PHOTOCHEMICAL TRANSFORMATIONS OF SOME β-SUBSTITUTED ENONES

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**Abstract**—The photochemical addition reaction of 3-cyano-, 3-chloro-, 3-methoxy-cyclohexanone, and some 3-aminocyclohexenones have been investigated. 3-Cyanocyclohexenone adds efficiently to olefins to give 2 + 2 cycloadducts. 3-Chlorocyclohexenone does not add readily and gives complex mixtures of products. The 3-aminocyclohexenones were photochemically completely unreactive. In contrast, a 3-amidocyclohexenone did cycloadd normally. 3-Methoxycyclohexenone (3) undergoes cycloaddition slowly (Φ ~ ·01). The cycloadducts or 3 are accompanied by products from reaction of 3 with radicals derived by hydrogen abstraction from solvent and olefin. The orientation of the cycloadducts was in all cases that predicted by consideration of the most stable π-complex. The results are discussed in terms of current theories of the mechanism of cycloaddition.

THE photochemical cycloaddition of cyclic α,β-unsaturated ketones to unactivated olefins has received considerable attention since its discovery in 1957.[1] The reaction has frequently been used in syntheses of complex molecules[2] and has recently received mechanistic scrutiny.[3] In a previous report[4] we described the results of an investigation of the synthetic utility and some mechanistic aspects of the reaction, in which the addition of 3-acetoxy-, 3-methyl-, and 3-phenyl-2-cyclohexen-1-one to various olefins was studied. These enones were found to add to several substrates to give mixtures of cycloadducts, occasionally accompanied by other products, such as Michael-type adducts of olefin to enone,[5a] and oxetanes.[5b] The electronic effects of the 3-substituents
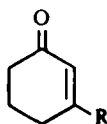
1: R = CN
2: R = Cl
3: R = OMe
4: R = NC₄H₈
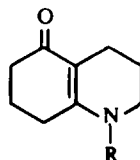
5a: R = H
5b: R = Me

on the product distribution were small and were outweighed in many cases by the steric effect of the substituent. The orientation of the products could be predicted in most cases by considering the most stable orientation of an intermediate π-complex between an excited enone molecule and a ground-state olefin, although in some instances steric factors were dominant. The results were consistent with a view of the reaction as preceding via an enone excited state with a relatively small degree of polar character, and involving a diradical-like intermediate.

It was considered worthwhile to investigate enones bearing other functional groups, especially those strongly electron-donating or withdrawing in character. We now report the results of a study of the photochemistry of 3-cyano-, 3-chloro-, and 3-methoxycyclohexenone (1, 2, 3), as well as three vinylogous amides (4, 5a, 5b) which may be regarded as 3-aminocyclohexenones.

3-Cyanocyclohexenone. On irradiation in the presence of an excess of several olefins, 3-cyanocyclohexenone (1) underwent efficient cycloaddition to give good yields of the expected cycloadducts, whose structures were evident from analytical and spectral data. Disappearance of 0·02 mole of material was usually complete within 60–90 min. The quantum yield of addition of 1 to cyclopentene was found to be $\sim$ 0·2. Irradiation of 1 in the presence of cyclopentene and of 1,1-dimethoxyethylene gave a single product in each case, the adducts 7 and 8 in 63 and 48 % yield, respectively. In establishing the structure of 7, mp 69–70°, the infrared saturated carbonyl stretching band at 1705 cm^{-1} and the absence of vinyl or cyclopropyl hydrogen signals in the NMR spectrum (no signals at τ 2–6·5 or > 8·8) were particularly helpful. The 6–4 ring fusion is believed to be *cis*, since prolonged exposure to base or alumina did not result in epimerization; bicyclo [4.2.0] octan-2-ones possessing *trans* ring fusions have been observed to readily epimerize to the *cis*-fused isomers under such conditions.[4, 6]

Similarly, adduct 8 showed no NMR signals in the τ 2–6 region and the position of the infrared carbonyl band (1708 cm^{1}) indicated the presence of a saturated ketone function. The NMR spectrum did exhibit at τ 7·3 the X portion of an ABX pattern, attributable to H-1 of 8. This adduct is therefore the 7,7-dimethoxybicyclo[4.2.0]octan-2-one 8, since the NMR spectrum of the 8,8-dimethyl isomer should show a singlet for H-1. The ketal function of 8 proved to be quite resistant to hydrolysis; the adduct was recovered unchanged after 8 hours at 60–70° in 3N HCl. A similar resistance to hydrolysis of ketals bearing a nearby carbonyl function has been previously noted, e.g., the adduct of 3-acetoxycyclohexenone and dimethoxyethylene.[4] In the present case, it seems likely that the cyano nitrogen is protonated in preference to the ketal oxygens, thus retarding hydrolysis of the ketal group.

