemical Cycloaddition of Cyclohexenone and Cyclopentenone to Conjugated Dienes[1a]

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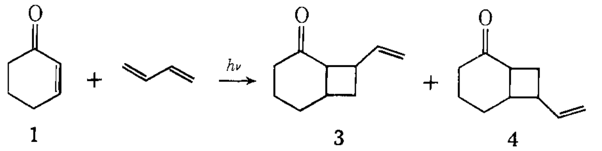
Cyclohexenone (1) and cyclopentenone (2) have been found to undergo [2 + 2] photochemical cycloaddition to conjugated dienes with moderate efficiency when the diene concentration is high, accounting for the erratic results sometimes obtained when certain 1,3-dienes are used as triplet quenchers for such enones. The products are mixtures of cyclobutanes resulting from [2 + 2] cycloaddition; in the addition of 1 and 2 to cyclopentadiene, the ratio of head-to-head to head-to-tail adducts was ~3:2. In the case of furan, a [4 + 2] cycloadduct was produced, as well as the usual [2 + 2] adducts. The experimental data are consistent with a mechanism involving attack of enone triplets on ground-state diene molecules.

The photochemical annelation of cyclic enones with unactivated olefins, developed only within the past decade,[2] has been the subject of recent intense interest with regard to its scope and mechanism. It is generally agreed that the reactive enone excited state is a triplet,[2b,3] that the annelation is nonconcerted, a radical- or diradical-like intermediate being involved, possibly preceded by complex formation between enone excited state and ground-state olefin.[3d,e,4] The reaction is usually limited to five- and six-membered cyclic enones, but these may bear certain substituents.[4] Such enones have been successfully added to olefins possessing a wide variety of either saturated or unsaturated substituents. It has been generally believed, even though no experimental observations appear to have been published, that enones add to conjugated dienes either not at all, or at best very inefficiently.[5] This seems reasonable, since energy transfer from the enone triplet excited states (E_T = 66–72 kcal) to a 1,3-diene (E_T = 53–60 kcal) should be exothermic by 6–20 kcal and therefore a rapid diffusion-controlled process, resulting in quenching of the enone triplet and production of diene triplets. Indeed, a powerful tool in mechanistic photochemistry, especially that of enones and dienones, has been the use of dienes such as 1,3-pentadiene and 1,3-cyclohexadiene as quantitative quenchers of triplet states of $E_T > 60$ kcal.[6]

Apparent exceptions have appeared. Schenck reported several years ago the benzophenone-sensitized addition of maleic anhydride ($E_T \cong 72$ kcal[7]) and dimethylmaleic anhydride to various dienes and trienes to give mixtures of [2 + 2] and [4 + 2] adducts.[8] Irradiation of duroquinone in the presence of dienes leads to both [2 + 2] and [4 + 2] adducts, as well as their products of further transformation;[9] however, transfer of triplet energy to the dienes should be inefficient here, since the quinone probably has $E_T \leq 50$ kcal. Also pertinent is the observation that saturated aldehydes and ketones undergo photoaddition to dienes to give vinyl oxetanes.[10] However, the evidence available implicates the intermediacy of carbonyl compound excited *singlet* states. On the other hand, Barltrop and Carless have very recently reported the isolation of photoadducts (oxetanes) from benzophenone and several 1,3-dienes, including 1,3-butadiene.[11] The oxetanes were formed inefficiently at the relatively low diene concentrations used (Φ = 0.0003 in 0.3–0.5 *M* diene) but were shown to arise from addition of ketone triplets to ground-state diene molecules. Finally, eucarvone (a 2,4-cycloheptadienone) has been reported to form [2 + 2] photoadducts with 1,3-dienes *via* triplet states.[12]

Results

We report here our observations that 2-cyclohexenone (1) and 2-cyclopentenone (2) do in fact undergo photochemical cycloaddition to several 1,3-dienes, usually in the [2 + 2] manner, and in the case of enone 1, with surprisingly high efficiency. By use of a large excess of the diene (≥10-mol excess) it is possible to obtain on a preparative scale good yields of most of the adduct mixtures under conditions of high conversion. For example, irradiation of 0.05 mol of 1 in the presence of a 20-fold excess of 1,3-butadiene gave an isolated yield of 72% of the adduct mixture of gross structures 3 and 4. In Table I are listed yields of adducts from irradiation of 1 and 2 with several representative dienes; these reactions were all run to essentially complete consumption of enone. There is usually observed concomitant formation of the diene dimers resulting from energy transfer from enone triplets to diene.[5] In those cases where this is a fairly efficient process, such as with 1 and 1,3-cyclohexadiene, there is a rapid early buildup of diene dimer and most of the enone is consumed by cycloaddition to the diene dimers.



1 3 4

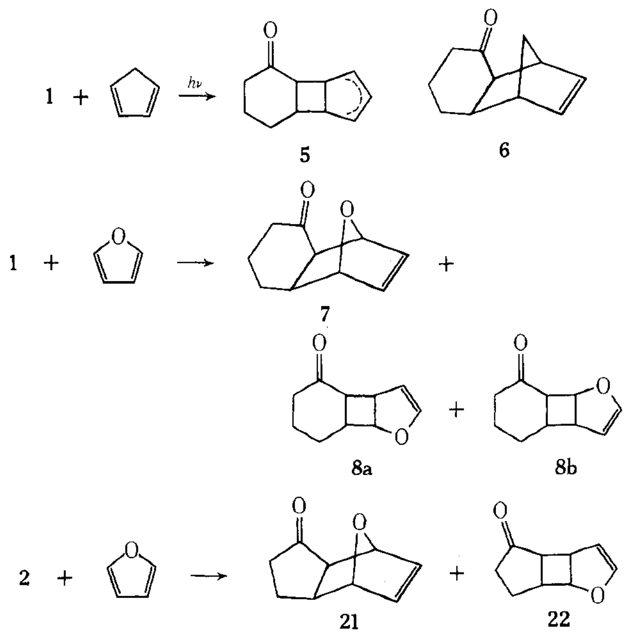
five isomers

The adduct mixtures from all dienes except furan and cyclopentadiene were shown in each case to contain only

Table I

Registry no.	Diene	Yield of adducts, %[a]	Relative efficiency[b]	Number of adducts	Ratio
		Photoadditions of 1[c]			
110-83-8	Cyclohexene		1.00	⩾3	
106-99-0	1,3-Butadiene	72	0.65	5	24:38:17:16:5
542-92-7	1,3-Cyclopentadiene	47	0.41	4	48:16:21:15
592-57-4	1,3-Cyclohexadiene	16	~0.3–0.35	⩾3	60:31:9
544-25-2	1,3,5-Cycloheptatriene	30	0.04	2	25:75
1700-10-3	1,3-Cyclooctadiene	78	0.58	3	13:70:17
27140-13-2	Spiro[2,4-hepta-2,5-diene]	55	0.5	3	
110-00-9	Furan	63	0.6	3	45:32:23
592-46-1	2,4-Hexadiene	40		⩾4	
111-78-4	1,5-Cyclooctadiene	66	0.7	2	29:71
		Photoadditions of 2[c]			
	1,3-Butadiene	32	0.10	3	
	Cyclopentadiene	27	0.14	2	37:63
	1,3-Cyclooctadiene	56	0.38	3	15:62:23
	Furan	47	~0.5	2	80:20

[a] Satisfactory elemental analyses and mass spectral molecular weight data were obtained on all adduct mixtures, and on individual compounds when the mixtures were resolvable. [b] Efficiency of addition to cyclohexene as standard; to obtain quantum yields for additions to dienes, multiply efficiencies by cyclohexene quantum yield ($\Phi = 0.45$) under identical conditions; compare ref 3e. [c] Standard conditions: [enone] = 0.25 *M*; [diene] = 5.0 *M*. Runs were carried to ⩽8% completion.