Irradiation of 1 in the presence of isobutylene gave a mixture of adducts (9 and 10) which could not be satisfactorily resolved on several GC columns. However, the composition of the mixture and the orientations of the adducts could be easily determined from the NMR spectrum of the mixture. Thus, there were exhibited two pairs of Me singlets whose areas were in the ratio 87:13, at τ 8·67 and 8·84, and 8·57 and 8·86, respectively. The major component exhibited a pair of doublets at τ 6·83 ($J = 10·6$ Hz, $J' = 9·2$) and is therefore the 7,7-dimethyl compound 9, whereas a smaller singlet at 7·05 is attributable to H-1 of the minor isomer 10.

Addition of 1 to 1,2-dichloroethylene proceeded in reasonable irradiation periods; the mixture of adducts produced, 11 and 12, was unstable to gas chromatography and was not separated.

The fact that the photoaddition of 1 to these electronegatively substituted olefins proceeds without difficulty attests to the wide applicability of the reaction with enone 1. Recently the addition of 1 to ethylene has been reported[7] to proceed smoothly.

3-Chlorocyclohexenone. The reactivity of this enone (2) in cycloaddition was lower than that of 1 and of most other enones studied. Thus, irradiation of 2 in the presence of cyclopentene for two days gave, in addition to substantial amounts of tarry material, a modest yield of the cycloadduct 13, together with a substance assigned structure 14.
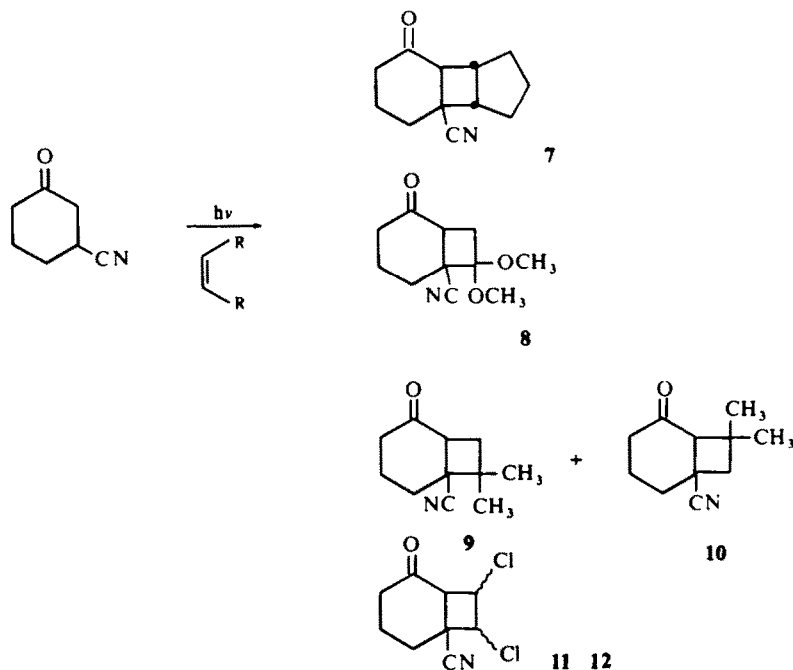
The structure of **13** was securely established by its conversion on sequential treatment with base and then hydrogen over palladium to a saturated ketone which was identical to the major (*cis*-fused) ketone from photoaddition of cyclohexenone to cyclopentene.