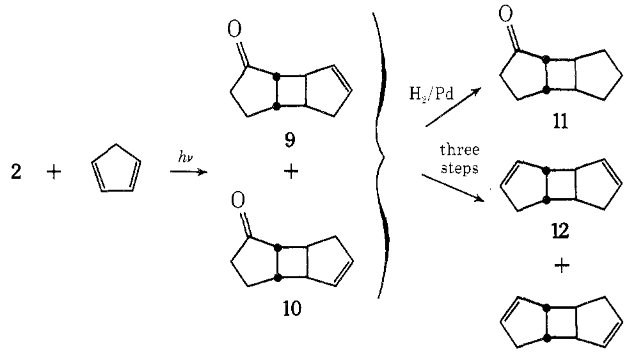


compounds resulting from [2 + 2] cycloaddition processes by the simple procedure of hydrogenation of the adducts and comparison of the resulting saturated ketones with those obtained by addition of **1** and **2** to the corresponding monoolefins. In some cases the individual components were isolated before hydrogenation, whereas in others the identification was simpler after hydrogenation, since the number of isomers was thus reduced by a factor of approximately 2. The composition of all product mixtures was checked at varying stages of completion and was found to be unchanged throughout the course of the reactions.

It would be anticipated that 1,4-addition would be most favorable in the case of a planar, cisoid 1,3-diene, such as cyclopentadiene or furan. In fact, **2** adds to cyclopentadiene entirely in the [2 + 2] fashion (*vide infra*) and **1** adds [2 + 2] to the extent of at least 85%. In the mixture from irradiation of **1** and cyclopentadiene, two of the four products were converted on hydrogenation to the known[3a] cis adduct of **1** and cyclopentene, and a third was reducible to the corresponding trans adduct. The fourth component of the product mixture, present to the extent of ~15% and not obtained entirely pure, exhibited nmr data [*inter alia*, signals at τ 3.9 (2 H, m) and for bridge methylene at 8.6 (2 H, m)], which are consistent with its formulation as a norbornene derivative (**6**). This material was not identical with the thermal [4 + 2] adduct of **1** and cyclopentadiene, prepared in low yield by heating the reactant at 170°. However, the thermal adduct is probably the isomer with the cyclohexanone ring fused endo,endo to the norbornene frame, whereas the photoadduct probably arises *via* a radical route (*vide infra*) not governed by orbital symmetry considerations and could have a different stereochemistry. Finally, if the adduct is the result of thermal addition of cyclopentadiene to a strained, photochemically produced trans enone, it should be one of the two trans-fused exo,endo isomers.[13]

Irradiation of **1** or **2** in furan resulted in both [2 + 2] and [4 + 2] addition. The stereochemistry of the [4 + 2] adducts, *e.g.*, **7**, is a matter of some interest since a trans ring fusion would imply the intermediacy of a strained ground-state trans enone *via* thermal [4 + 2] addition. However, the [4 + 2] adducts from **1** and **2** and furan proved to be thermally unstable and on attempted gas chromatographic purification underwent retro Diels–Alder reaction, reverting to **1** and **2**, respectively, and furan. The presence of **7** in the product mixture from **1** and furan was clear from the spectral properties of the mixture, the nmr signals for **7** at τ 3.7 (2 H, A part of AA′XX′), 5.1 and 5.4 (1 H each, broad singlets, -CHO-), and 6.5 (2 H, m, $-CH_2C{=}O$) being clearly separated from those attributable to **8a** at τ 3.6 (1 H, 2 d, $J = 7.4$, $J' = 4.2$ Hz, -OCH-) and 6.7 (2 H, m, $-CH_2C{=}O$) and to **8b**. The major [2 + 2] adduct, **8a**, obtained pure by gc, was identified by comparison of the product of its hydrogenation over palladium on charcoal with the major photoadduct from **1** and 2,3-dihydrofuran. Similarly, reduction of the major [2 + 2] adduct from **2** and furan gave a compound identical with the adduct of **2** and 2,3-dihydrofuran.

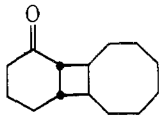
The addition of **2** to cyclopentadiene gave two products, **9** and **10**, in a 63:37 ratio. That these were [2 + 2] adducts differing only in the position of the double bond was shown by their conversion upon catalytic hydrogenation to the same saturated tricyclic ketone, **11**, identical with the adduct of **2** and cyclopentene, whose structure has been established as being the anti [2 + 2] product.[14]



The orientation of the adducts from 2 and cyclopentadiene, and also from 1 and 1,3-cyclohexadiene, was established by a combination of chemical degradation and synthesis. The adduct mixtures were converted to diolefins by a three-step sequence of (1) reduction with lithium aluminum hydride, (2) conversion to the corresponding secondary tosylates, and (3) elimination with *tert*-butoxide. The individual diolefins 12 and 13 were separated by gc and compared with authentic samples prepared by similar sequences from the photodimers of 1 and 2 whose structures have been rigorously proved.[15] In this way it was shown that the ratio of "head-to-head" to "head-to-tail" adducts from 2 and cyclopentadiene (9 and 10) was 63:37. Application of this method to the adduct mixture from 1 and 1,3-cyclohexadiene resulted in the isolation of the two major diolefins from the mixture, which were found to be identical with samples produced by degradation of the two *major* photodimers of 1.[15b] The two major adducts from 1 and 1,3-cyclohexadiene were formed in a head-to-head:head-to-tail ratio of 69:31.

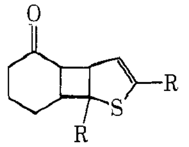
The predominance of head-to-head adducts is at first somewhat surprising, since the π-complex rule of orientations in photochemical cycloadditions would predict that in the more favored complex the more electron-rich terminal carbon of the diene should lie nearest C-2 of the enone, giving rise to head-to-tail adducts. The orientational selectivities observed here are not large in either case, and predictive rules appear irrelevant. However, the concept of the stability of the presumed biradical intermediate may have mechanistic implications here, if not predictive power. Since initial bond formation to the diene almost certainly takes place at one of the terminal diene carbons, it might appear that initial bonding to the enone occurs to an appreciable extent at both C-2 and C-3, with that at C-3 predominating. The only experimental results yet available having a bearing on the site of initial bonding to enone in photocycloadditions indicate that in the case studied (2 to the symmetrical substrate 1,2-dichloroethylene) bonding occurs initially entirely at C-3.[16] The quantitative validity of this result has been questioned, however.[2b] Further, the initial bonding step may be reversible, in which case no conclusions can be drawn from the orientations observed here.

The product yields and relative quantum yields in the photochemical cycloaddition of 1 and 2 to the other dienes studied are given in Table I and do not require further comment. The facile addition of 1 to 1,3-cyclooctadiene was unsurprising and was expected even before the fact, since this twisted diene probably has a triplet energy of 70-72 kcal[17] and energy transfer from enone triplets should be endothermic and thus not favored. The addition of 1 and 2 to 1,5-cyclooctadiene was studied in order to search for products resulting from 1,5-cyclization of the presumed diradical intermediate. 1,5-Cyclooctadiene undergoes bridging during the addition of many, but not all, radicals to yield 2,6-disubstituted bicyclo[3.3.0]octanes.[18] In fact, the two adducts, formed in a 42:58 ratio by photochemical addition of 1 to 1,5-cyclooctadiene, were converted upon hydrogenation to two saturated tricyclic ketones. These proved to be identical with the two major adducts from 1 and cyclooctene itself, and must therefore by the cis- and trans-fused isomers of structure 14. Base-catalyzed equilibration experiments indicated the major (58%) isomer to be that possessing the cis 6:4 ring fusion.

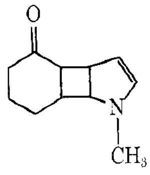


14

Finally, we studied the behavior of excited 1 toward thiophene, 2,5-dimethylthiophene, and *N*-methylpyrrole, and of carbostyril [(1*H*)-2-quinolone, 15] to furan. Irradiation of 1 in neat thiophene gave mainly dimers of 1, but there could be isolated by repeated fractional distillation 8% of an adduct whose spectral data indicate it to be the result of [2 + 2] addition of 1 to thiophene. The two vinyl hydrogens in the adduct's nmr spectrum appear at τ 3.84 and 4.41. In the spectrum of 2,3-dihydrothiophene itself H_4 and H_5 appear at τ 4.52 and 3.94.[19a] In 2,5-dihydrothiophenes with almost identical alkyl substituents on C-2 and C-5, such as 7-thianorbornenes, the vinyl hydrogens have almost identical chemical shifts.[19b] 2,5-Dimethylthiophene has been reported to be considerably more reactive than thiophene itself toward benzophenone triplets.[20] This difference in reactivity extended to excited 1 and we were able to isolate 43% of a mixture of [2 + 2] adducts, 17. The orientation of 16 and 17 was not experimentally determined, but was inferred by analogy with the orientation of 8 and 22, established as described earlier (*vide supra*).



16, R = H
17, R = CH$_3$



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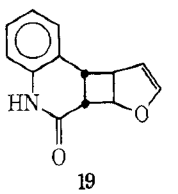
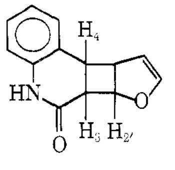
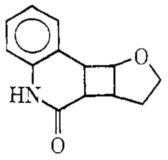


19

Irradiation of 1 in the presence of *N*-methylpyrrole gave a mixture of unstable adducts which underwent hydrolysis to give material whose ir and nmr spectra exhibited signals characteristic of aldehydic C-H bonds. This would appear to indicate the presence of an enamine function and, consequently, a [2 + 2] structure such as 18 for at least one of the adducts.

Irradiation of carbostyril in ethanol-furan mixtures gave the known carbostyril photodimer and a single adduct, 19, mp 201-202°; hydrogenation of this adduct gave dihydro-19, mp 194-195°. Photochemical addition of carbostyril to 2,3-dihydrofuran gave an adduct, 20, mp 174-175°, whose orientation and stereochemistry were assigned as shown by analogy with the known photoproduct from carbostyril and ethyl vinyl ether.[21] Compound 20 was in every respect





20

Table II

Diene concn, M^a	Ratio of diene dimers/adducts^b
0.12	0.28
0.25	0.35
0.50	0.48
1.0	0.90
2.0	1.8
4.0	3.2

[a] Enone concentration in all runs was 0.10 *M*. [b] Runs were carried to 8% completion.

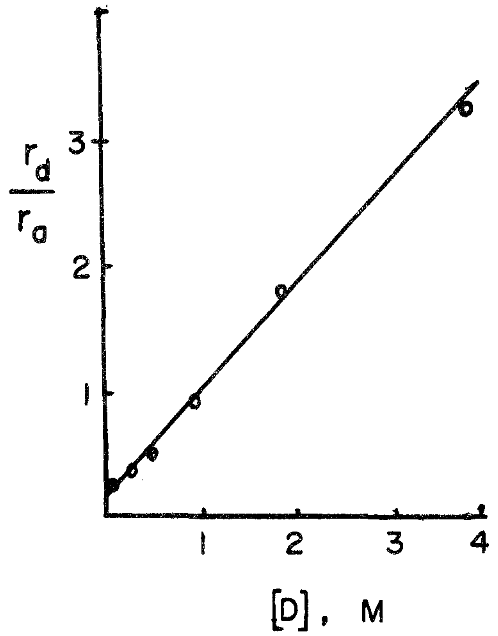


Figure 1. Plot of data in Table II.

different from dihydro-19, eliminating from consideration the anti, head-to-tail structure for **19**. That **19** possesses the orientation shown (head-to-head) was deduced from examination of its 220-MHz nmr spectrum. Previous workers have reported that in the nmr spectra (220 MHz) of adducts from carbostyril and several olefins, the signal due to H-3 appeared in every case at higher field (0.15–0.87 ppm) than that due to H_4. Consequently, we assign the signals at τ 6.28 and 6.51 in the spectrum of **19** to H-4 and H-3, respectively. When the spectrum was scanned while simultaneously irradiating the signal at τ 4.85, attributable only to the proton α to the furan oxygen (H-2′ in the formula below), the H-3 multiplet collapsed from a doublet of multiplets to a single multiplet. This demonstration that H-2′ and H-3 are strongly coupled (J = 7.4 Hz) leads to the above orientational assignment. In the photochemical additions of carbostyril examined by Evanega and Fabiny in which more than one adduct was isolated, analysis and decoupling experiments invariably indicated the major adduct to have the head-to-tail anti stereochemistry. One may conclude from this that photoexcited carbostyril adds initially at C-3, since excited triplet benzophenone adds to furan to give solely the product from reaction of the carbonyl oxygen with C-2 of furan.[22]

Finally, the rates of formation of both adducts and diene dimers were measured for the cyclohexenone–butadiene system at several diene concentrations. The data (Table II) show that the rate of adduct formation increases with increasing diene concentration, and that the rate of diene dimer production shows an even greater dependence on diene concentration. Interestingly, the ratio of these two rates showed an approximately linear dependence on diene concentration (Figure 1). Unfortunately, we have no quantitative explanation for this behavior. Since at least one step in the enone photoannelation process (and, presumably, in the dimer-forming process) is thought to be reversible,[23] the kinetics of these systems is quite complex. The photoannelation of enones with monoolefins is generally regarded as originating *via* excited triplet ketone;[2] it seems most likely that the presently observed adducts with dienes arise *via* a similar intermediate. However, a satisfactory analysis which accounts for both (a) the success of the adduct-forming process in competition with energy transfer to ground-state diene, and (b) why cyclopentenone adds more slowly to dienes than does cyclohexenone and yet gives diene dimers faster than **1** awaits the availability of additional quantitative data.

Experimental Section

General. All dienes were the purest grade commercially available and were freshly distilled before use in each case. The enones employed, 2-cyclopentenone and 2-cyclohexenone, were obtained from the Aldrich Chemical Co. and were redistilled under reduced pressure and stored at −20°. Gas chromatography indicated each to be >98% pure. Analytical gas chromatography was performed on the following columns: column A, 5 ft × 0.25 in., 5% SE-30 silicone rubber on Chromosorb P; column B, 5 ft × 0.25 in., 5% Carbowax 20M on Chromosorb P; column C, 10 ft × 0.25 in., 10% QF-1 fluorosilicone rubber on Chromosorb W; column D, 10 ft × 0.125 in., 5% Carbowax 20M on Chromosorb W; and column E, 12 ft × 0.125 in., 5% Apiezon L on Chromosorb P. Preparative gas chromatographic separations were accomplished on columns B and C, mentioned above, or on column F, 6 ft × 0.375 in., 20% SE-30 on Chromosorb P, and column G, 10 ft × 0.375 in., 20% Carbowax 20M on Chromosorb P. The instrument was a Varian Aerograph Model 202-1B, equipped with a thermal conductivity detector. Infrared spectra were obtained on a Beckman IR-8 instrument, while nuclear magnetic resonance spectra were determined on a Varian A56-60A instrument operating at 47°. Elemental analyses were performed by the Elek Co., Torrance, Calif.

General Procedure for Enone–Diene Photoadditions. The apparatus consisted of a cylindrical Pyrex vessel which surrounded a Pyrex immersion well and was fitted by means of side arms to a condenser and a small serum bottle cap. Ice water at 5–8° was circulated through the annular space of the Pyrex well and also through an external bath in which the apparatus was immersed. In irradiations involving 1,3-butadiene or cyclopentadiene, coolant at −25° was circulated through the immersion well in order to prevent loss of 1,3-butadiene by evaporation and to retard thermal dimerization of cyclopentadiene. Solutions of 0.02 mol of enone, 0.2–0.4 mol of diene, and sufficient benzene to give a total volume of *ca.* 100 ml were prepared and flushed with prepurified nitrogen for 1 hr. The solutions were then irradiated with a Hanovia 450-W medium-pressure mercury arc, under a slight positive pressure of nitrogen. The progress of the reactions was monitored by gas chromatographic or infrared spectral means. After evaporation of the excess diene, the residue was fractionally distilled to separate diene dimers and the adducts. In many cases (see below) individual components of the adduct mixtures could be isolated by preparative gc. Yields of adduct mixtures are given in Table I.