Irradiation of **2** in the presence of excess isobutylene for extended periods gave a mixture of eight products which could not be completely separated on our gas chromatography columns. The mixture was unstable to storage and was not characterized.
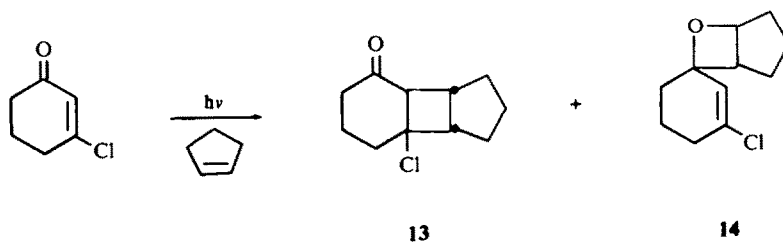
However, the low intensity of the infrared carbonyl stretching band indicates bicyclo[4.2.0]octanones comprise only a minor portion of the mixture.

3-Methoxycyclohexenone. It was thought initially that photocycloaddition of 3-alkoxycycloalkenones to olefins might be quite facile, since the previously studied 3-methylcyclohexenone, which likewise bears a mildly electron-donating, non-bulky substituent, underwent clean, rapid addition to several olefins.[4, 6] We were somewhat surprised, therefore, when **3** proved to add only slowly ($\Phi \sim \cdot01$ for **15**), with complications from competing reactions. Irradiation of 3-methoxycyclohexenone (**3**) in ether-cyclopentene mixtures led to complex mixtures of products, some of which arise from

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secondary reactions of primary products. The compounds isolated and identified are shown in Eq 1, while the yields after various irradiation periods are shown in Table 1.

TABLE 1

Conditions	Time (hr)	% Composition of Reaction Mixture				
		3	15	16	17	tar
A	30	37	38	13	4	
A	60	15	21	27	13	25%
B	30	90	—	—	—	10
B	60	50	—	20	13	15
B	90	25	—	14	26	30
C	50	24	40	—		

A: ·02 mole 3 + 0·5 mole cyclopentene in ether.
B: 0·02 mole 3   in ether.
C: 0·02 mole 3 + 0·5 mole cyclopentene in methylene chloride.

Identification of the various products was performed by means of analytical and IR, UV, NMR and mass spectral data. Cycloadduct **15** was assigned the *cis* stereochemistry at the 6–4 ring fusion on the basis of its stability to methanolic sodium methoxide and to alumina.[4, 6] While appreciable quantities of cycloadduct **15** are produced in cyclopentene-ether mixtures, the major portion of the reaction mixture consists of compounds formed by ground-state reactions of 3 with cyclo-pentenyl and α-ethoxyethyl radicals produced by abstraction of a hydrogen atom from the solvent or from cyclopentene. Somewhat cleaner reaction mixtures were obtained when methylene chloride was used as solvent (*cf* Table 1). Since compounds **16** and **17** are
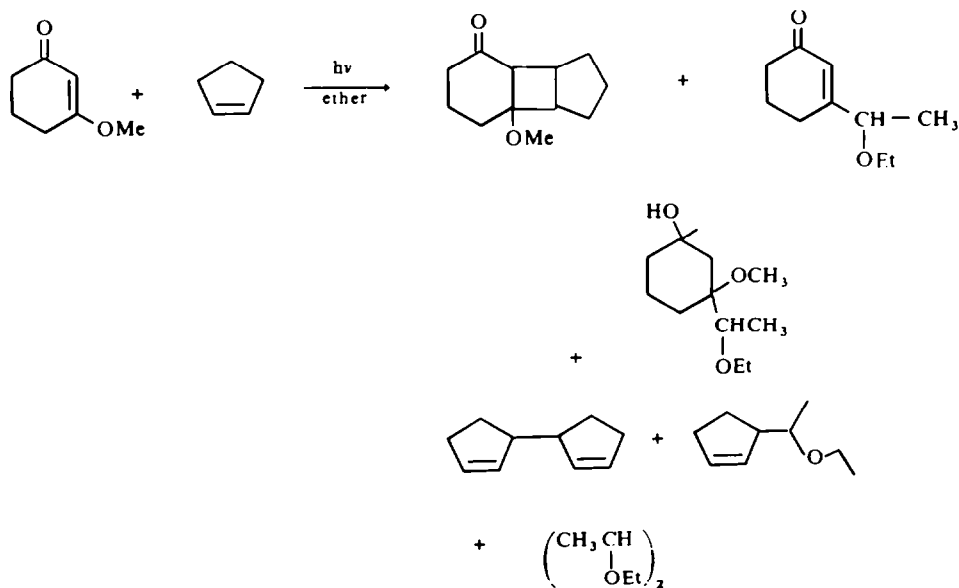
formed at rates only slightly slower than **15**, the latter adduct is best isolated after shorter irradiation periods and separated from unchanged **3** by fractional distillation or gas chromatography. Prolonged irradiation of the reaction mixture causes destruction of **15**.