Cyclohexenone and 1,3-Butadiene. Irradiation of a solution of 2-cyclohexenone (**1**, 4.0 g, 0.040 mol) and freshly distilled 1,3-butadiene (56 g, 1.0 mol) made up to 200 ml in benzene for 4 hr resulted in the isolation of 5.4 g of butadiene dimers, bp 40–44° (16 mm), and the recovery of 0.6 g of unchanged cyclohexenone (**1**). The mixture of [2 + 2] cycloadducts, **3** and **4**, was obtained as a colorless, sweet-smelling oil: bp 50–52° (0.3 mm) (3.7 g, 72%); ir (film) 1722, 1709 cm^{-1} (C=O); nmr ($CDCl_3$) τ 3.8–4.5 (1 H, X parts of ABX's); 4.7–5.3 (2 H, AB portions of ABX's), and 7.0–8.7 (11 H, m); mass spectrum m/e (rel intensity) 150 (parent, 87), 121 (62), 93 (56), and 78 (100). *Anal.* Calcd for $C_{10}H_{14}O$: C, 80.04; H, 9.30. Found: C, 79.82; H, 9.17.

Analysis on column C showed five partially resolved peaks with areas in the ratio (in order of increasing retention time) 21:17:26:30:6.

A solution of the above-described cyclohexenone–butadiene adduct mixture (1.5 g, 0.010 mol) in ethyl acetate was shaken with 10% palladium on charcoal (0.10 g) under 2 atm hydrogen pressure until absorption had ceased (20 min). Filtration of the catalyst, evaporation of the solvent, and distillation gave the dihydro adduct mixture, bp 49–52° (0.3 mm) (1.3 g, 88%). A solution of this mixture in ether (50 ml) was stirred with neutral, activity I Woelm alumina for 44 hr. Filtration of the mixture and evaporation of the ether gave a colorless oil which showed three peaks on column D in the ratio 24:55:21.

Irradiation of a solution of 2-cyclohexenone (1, 1.0 g, 0.01 mol) and 1-butene (20 g, 0.50 mol) in benzene (90 ml) for 2 hr, followed by distillation of the solvent and excess 1-butene, gave an adduct mixture, bp 52–54° (0.5 mm), ir (film) 1710 cm^{-1}, *m/e* 152 (parent), which showed three peaks on columns D and E of the same retention times as those mentioned above, in the ratio 35:48:17.

Cyclohexenone and Cyclopentadiene. A solution of 2-cyclohexenone (4.0 g, 0.040 mol) and freshly distilled cyclopentadiene (66 g, 1.0 mol), made up in benzene to 220 ml, was irradiated at −20° for 3 hr. The solvent and excess cyclopentadiene were removed by evaporation under reduced pressure, maintaining the reaction mixture at 0° or below. Fractional distillation gave the following fractions: (A) cyclopentadiene dimers, bp 32–36° (5 mm), 6.1 g; (B) a mixture of adducts, bp 72–74° (0.3 mm), 4.7 g (0.026 mol. 66%); and (C) a fraction. bp 150–160° (0.2 mm), 0.9 g, which appeared to be composed of adducts of 1 with cyclopentadiene dimers. The 1:1 adduct mixture, fraction B (5 and 6), showed the following spectral data: ir (film) 1710 (s) and 1601 cm^{-1} (w); nmr (CCl_4) τ 3.9–4.4 (2 H, m), 6.7 (1 H, m), 6.9 (1 H, m), and 7.4–8.6 (10 H, m, $-CH_2$'s); mass spectrum *m/e* (rel intensity) 162 (parent, 24), 106 (27), 97 (100), and 91 (63). *Anal.* Calcd for $C_{11}H_{14}O$: C, 81.51; H, 9.63. Found: C, 81.20; H, 9.77.

This material was shown by analysis on column D at 200° to be a mixture of four isomers of the following relative areas: 48:16:21:15.

A sample of the mixture in ethyl acetate (50 ml) was shaken under 15 psig hydrogen pressure for 2 hr; filtration and evaporation gave a colorless oil which showed two major and one minor components on columns B and D, of retention times (column B, 190°) 10.5 (63%), 12.1 (21%), and 12.5 min (15%). Photoaddition of 1 to cyclopentene as described by Corey, *et al.*,[3a] gave a mixture of the two major components in a 73:27 ratio (the cis- and trans-fused compounds, respectively) in our hands. The identity of the two saturated tricyclic ketones from the two sources was shown by comparison of the infrared spectra of collected samples and by identity of retention times on columns A, B, and D. The spectral features of the third component were given earlier, in the text.

Cyclohexenone and 1,3-Cyclohexadiene. A solution of 1 (5.0 g, 0.050 mol) and 1,3-cyclohexadiene (30 g, 0.38 mol) in sufficient benzene to make 220 ml of solution was irradiated under the standard conditions for 4.5 hr. Distillation gave first cyclohexadiene dimers (21 g), bp 45–53° (0.4 mm), and then a fraction showing carbonyl absorption (3.8 g), bp 60–120° (0.3 mm). Redistillation of the second fraction through a wire-spiral column gave a mixture of 1:1 adducts: bp 92–94° (0.3 mm) (1.6 g, 0.09 mol, 18%); ir (film) 1702 cm^{-1}; nmr (CCl_4) τ 4.17 (2 H, s, br) and 7.0–8.9 (14 H, m); mass spectrum *m/e* 178 (parent). *Anal.* Calcd for $C_{12}H_{16}O$: C, 81.84; H, 9.08. Found: C, 82.29, H, 9.14. The mixture showed three poorly resolved peaks on columns C and D, of approximate ratio 40:50:10.

Conversion of the 1-Cyclohexadiene Adducts to Tricyclo[6.4.0.0]dodecadienes. A solution of the mixture of adducts from 1 and 1,3-cyclohexadiene (1.5 g) in methanol (30 ml) was added slowly to sodium borohydride (2.0 g) in 90% aqueous methanol at 30–40°. The solution was stirred for an additional 4 hr, after which the solvent was evaporated, water was added, and the reaction mixture was extracted four times with ether. Drying and evaporation of the ether extracts gave the mixture of alcohols (1.3 g), ν_{max} 3450 cm^{-1} (br).

The crude mixture of alcohols thus obtained (1.3 g) was converted directly to the corresponding tosylates by treatment with *p*-toluenesulfonyl chloride (2.5 g) in dry ether (50 ml) at 0–5° for 30 hr. Treatment with ice and water and extraction with ether (4 × 50 ml), followed by washing of the extracts with dilute hydrochloric acid solution, dilute sodium bicarbonate, and saturated brine, drying, and evaporation of the ether gave the tosylate mixture as a colorless oil (2.0 g). This material was dissolved in dry dimethyl sulfoxide (10 ml) and treated at 25–35° with a solution of freshly sublimed potassium *tert*-butoxide (0.90 g) in dimethyl sulfoxide (15 ml). After the solution has stood at room temperature for 2 hr, it was poured onto an ice–water slurry and the resulting mixture was extracted three times with pentane. The combined extracts were tricyclic dienes as a colorless oil, bp 46–49° (0.4 mm) (0.62 g, 41%). This material was sufficiently well resolved on a 10 ft × 0.25 in. Apiezon L column to allow collection of the two major components, which amounted to 56 and 34% of the total. These were found to be identical with the independently prepared samples of tricyclo[6.4.0.$0^{2,7}$]dodeca-3,11-diene and the 3,9-diene, respectively (*vide infra*).

Synthesis of Authentic Tricyclododecadienes. A mixture of the photodimers of 1 was prepared according to the procedure of Hammond, *et al.*, which was stated to give the head-to-head anti, the head-to-tail anti, and two other isomers in a ratio of 25:60:15. Degradation of this mixture was performed in the same way as was the conversion of the individual cyclopentenone photodimers to the corresponding diolefins (*vide infra*). Thus, a solution of 5.0 g of the dimer mixture in ether (100 ml) was added to excess lithium aluminum hydride, and the solution was refluxed for 2 hr and worked up in the fashion described below. Treatment of the crude oily mixture of diols with tosyl chloride (12 g) in dry pyridine (50 ml) at 0–5° for 4 hr, dilution with ice water, and repeated extraction with ether gave a thick oil. To this oil (6.5 g) in *tert*-butyl alcohol (30 ml) was added freshly sublimed potassium *tert*-butoxide (4.0 g) in portions, with cooling to keep the temperature below 25°. The mixture was shaken at 25° for 0.5 hr and then poured into ice water. Extraction with pentane, washing several times with water, and evaporation of the solvent gave a colorless oil, which was distilled to give a diolefin mixture, bp 45–49° (0.4 mm) (0.9 g). The two major components of the mixture (62 and 27% of the total) were found to be identical with the two major components of the mixture obtained by degradation of cyclohexenone–cyclohexadiene adduct mixture.

Photoaddition of 2-Cyclohexenone to 1,3,5-Cycloheptatriene. A solution of 1 (2.0 g, 0.020 mol) and redistilled cycloheptatriene (46 g, 0.50 mol) in sufficient benzene to make 120 ml of solution was irradiated for 30 hr under the standard conditions. There was obtained 2.6 g of a yellow oil, bp 70–80° (bath) (0.1 mm). Preparative gc on column F gave first a mixture of cycloheptatriene dimers (30% of total area, two peaks on column C, in the ratio 28:72): ir (film) 1657 cm^{-1} (m); nmr (CCl_4) τ 4.0–4.7 (8 H, m) and 6.8–8.4 (8 H, m); mass spectrum *m/e* (rel intensity) 184 (parent, 48), 92 (100), and 91 (86). *Anal.* Calcd for $C_{14}H_{16}$: C, 91.34; H, 8.66. Found: C, 91.02; H, 8.31.

The third and fourth peaks (70% of area, 44% yield) were incompletely resolved, but were obviously adducts of 1 and cycloheptatriene: ir (film) 1703 cm^{-1}; nmr ($CDCl_3$) τ 4.1 (4 H, m) and 6.8–8.6 (12 H, br, m); mass spectrum *m/e* (rel intensity) 188 (parent, 46), 104 (51), 92 (96), 91 (100); uv (EtOH) 250 nm (ϵ 2300). *Anal.* Calcd for $C_{13}H_{16}O$: C, 82.13; H, 8.41. Found: C, 82.36; H, 8.19. Hydrogenation of this adduct mixture (0.50 g) over palladium on charcoal in ethyl acetate led to the uptake of 2 equiv of hydrogen and gave, after work-up, 0.44 g of a saturated tricyclic ketone mixture, ν_{max} 1704 cm^{-1}, which showed two peaks on column B at 180°. Their retention times were identical on columns A, B, and C, to those of the two components of the ketone mixture obtained in 61% yield on photochemical addition of 1 to cycloheptene. The ir spectra of the collected ketones were superimposable.

Photoaddition of 2-Cyclohexenone to 1,3-Cyclooctadiene. A solution of 1 (2.0 g, 0.020 mol) and 1,3-cyclooctadiene (43 g, 0.40 mol) in sufficient benzene to make 125 ml of solution was irradiated under the standard conditions for 2.5 hr. Evaporation of the excess diene under reduced pressure and short-path distillation of the residue gave the adduct mixture, bp 90–95° (bath) (0.2 mm) (2.35 g, 66%). This material was shown by analysis on column C at 190° to be composed of three isomers, in the ratio 13:70:17, of retention times 15.5, 17.2, and 18.3 min, respectively. The first and second components were collected from column G at 230°. The first peak, obtained as a colorless oil, showed ir (film) 1700 cm^{-1}; nmr (CCl_4) τ 4.3 (2 H, br) and 6.9–8.6 (18 H, br); mass spectrum *m/e* (rel intensity) 204 (parent), (41), 175 (33), 108 (29), 105 (40), and 79 (100). *Anal.* Calcd for $C_{14}H_{20}O$: C, 82.38; H, 9.80. Found: C, 82.57; H, 9.71.

The second major component was a solid and could be obtained pure by direct low-temperature crystallization of the mixture, as well as by gc. Recrystallization from 10% chloroform–hexane at 0° gave thick white prisms: mp 78.5–79.5°; ir (KBr) 1698 cm^{-1}; nmr ($CDCl_3$) τ 4.1–4.7 (2 H, m) and 6.9–8.5 (18 H, m, br); mass spectrum *m/e* (rel intensity) 204 (parent, 57), 175 (43), 147 (18), 133 (16), 119 (16), 108 (25), 105 (32), 91 (73) 79 (100), and 67 (54). *Anal.* Found: C, 82.25; H, 9.62.

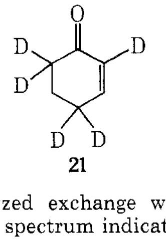
A solution of the adduct mixture (0.50 g) in ethyl acetate (20 ml) was shaken for 1 hr over palladium on charcoal under 15 psig hydrogen pressure. The colorless oil obtained after filtration of the catalyst and evaporation of the solvent showed two peaks on columns C and D at 180° in the ratio 87:13. Collection of the peaks and infrared analysis showed them to be identical with the two major adducts from 1 and cyclooctene. Thus, all three adducts must result from [2 + 2] cycloaddition.

Photochemical Cycloaddition of 1 to 1,5-Cyclooctadiene. A solution of 1 (2.0 g, 0.020 mol) and freshly distilled 1,5-cyclooctadiene (32 g, 0.030 mol) in sufficient benzene to make 130 ml of solution was irradiated for 3 hr under the standard conditions. The usual work-up gave a colorless oil: bp 116-120° (0.1 mm) (2.9 g, 64%); ν_{max} 1700 cm^{-1}; nmr (CCl_4) τ 4.4 (2 H, m) and 7.4-8.7 (18 H, complex m); mass spectrum *m/e* (rel intensity) 206 (parent, 91), 178 (35), 163 (35), 97 (100), 91 (70), 79 (100), and 67 (66). *Anal.* Calcd for $C_{14}H_{20}O$: C, 82.38; H, 9.80. Found: C, 82.10; H, 9.59.

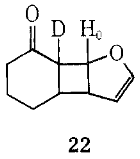
Hydrogenation of this ketone mixture (0.70 g) in ethyl acetate solution in the presence of 10% palladium on charcoal (50 mg) for 1 hr led to solvent, and distillation gave 0.62 g (90%) of a colorless oil which showed two peaks in the ratio 42:58 (column C at 190°) which were identical (ir, retention times) with the two saturated ketones obtained in a ratio of 87:13 from reduction of the 1-1,3-cyclooctadiene adducts. Photochemical addition of 1 to *cis*-cyclooctene (3 hr through Pyrex) gave 66% of a mixture of three saturated tricyclic ketones in the ratio 56:40:4. The first two of these were identical (ir, gc) with the two saturated ketones obtained from reduction of the adducts from 1,3- and 1,5-cyclooctadiene, thus showing that both adducts from the two dienes resulted from 1,2-addition.

Exposure of an ether solution of the adduct mixture from 1 and cyclooctene (200 mg in 20 ml) to sodium methoxide (40 mg) for 12 hr at 25° resulted in isomerization of the first and third components. After neutralization, pouring into water, and work-up, the recovered ketone mixture was found to contain the first and second components in the ratio 73:27. Apparently the second isomer possesses a trans 6-4 ring transfusion.