The structure of compound **16**, 3-(α-ethoxyethyl)cyclohexenone, was evident from its high-intensity ultraviolet absorption maximum (λ_{max} 234 nm, $\varepsilon = 13,000$) and its NMR spectrum, which exhibited signals for one vinyl hydrogen (τ 3·8) and for an α-ethoxyethyl group (3-proton triplet and doublet at τ 8·79 and 8·68; one-proton and two-proton quartets at τ 5·95 and 6·49). A reasonable mechanism for the formation of **16** is shown below; thus, a molecule of excited **3** abstracts a hydrogen atom from a solvent molecule, followed by coupling of the two radicals produced. Loss of the elements of methanol then gives **16**. Photolysis of **3** in THF gave the analogous
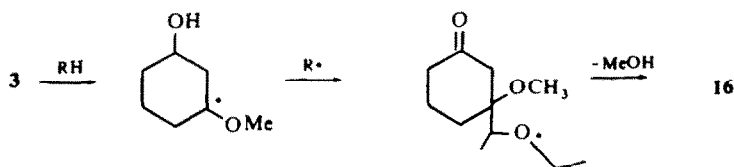

product produced by addition of a solvent-derived radical, 3-(2-tetrahydrofuryl)-cyclo-hexenone. However, use of other solvents with easily abstractable hydrogens such as methanol and isopropanol did not lead to the corresponding cyclohexenones.

The structure of **17** was assigned on the basis of spectral data, including infrared bands characteristic of OH (3450 cm^{-1}) and C-O ($\sim$ 1100 cm^{-1}) groupings, and NMR signals characteristic of α-ethoxyethyl (τ 8·8, 3H, doublet, τ 8·77, 3H, triplet, $\sim$ τ 6·1, 2H and 1H, multiplets) OMe, (6·6, 3H, singlet) and hydrogen α to OH (5·9,m).

The formation on irradiation of **3** of the coupling and cross-coupling products from solvent-derived radicals, and of **16** and **17** indicates that there is present an excited state of **3** whose CO oxygen possesses considerable H-abstracting capability, resembling in this respect the n → π* excited states of saturated and aryl ketones.[8]

Irradiation of 3-methoxycyclohexenone in 1,1-dimethoxyethylene effected slow conversion to tarry materials and adduct **19** (37%; $\Phi \sim$ 0·02). This compound was thermally unstable and was not obtained analytically pure. Its identity was determined from its IR, UV, NMR, and mass spectra (Experimental). The location of the OMe of **19** at C-6 was established by acid catalyzed hydrolysis to a diketone whose IR band at 1779 cm^{-1} indicated it to be the nonenolized γ-dione **20**. Attempted preparative gas chromatographic purification of **19** at 220° gave a product whose analysis and mass spectral mol wt indicated it to be derived by thermal loss of methanol, possibly followed by subsequent rearrangement. The IR spectrum of the product exhibits strong bands at 1757 and 1640 cm^{-1}, indicative of a molecule possessing either an enol ester, or both cyclobutanone and enol ether functions. This question is apparently answered by examination of the NMR spectrum, which shows two 3-proton singlets attributable to OMe groups at τ 6·23 and 6·60. The two OMe's leave only one O atom to make up the CO moiety; this latter must be a ketone, rather than an ester function. The NMR spectrum of the product can generally be rationalized in terms of any of the structures **21 - 23** (other signals besides those mentioned above occur at τ 5·04

[1H, d, J = 3·3]; 7·4 [1H, m]; and 8·3–8·5 [6H, m]). However, the UV spectrum eliminates 22 from consideration. The splitting of the signal at τ 5·04 is most consistent with the unrearranged structure 21 in which the vinyl hydrogen β to alkoxyl should be a sharp doublet, whereas the corresponding hydrogen of 23 would be at least coupled to the second hydrogen on the α-methylene group and would very likely be further broadened by virtual coupling. Further militating against structure 23 is the complexity of any rational process accounting for its formation. On the other hand, it is difficult to reconcile the observed CO stretching frequency (1767 cm^{-1}) with 21; a decision between structures 21 and 23 must await the results of chemical degradation.
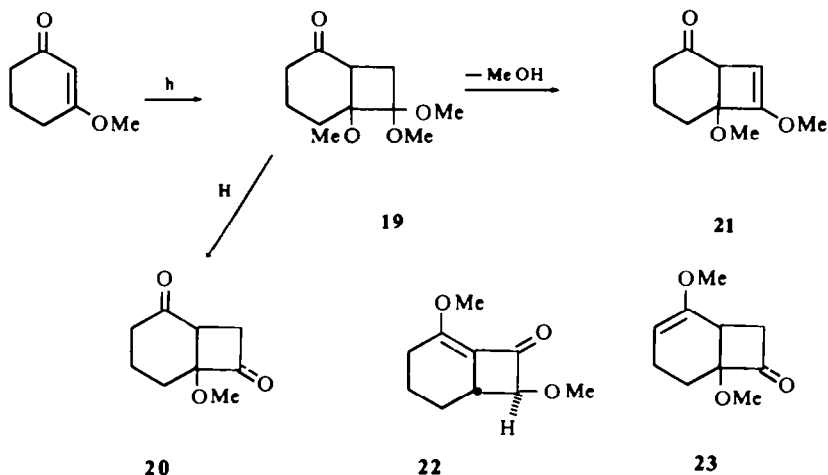
Irradiation of 3-(N-pyrrolidinyl)cyclohexenone (4) in the presence of cyclopentene, 1,1-dimethoxyethylene, or acryonitrile caused only slow decomposition of the starting material and tar formation. It seemed possible that the cycloaddition reaction might be facilitated in a system in which the 3-substituent is required to be more nearly coplanar with the remainder of the molecule. However, the octahydroquinolones 5a and 5b proved to be similarly inert to Pyrex-filtered light and underwent slow decomposition to tars when irradiated through a Corex filter.

The vinylogous imide 24 did undergo addition to cyclopentene to form the simple cycloadduct in good yield. Compound 24 can be regarded as a 3-amidocyclohexenone; evidently the greatly reduced electron-donating ability of the amido function as compared to the amino group results in an excited state similar to those of the normal cyclohexenones, rather than the vinylogous amides 4 and 5. Other examples of photochemical cycloaddition of vinylogous imides related to 24 have been reported.[9]
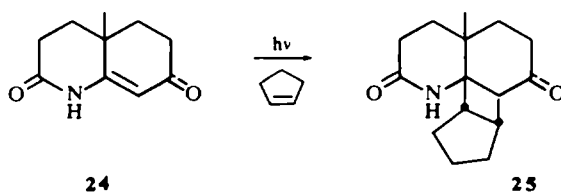
Yang has reported the formation of vinylogous amides by irradiation of N-vinyl amides;[10] the product vinylogous amides have structures analogous to **4** and **5** and were inert to continued irradiation. The inertness of Yang's acyclic compounds is not unexpected, since their excited state can dissipate energy by *cis-trans* isomerization.

DISCUSSION OF RESULTS

The photochemical cycloaddition of cyclohexenone and of 3-acetoxy-, 3-methyl-, and 3-phenylcyclohexenone with several olefins can be interpreted as occurring *via* a mechanism involving radical-like intermediates and in which the rule of the most favorably oriented π-complex of enone and olefin predicts the sole or predominant product.[4, 6] Thus, olefinic substrates bearing electron-donating substituents usually produce 7-substituted bicyclo[4.2.0]octan-2-ones and those olefins possessing electron-withdrawing groups give rise to 8-substituted bicyclooctanones. Consideration of the most stable diradical intermediate correctly predicts the major products in thermal 4 + 2 cycloaddition; however this procedure predicts the major cyclobutane in 2 + 2 photocycloadditions only if C-2 is assumed to be the site of initial bonding. The position of initial bonding in such cycloadditions is, however, currently a matter of uncertainty.[11, 12] Exceptions do exist to the π-complex rule. It has recently been observed by us[4] and others [2a] that in the case of cycloadditions to olefins which are very mildly polarized (e.g., by mildly electron-donating groups such as alkyl or aryl) that the steric effects of a moderately bulky 3-substituent is sufficient to reverse the orientation of the components in the π-complex, and consequently, the orientation in the predominant cycloadduct.