Photoaddition of 1 to Furan. A solution of 2-cyclohexenone (4.0 g, 0.040 mol) in furan (125 ml) was irradiated under the standard conditions for 3 hr. The residue remaining on evaporation of the excess furan was evaporatively distilled in a short-path apparatus to afford an adduct mixture as a faintly yellow oil, bp 70° (bath) (0.08 mm) (4.1 g, 63%). *Anal.* Calcd for $C_{10}H_{12}O_2$: C, 73.19; H, 7.30. Found: C, 72.88; H, 7.35. The nmr spectrum of the mixture showed, in addition to signals due to **8a** and **8b** (*vide infra*), additional signals for 7 at τ 3.72 (2 H, A part of AA′XX′, vinyls), 5.13 (1 H, m, HCO), 5.40 (1 H, m, HCO), and 6.5 (1 H, m, CHC=O). From the respective area ratios, the mixture contained *ca.* 40% of 7. Adduct 7 underwent retro Diels-Alder cleavage on attempted glc separation. On column A at 180°, three peaks were present, of retention times 4.0, 13.7, and 14.5 min, of relative areas 40:35:25. The first of these was shown to be 1 by comparison of infrared spectra. The second peak was identified as the [2 + 2] adduct **8a**: nmr ($CDCl_3$) τ 3.61 (1 H, 2 d, J = 2.8, J' = 1.4 Hz, -C=CHO), 4.80 (1 H, apparent t, J = 2.8 Hz, -OCH=CHC), 5.01 (1 H, 2 d, J = 7.4, J' = 4.2 Hz, -OCH-), 6.7 (2 H, m, -CH_2C=O), and 7.2-8.6 (7 H, m); ir (film) 1706 (s, C=O), 1600 cm (s, -OC=C); mass spectrum *m/e* (rel intensity) 166 (parent, 15), 81 (17), 79 (13), 68 (100), and 55 (28). The third peak [ir (film) 1704 cm^{-1}; nmr ($CDCl_3$) τ 3.7 (1 H, m), 4.81 (1 H, apparent t, J = 3.0 Hz), 5.24 (1 H, 2 d, br, J = 8.4, J' = 4.5 Hz), and 6.7-8.2 (9 H, m); mass spectrum *m/e* (rel intensity) 166 (18), 68 (100)] is assigned structure **8b** on the basis of (a) the establishment of structure **8a** for the major [2 + 2] adduct (*vide infra*), and (b) the nmr spectrum of deuterated adduct **22**. 2,4,4,6,6-Pentadeuterio-2-cyclohexen-1-one (**21**) was prepared by the usual base-catalyzed exchange with D_2O. Two cycles gave material whose nmr spectrum indicated was ~85% deuterated in the 2 position. Irradiation of **21** in the manner described above, distillation of the product, and collection of the minor peak (that of longer retention time) from column A gave a colorless oil, whose nmr spectrum showed a signal at τ 5.2 which had collapsed from the pair of doublets in the spectrum of **8b** to a single broad doublet ($J \cong$ 8 Hz). This signal must be due to H_0 and its appearance in the spectrum of the deuterated adduct demonstrates that H_0 and the proton α to carbonyl are strongly coupled, and must be on adjacent carbon atoms, as in **22**.



21



22

A sample of the distilled adduct mixture (1.2 g) in ethyl acetate was shaken under 15 psig hydrogen pressure with 10% palladium on charcoal (50 mg). After 45 min, reduction was complete; the catalyst was then filtered and the solvent was evaporated. Analysis of the residue on column C at 180° showed three peaks at 8.5, 9.2, and 11.0 min, in the ratio of 16:44:40. The second peak was collected and found to be identical (ir, gc retention times on columns B and C) with the major product of addition to 1 to 2,3-dihydrofuran. The minor peaks were not further investigated.

Irradiation of 1 with 2,3-Dihydrofuran. A solution of 1 (2.0 g) and 2,3-dihydrofuran[24] (35 g) in benzene (80 ml) was irradiated under the standard conditions for 3 hr. Distillation of the excess olefin and evaporation of the benzene, followed by distillation of the residue, gave 2.3 g (64%) of a colorless oil, bp 74-80° (0.1 mm), ir 1706 cm^{-1}. Analysis on column C at 180° showed two peaks, of retention times 9.2 and 11.5 min, in the ratio 69:31. The major peak was identical with one of the components from the hydrogenation of the 1-furan product mixture (*vide supra*).

Photochemical Cycloaddition of Cyclopentenone (2) to Cyclopentadiene. A solution of 2 (4.1 g, 0.050 mol) and freshly distilled cyclopentadiene (60 g, 0.90 mol) in sufficient benzene to afford 220 ml of solution was irradiated in the usual fashion while being cooled externally with an ice-salt bath at −15°, and with chilled glycol-water (−20°) being circulated through the immersion well. After 3 hr of irradiation, the solvent and excess cyclopentadiene were evaporated under reduced pressure, care being taken to keep the solution below 5°. Fractional distillation under reduced pressure of the residue thus obtained afforded three fractions: (a) cyclopentadiene dimers, bp 30-32° (1 mm), 6.1 g; (b) an adduct mixture, bp 51-54° (0.3 mm), 2.3 g (37%); and (c) enone-dimer adducts, bp 115-130° (0.3 mm), 2.0 g (24%), in addition to a tarry residue. Redistillation through a 15-cm Vigreux column of fraction b from two such reactions gave the mixture of the adducts **9** and **10** as an almost colorless oil: bp 51-53° (0.3 mm); ir (film) 1730 cm^{-1}; nmr ($CDCl_3$) τ 3.8-4.6 (2 H, m), 6.9-8.7 (10 H, m); mass spectrum *m/e* (rel intensity) 148 (parent, 27), 106 (36), 83 (60), 82 (100), and 65 (48). *Anal.* Calcd for $C_{10}H_{12}O$. A solution of the above adduct mixture (2.1 g, 0.015 mol) in methanol (20 ml) was treated with excess sodium borohydride in methanol, with external cooling to keep the temperature below 30°. After being stirred for 2 hr further at room temperature, the reaction mixture was poured onto an ice-water slurry and extracted with ether. The ether extracts were washed exhaustively with water, dried ($MgSO_4$), and evaporated to yield the alcohol mixture (1.9 g). This material, without further purification, was treated in pyridine (10 ml) with *p*-toluenesulfonyl chloride (2.8 g) in pyridine at 0-4° and stirred at that temperature for 5 hr, then let stand overnight in the refrigerator. The reaction mixture was poured into ice-cold 10% hydrochloric acid and extracted with ether (3 × 15 ml), and the extracts were washed once with cold 10% HCl, twice with cold 5% sodium bicarbonate, and then with cold water, and dried. Evaporation of the ether gave the tosylate mixture as a viscous oil which was dissolved in dry dimethyl sulfoxide (25 ml) and treated at 20-25°, while being vigorously stirred, with freshly sublimed potassium *tert*-butoxide (2.2 g). After 1 hr, the dark brown reaction mixture was poured into water and extracted with pentane (3 × 15 ml). The pentane extracts were washed with water, dried, and evaporated to give a colorless oil, bp 35-39° (4 mm) (0.82 g), which was shown by analysis on column A to consist of two components in the ratio 38:62. These were collected from column D and were found to be identical with authentic samples of tricyclo[5.3.0.0]deca-3,9- and -3,11-diene, respectively (*vide infra*).

The head-to-head and head-to-tail dimers of cyclopentenone, mp 65 and 126°, respectively, were prepared as described by Eaton.[15a] A solution of the head-to-head dimer (3.0 g) was dissolved in tetrahydrofuran (200 ml) and added dropwise to 1.8 g of lithium aluminum hydride in refluxing 1:1 ether-tetrahydrofuran (100 ml). The reaction mixture was treated successively with water (1.8 ml), 10% sodium hydroxide (1.8 ml), and water (6 ml). After stirring for an additional 1 hr, the resulting white suspension was filtered and the solid was washed twice with tetrahydrofuran. The combined filtrates were evaporated to give the product diols as a white solid (2.8 g). Recrystallization gave the major isomer as white prisms, mp 188-189° (1.8 g). *Anal.* Calcd for $C_{10}H_{16}O_2$: C, 71.47; H, 9.53. Found: C, 71.65; H, 9.71.

The major diol (1.7 g) in dry pyridine (20 ml) was treated with *p*-toluenesulfonyl chloride (3.2 g) in pyridine (20 ml) at 0-5°, and stirred at that temperature for 6 hr. The reaction mixture was poured into ice water and extracted with ice-cold ether (4 × 15 ml) and the ether extracts were washed with cold 15% hydrochloric acid (4 × 30 ml), 5% sodium bicarbonate, and water. Drying and evaporation of the extracts gave the corresponding ditosylate as a white solid (2.9 g). A sample had mp 177–178° dec after recrystallization from tetrahydrofuran. Treatment of the ditosylate (2.5 g) in dry dimethyl sulfoxide (25 ml) with freshly sublimed potassium *tert*-butoxide (3.0 g) at 40° for 35 min gave, after pouring the reaction water, extraction with pentane, and work-up, diene **13**, tricyclo[5.3.0.0]deca-3,9-diene, as a clear liquid, bp 42–44° (4 mm) (0.65 g). This diene was identical with the *minor* diene obtained from degradation of the adduct mixture from **2** and cyclopentadiene, as shown by the identity of their ir spectra and gc retention times on columns A, B, and D.