The present results are consistent with the general picture outlined above and serve to supplement it and to amplify certain features. In those cases where photoannelation was in fact observed with **1** and **3**, the rates of addition and product orientations were similar to that in analogous reactions of the parent enone. The photochemical behavior of **1** was difficult to predict, since it no longer has the π-system of a simple enone. Others have recently reported straightforward behavior for **1** and for 3-carbomethoxy-cyclohexenone when irradiated in the presence of ethylene.

On the other hand, enones **2** and **3** are far less reactive than cyclohexenone itself and **1**; the major result of the present study is the reluctance of **2** and **3**, and the complete refusal of **4** and **5** to undergo cycloaddition. The predominant products from irradiation of **2** and **3** in solvents bearing abstractable hydrogens arise from species derived from attack on these enones of radicals produced by hydrogen abstraction from solvent or olefin. This type of behavior is well known for n → π* triplets of saturated and aryl ketones.[13] One explanation of the observed effect of 3-substituents is that the reactive enone excited state in cycloaddition is the π → π* triplet, as suggested by Wagner,[12] and is electron deficient at both C-2 and C-3. Strongly electron-donating substituents would thus slow down the rate of cycloaddition by altering the electron distribution in that excited state. It would then seem reasonable that in many enones with an unreactive π → π* state there are observed simultaneously with, or instead of, cyclo-addition, reactions such as hydrogen abstraction which are characteristic of n → π* triplets (a higher excited state if the π → π* triplet is indeed the reactive state in cycloaddition). Such reactions are relatively inefficient and are rarely observed for enones more reactive to cycloaddition than **2–5**. The evidence available from the present and other work on the effects of enone substituents and on the reactivities of

olefinic substrates is therefore consistent with Wagner's contention that a lowest-lying enone $\pi \to \pi^*$ triplet is the reactive species in cycloadditions, but certainly does not require this conclusion. It may be that in photocycloadditions an n $\to \pi^*$ triplet is the reactive excited state after all, and electron-withdrawing substituents simply make C-2 and C-3 unreactive, while leaving unchanged the odd-electron character of the O atom, and consequently its H-abstracting property. More information on the site of initial bonding in these cycloadditions should shed light on the nature of the reactive species; we are currently pursuing studies designed to provide evidence concerning the initial reactive site in photocycloadditions of enones to unsymmetrical olefins.

EXPERIMENTAL

General procedure for irradiations. The reactions were conducted as previously described.[4] Thus, the apparatus consisted of a cylindrical Pyrex irradiation vessel which surrounded a quartz immersion well and was fitted by means of side arms with a cold-finger condenser and a small serum bottle cap. Chilled water at 5–8° was passed through the annular space of the quartz well and also through an external bath in which the entire apparatus was immersed. For those reactions in which isobutene was employed, an ethylene glycol–water mixture cooled to −20° was passed through the well and through a cooling coil in an external glycol–water bath. Solns of the enones and substrates in dry solvent were placed in the vessel and were deoxygenated by flushing with purified N_2 for 1.5 hr. A slight positive pressure of N_2 was maintained throughout the irradiations. The solns were irradiated by a Hanovia Type L medium pressure 450-W mercury arc. A Corex filter sleeve was employed; this filter is opaque to light of wavelength shorter than 260 nm. The progress of the reactions was monitored by removing aliquots with a syringe and examination by gas chromatography or IR techniques. Gas chromatographic work was performed on the following columns: (1) 5 ft × 0.25 in 5% SE-30 silicone rubber on Chromosorb P (column A), (2) 5 ft × 0.25 in 5% Carbowax on 20-M on Chromosorb P (column B), and (3) 12 ft × 0.25 in 10% QF-1 fluorosilicone rubber on Chromosorb W (column C). Preparative gas chromatographic separations were accomplished using either a 10 ft × ⅜ in 20% Carbowax on Chromosorb P (column D) or a 6 ft × ⅜ in 20% SE-30 on Chromosorb W (column E). NMR spectra were obtained on a Varian A56-60A instrument operating at 46°.

Photoaddition of 3-cyanocyclohexenone (1) to cyclopentene. A soln of 3-cyanocyclohexenone (2.42 g, 0.020 mole) and cyclopentene (41 g, 0.6 mole) in dry ether (150 ml) was irradiated under the standard conditions for 1.5 hr. Evaporation of the solvent and excess cyclopentene, trituration of the residue with ether–pentane, and filtration gave the crude adduct.[i] Recrystallization from MeOH gave pure 7 as white prisms, mp 69–70° (2.4 g, 63%); IR (KBr) 2238 and 1710 cm⁻¹; NMR (CHCl₃) τ 7.35 (1H, half of AB, $J \sim 8$, Hα to CO) and 7.2–8.7 (14H). (Found: C, 75.93; H, 8.03. Calcd. for $C_{12}H_{15}NO$: C, 76.21; H, 7.94%). Gas chromatographic examination of the reaction mixture revealed no other volatile components.

Photoaddition of 1 to 1,1-dimethoxyethylene. Irradiation of 1 (1.21 g, 0.010 mole) and 1,1-dimethoxy-ethylene (30 g, 0.34 mole) in ether (170 ml) for 3 hr, followed by evaporation of the solvent and distillation at 100 mm of the excess dimethoxyethylene gave a brown oil which was evaporatively distilled to give adduct 8 (1.18 g, 58%) as a colorless oil which darkened on standing at room temp; IR(film)2240 and 1709 cm⁻¹; NMR (CCl₄) τ 6.67 and 6.79 (3H each, s, OCH₃), 7.3 (1H, X part of ABX $J = 8.6$, $J' = 5.2$, H-1) m/e (P) 209. An analytical sample was collected from column E at 210°. (Found: C, 62.97; H, 7.31. Calcd. for $C_{11}H_{15}NO_3$: C, 63.22; H, 7.18%).

Treatment of 8 with 2:1 THF-3N HCl for 4 hr at 50° resulted in no change; more vigorous acid treatment caused decomposition to tarry material.

Photoaddition of 1 to isobutylene. A soln of 2.42 g of 1 (0.2 mole) and isobutene (56 g, 1.0 mole) in ether (140 ml) was irradiated at −20° for 4 hr. Evaporation of solvent and excess isobutene gave a brown oil which was evaporatively distilled to give a mixture of adducts 9 and 10 (2.6 g, 78%) bp 70° (bath)/0.2 mm. Analytical GC showed the presence of two components in a ratio of 87:13. The adducts decomposed on attempted preparative GC, but the NMR spectrum of the mixture was sufficiently informative as to allow structure assignments to be made.

IR (film) 2238 (CN) and 1705 (C = O) cm⁻¹; NMR (CCl₄); τ 6.83 (1H, 2 d, $J = 10.6$, $J' = 9.2$ Hz, H-1 of 9; 7.1 (1H, s, H-1 of 10); 8.57 and 8.86 (k H each, s, Me's of 9); 8.67 and 8.84 (3H, s, Me's of 10).

Photoaddition of 1 to 1,2-dichloroethylene. A soln of 1 (1·2 g, 0·01 mole) and 1,2-dichloroethylene (48 g, 0·50 mole) in ether (160 ml) was irradiated for 3·5 hr. Evaporation of the solvents gave an unstable brown oil which evolved HCl at room temp. This material, a mixture of adducts of gross structure, 11, exhibited the following spectral data: IR (film): 2245 (CN) and 1710 (C = O) cm^{-1}; NMR (CCl$_4$) τ 6·3 (2d, J = 9, J = 7, Hα to Cl; 6·8–8·2 (7H, multiplets); mass spectrum: 217, 219, 221 (P, P + 2, P + 4).