Similarly, the head-to-head dimer of cyclopentenone was converted to the corresponding diolefin; no sharp-melting diols or ditosylates were obtained during the sequence. The diene thus obtained was identical in all respects with the *major* product from degradation of the adduct mixture from **2** and cyclopentadiene.

Photochemical Cycloaddition of 2-Cyclopentenone to 1,3-Butadiene, 1,3-Cyclooctadiene, and Furan. Irradiation of **2** (3.5 g) and 1,3-butadiene (50 g) for 5 hr gave, in addition to 1.5 g of recovered **2**, an adduct mixture (1.2 g, 37% based on unrecovered enone): bp 41–44° (0.3 mm); ir 1731 cm^{-1}; nmr (CDCl$_3$) τ 4.2–4.4 (1 H, m), 5.1–5.3 (2 H, m), and 6.6–8.5 (9 H, m); *m/e* 138. *Anal.* Calcd for $C_9H_{12}O$: C, 79.43; H, 8.82. Found: C, 79.20; H, 8.68.

Irradiation of **2** and excess of 1,3-cyclooctadiene for 3 hr gave 56% of a colorless oil: bp 105–108° (0.3 mm); ir 1729 cm^{-1}; nmr (CCl$_4$) τ 4.2–4.4 (2 H, m) and 6.7–8.3 (14 H, m); *m/e* 190 (parent). Analysis on column C showed three components of relative areas 15:62:23.

Similarly, irradiation for 3 hr of **2** (3.0 g) and furan (100 ml) gave an adduct mixture, bp 78–80° (0.4 mm), ir (film) 1741 cm^{-1}, which appeared to consist of both [2 + 2] and [4 + 2] adducts, as shown from the nmr spectrum [*inter alia,* τ 3.62 (t, J = 1.4 Hz, vinyl H of [4 + 2] adduct), 4.80 (t, J = 2.8 Hz, -CH=CHO- of [2 + 2] adduct), and 5.0 and 5.1 (s, m, -CHO- of [4 + 2] adduct)]. As with the products from **1** and furan, the temperature required for gas chromatographic purification caused cycloreversion of the [4 + 2] adduct and at least partial decomposition of the [2 + 2] adduct(s).

Analysis was feasible, at least, and there appear to be present three components, of areas ~ 5:4:1. Even with partial decomposition occurring, enough of the major [2 + 2] adduct was collected for infrared spectral comparison of its hydrogenation product with the major product from **3** and 2,3-dihydrofuran, with which it proved to be identical, and thus must have structure **22**. The sample obtained in the latter fashion (66% yield) had ir (film) 1733 cm^{-1}; nmr (CDCl$_3$) τ 3.71 (1 H, t, J = 2.8 Hz), 4.80 (1 H, t, J = 2.8 Hz), 5.1 (1 H, m), and 6.8–8.2 (7 H, m); mass spectrum *m/e* (rel intensity) 166 (parent, 6.5) and 68 (100). *Anal.* Calcd for $C_9H_{10}O_2$: C, 72.04; H, 6.64. Found: C, 71.88; H, 6.50.

Photochemical Reaction of 1 with Thiophene. A solution of **1** (1.5 g) in thiophene (110 ml) was irradiated for 10 hr. Evaporation of the excess thiophene and distillation gave 0.42 g of material, bp 81–90° (0.2 mm), as well as 0.89 g of enone dimers, bp 115–125° (0.2 mm). Two fractional distillations of the first fraction through a micro wire-spiral column gave 0.18 g (8%), bp 85–88° (0.2 mm), of **16**: nmr (CDCl$_3$) τ 3.84 (1 H, d, J = 5.4, J' = 1.6 Hz), 4.40 (1 H, 2 d, J = 5.4, J' = 2.6 Hz), 5.73 (1 H, 2 d, J = 8.0, J' = 5.4 Hz), and 6.8–8.6 (9 H, m); ir (film) 1705 (s) and 1600 (w) cm^{-1}; mass spectrum *m/e* (rel intensity) 180 (parent, 15), 97 (20), 84 (100), and 55 (76). *Anal.* Calcd for $C_{10}H_{12}OS$: C, 66.70; H, 6.62. Found: C, 66.45; H, 6.51.

Photochemical Addition of 1 to 2,5-Dimethylthiophene. A solution of **1** (2.0 g) and 2,5-dimethylthiophene (20 g) in benzene (100 ml) was irradiated through Pyrex for 3 hr. Evaporation of the solvent and excess 2,5-dimethylthiophene, followed by fractional distillation of the residue, gave crude **17**. Two more distillations gave **17** as a colorless oil: bp 112–114° (0.1 mm) (2.1 g, 51%); ir (film) 1699 cm^{-1}; nmr (CDCl$_3$) τ 4.72 (1 H, m), 6.7 (1 H), 8.1 (2 H, d, allyl CH$_3$), 8.50 (3 H, s), 8.50 (s), and 7.0–8.4 (7 H, m); mass spectrum *m/e* (rel intensity) 208 (parent, 16), 193 (35), and 110 (100). *Anal.* Calcd for $C_{12}H_{16}O_2$: C, 69.25; H, 7.81. Found: C, 69.58; H, 7.55. Analysis on column A showed two incompletely resolved peaks in a ratio of ~ 2:1.

Photochemical Reaction of 1 with 1-Methylpyrrole. A solution of **1** (3.0 g, 0.03 mol) and 1-methylpyrrole (25 g) in benzene (100 g) was irradiated for 5 hr. Work-up in the usual manner gave, besides 1.4 g of recovered **1**, a golden oil, bp 80–95° (0.1 mm) (0.86 g), which darkened on standing in the presence of air: ir (film) 1700 cm^{-1} (s, br); nmr (CCl$_4$) τ 3.8 (1 H, m, br), 4.3 (1 H, m, br), 6.5 (3 H, 2 s, NCH$_3$), 6.7–8.3 (8 H, m).

Reaction of Carbostyril (15) with Furan. A solution of carbostyril (2.0 g, 13 mol) and furan (100 ml) in 95% ethanol (100 ml) was irradiated through Pyrex for 10 hr. Filtration of the suspension, after evaporation of excess furan, gave 47% of the known photodimer of carbostyril, mp 300–302°. Evaporation of the filtrate under reduced pressure gave a yellow semisolid residue which was chromatographed on a 25 × 300 nm column of silica gel. Elution with chloroform (500 ml) and 10:1 chloroform–ethyl acetate (700 ml) gave in the earlier fractions 0.96 g (75 ml each) of adduct **19** as an off-white solid, and in the later fractions 48% of unchanged **15**. Recrystallization of the combined product fractions from ethyl acetate–hexane gave pure **19** as white prisms: mp 201–202° (0.43 g, 37% based on unrecovered **15**); ir (KBr) 1663 (C=O) and 1594 cm^{-1} (vinyl ether); nmr (CDCl$_3$) τ 1.12 (1 H, br, NH), 2.9–3.1 (4 H, m), 3.60 (1 H, 2 d, J = 2.7, J' = 1.1 Hz), 4.68 (1 H, t, J = J' = 2.7 Hz), 4.85 (1 H, d of m, J = 7.4 Hz), 6.28 (2 H, br, s), 6.51 (1 H, 2 t, J = 7.4, J' = 1.5 Hz); mass spectrum *m/e* (rel intensity) 213 (parent, 0.5), 145 (61), 90 (80), and 68 (100). *Anal.* Calcd for $C_{13}H_{11}O_2N$: C, 73.24; H, 5.16. Found: C, 72.95; H, 5.30. Shaking a sample of **19** (0.10 g) in ethyl acetate (40 ml) with 10% palladium on charcoal under 1 atm pressure of hydrogen for 8 hr, followed by filtration of the catalyst and evaporation of the solvent, gave dihydro-**19** as white needles, mp 194–195° after recrystallization from ethyl acetate–hexane: ir 1671 (C=O, s), 1598 cm^{-1} (w); nmr (CDCl$_3$) τ 1.02 (1 H, br), 2.7–3.1 (4 H, m), 4.9 (1 H, m), 5.48 (2 H, m), 6.93 (1 H, m), 7.0–7.8 (5 H, m).

Photochemical Addition of 15 to 2,3-Dihydrofuran. A solution of **15** (1.0 g) and 2,3-dihydrofuran (20 g) in ethanol (200 ml) was irradiated through Pyrex for 6 hr. Evaporation of the ethanol and excess olefin gave a semisolid residue which was chromatographed on silica gel. Elution with 10:1 chloroform–ethyl acetate gave first four fractions containing crude 20 and, later, unchanged **15** (0.08 g). Recrystallization of the crude **20** from ethyl acetate–hexane gave the pure material as white leaflets: mp 174–175°; ir (KBr) 1660, 1592, 1410 cm^{-1}; nmr (CDCl$_3$) τ 2.7–3.0 (4 H, m), 4.8 (1 H, m), 5.6 (2 H, m), 6.4 (1 H, s, br), 6.8 (1 H, m), and 7.0–7.9 (5 H, m). *Anal.* Calcd for $C_{13}H_{13}NO_2$: C, 72.58; H, 6.04. Found: C, 72.69; H, 5.86.

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Registry No.—**1**, 930-68-7; **2**, 930-30-3; **3**, 51519-59-6; **4**, 51519-60-9; **5** isomer 1, 51519-61-0; **5** isomer 2, 51519-62-1; **5** isomer 3, 51519-64-3; **6**, 51519-65-4; **7**, 51519-66-5; **8a**, 51519-67-6; **8b**, 51519-68-7; **9**, 51567-37-4; **10**, 51519-69-8; **13**, 51519-70-1; **15**, 493-62-9; **16**, 51567-38-5; **17**, 51519-71-2; **18**, 51519-72-3; **19**, 51519-73-4; dihydro-**19**, 51519-74-5; **20**, 51519-75-6; **21**, 51519-76-7; **22**, 51519-77-8; 2,3-dihydrofuran, 1191-99-7; thiophene, 110-02-1; 2,5-dimethylthiophene, 638-02-8; 1-methylpyrrole, 96-54-8; cyclohexenone-1,3-cyclohexadiene adduct A, 51519-78-9; cyclohexenone-1,3-cyclohexadiene adduct B, 51519-79-0; 1,3,5-cycloheptatriene dimer, 31510-69-7; cyclohexenone–cycloheptatriene adduct, 51519-81-4; cyclohexenone-1,3-cyclooctadiene adduct A, 51519-82-5; cyclohexenone-1,3-cyclooctadiene adduct B, 51519-83-6; *trans*-cyclohexenone-1,5-cyclooctadiene adduct, 51519-84-7; *cis*-cyclohexenone-1,5-cyclooctadiene adduct, 51607-06-8; 2-cyclopentenone-1,3-butadiene adduct A, 51519-85-8; 2-cyclopentenone-1,3-butadiene adduct B, 51519-86-9.

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Cycloaddition of 1-Azirines with Cyclopentadienones. Formation of 2*H*- and 3*H*-Azepines, and Mechanistic Interpretation[1,2]

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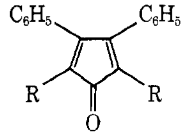
Cyclopentadienones **1** and 1-azirines **2** react in refluxing toluene to afford 3*H*-azepines **3** directly, with loss of CO. Azirines **2** react similarly with 1,3-diphenylinden-2-one (**16**) and phencyclone (**17**) to give 2*H*-azepines **18** and **19**. The phenanthro-2*H*-azepines **19** rearrange under basic or thermolytic conditions to the more stable 3*H* isomers with the ring proton at the 9 position of the phenanthrene nucleus. Analogous cycloadditions of **16** and **17** with 1,2,3-triphenylcyclopropene (**22**) lead to cycloheptatrienes and exo bridging carbonyl compounds. The mechanism of azepine formation is rationalized in terms of an *endo*-2-azatricyclo$[3.2.1.0^{2,4}]$oct-6-en-8-one intermediate (**13**) which extrudes CO with disrotatory ring opening of the aziridine C–N bond, to afford primarily 2*H*-azepines which may or may not then rearrange to the 3*H* isomers. Analysis of the nmr spectra, with particular attention to the conformational preference of the azepine ring, is also recorded.

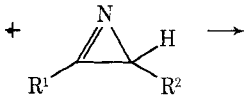
During the last decade 1-azirines have become readily available and their synthetic utility has been extensively developed.[3] Recently the first cycloadditions of these heterocyclic systems have been reported. These include thermal reactions with ketenes,[4,5] ketenimines,[5] nitrile oxides,[6] cyclopentadienones,[2,7] cyclopentadiene,[8] diphenylisobenzofuran,[9] and diazomethane[10] to yield a variety of products. 1-Azirines also react photochemically (*via* the nitrile ylide) with themselves,[11-13] as well as with various carbon–carbon[14,15] and hetero double bonds.[15,16]

The synthesis and chemistry of azepines has likewise evolved largely during the last decade.[17] Although a number of examples of N-substituted 1*H*-azepines are known,[17] attempts to prepare the unsubstituted system have led to the formation of 3*H*-azepines.[18] 4*H*-Azepines rearrange under thermal or basic conditions to the 3*H* isomers.[19-22] No example of the 2*H*-azepine was known prior to this study.[2] This has led to the generalization[21] that the relative stabilities of the azepine systems are in the order 2*H* < 4*H* < 3*H*. It has also been calculated[23] that for the parent systems, 1*H*-azepine has a resonance energy of −1.80 kcal mol^{-1}, whereas that of the 3*H*-azepine is +0.23.

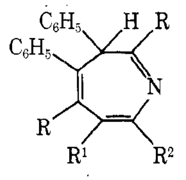
We report here our detailed findings on the reaction of 1-azirines with a variety of cyclopentadienones to give 2*H*- and 3*H*-azepines.



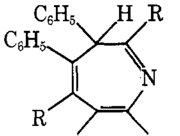
1a, R = C_6H_5
b, R = CH_3
c, R = C_2H_5



2a, $R^1 = C_6H_5$; $R^2 = H$
b, $R^1 = C_6H_5$; $R^2 = CH_3$
c, $R^1 = R^2 = C_6H_5$
d, $R^1 = C_6H_5$; $R^2 = CH_2OH$
e, $R^1 = C_6H_5CH_2$; $R^2 = H$



3a, $R = R^1 = C_6H_5$; $R^2 = H$
b, $R = R^1 = C_6H_5$; $R^2 = CH_3$
c, $R = R^1 = R^2 = C_6H_5$
d, $R = R^1 = C_6H_5$; $R^2 = CH_2OH$
e, $R = C_6H_5$; $R^1 = C_6H_5CH_2$; $R^2 = H$
f, $R = CH_3$; $R^1 = C_6H_5$; $R^2 = H$
g, $R = R^2 = CH_3$; $R^1 = C_6H_5$
h, $R = CH_3$; $R^1 = R^2 = C_6H_5$
i, $R = CH_3$; $R^1 = C_6H_5CH_2$; $R^2 = H$
j, $R = C_2H_5$; $R^1 = C_6H_5$; $R^2 = H$
k, $R = C_2H_5$; $R^1 = C_6H_5$; $R^2 = CH_3$



4a, R = C_6H_5
b, R = CH_3

Results and Discussion

Though no reaction occurs between tetracyclone (**1a**) and azirine **2b** in refluxing benzene overnight, clean conversion into an azepine **3b** with loss of CO takes place in refluxing toluene after 4 days.[2] The structural assignment to 3*H*-azepines **3** was facilitated by the use of dimethylcyclone (**1b**) and 2-phenylazirine (**2a**) as substrates. The resulting azepine **3f**, produced in 86% yield, displayed two methyl singlets at τ 8.24 and 7.72, the latter exhibiting