Irradiation of 3-chlorocyclohexenone (2) and cyclopentene. A soln of 3-chlorocyclohexenone[14] (2·2 g, 0·02 mole) and cyclopentene (50 g, 0·68 mole) in ether (140 ml) was irradiated under the standard conditions for 36 hr. Evaporation of the solvent and distillation of the excess cyclopentene and evaporative distillation of the brown oily residue gave 0·94 g of pale yellow oil, bp 70–80°/0·2 mm (bath), a mixture of four components as shown by GC on column A. Attempted preparative GC led to loss of HCl and decomposition to ill-defined material. Slow evaporative distillation led to fractions rich in the two major components. Fraction 1, bp 60–70°/0·2 mm (bath) exhibited the following spectral data; IR (film) 1050–1200 (s, br, C—O); NMR (CCl$_4$) τ 3·22 (1H, m) and 8·0–9·5 (14H, m); m/e (P) 198, 200; Fraction 2, bp 75–80° (bath/0·2 mm) 0·2 mm; IR (film): 1705 cm^{-1}; NMR (CDCl$_3$): τ 7·3 (1H, d, J ~ 5, Hα to CO) and 7·4–8·5 (14H, m) m/e (P) 198, 200. A soln of fraction 2 (0·50 g) in t-BuOH was stirred overnight with a soln prepared by dissolving K (0·2 g) in t-BuOH. Most of the BuOH was removed under reduced pressure and the residue was poured into water and extracted several times with ether. The oil remaining after evaporation of the ether extracts was shaken for 1 hr in EtOAc with 10% Pd-C under 10 psi hydrogen pressure. The catalyst was filtered off, the solvent evaporated, and the residue distilled, giving 0·21 g, bp 60–62°/0·3 mm of colorless oil. The oil showed two peaks on column B at 160°; the major (78%) component was identical (IR, GC on 3 columns) with the major isomer from addition of cyclohexenone to cyclopentene.[6]

Photolysis of 3-methoxycyclohexenone (3) in ether-cyclopentene. A soln of 3-methoxycyclohexenone (2·52 g, 0·020 mole) and cyclopentene (45 g, 0·67 mole) in dry ether (150 ml) was irradiated under the standard conditions for 60 hr. Distillation of the ether and excess cyclopentene gave a yellow oil (4·1 g) which was vacuum distilled to afford three fractions: A, bp 30–46°/0·3 mm, (2·0 g); B, bp 64–70°/0·3 mm; and C, bp 70–120°/0·3 mm (2·6 g).

Analysis of fraction A on column A showed the presence of three major components, amounting to 20, 37, and 31% of the total mixture. These were identified as (1) 3,3'-bicyclopentenyl, by comparison with an authentic sample; (2) 3-(α-ethoxyethyl)cyclopentene; NMR (CCl$_4$; *inter alia*) τ 4·0 (2H, m) 5·8 (1H, m, H on C-3), 8·9 (3H, d, J = 7 Hz), and (3) 2,3-diethoxybutane, by comparison with a sample obtained by a method previously described.[15]

Fraction B was shown by IR and GC to consist of unchanged 3 (95% pure).

Fraction C consisted of four components which were isolated by collection from column E. These were, in the order of elution at 210°: **15**, 3-(α-ethoxyethyl)cyclohexenone(retention time 4·3 min) (33% of area, 21% yield by GC); IR (film) 1670, 1629, and 1097 cm^{-1}; UV (CH, OH) max 234 nm (ε = 13,000); NMR (CCl$_4$): τ 3·8 (1H, br, s, H-2), 5·95 (1H, q, J = 7·5, CH$_3$CH—O—), 6·49 (2H, q, J = 7·0, —CH$_2$—CH$_3$), 7·3–8·5 (6H, m), 8·68 (3H, d, J = 7·5), and 8·79 (3H, tr, J = 7·0); mass spectrum, m/e (rel intensity) 168 (1·0P), 167 (10·2), 126 (4·1) and 113 (23). Found: C, 71·29; H, 9·35. Calcd. for C$_{10}$H$_{16}$O$_2$: C, 71·44; H, 9·52.

The second peak to be eluted (retention time 5·8 min) was unchanged starting material, **3** (11% of area). The third peak (retention time 12·3 min) was identified as adduct **16**, 7-methoxy-tricyclo[6.3.0.0^{2,7}] undecan-3-one (42% of area, 27% yield); IR (film) 1706 cm^{-1}; NMR (CCl$_4$): τ 6·84 (3H, s, OCH$_3$) and 7·2–8·6 (15H, m); mass spectrum: m/e 194(P). (Found: C, 74·01; H, 9·53. Calcd. for C$_{12}$H$_{18}$O$_2$: C, 74·24; H, 9·27%).

The fourth peak (retention time 19·6 min) was assigned structure **17** (18% of area, 13% yield); IR (film)

$$ \overset{\text{H}}{\underset{|}{} } $$

3500 and 1060 cm^{-1}; NMR (CCl$_4$) τ 6·0–6·7 (4H, m, —C—O—) 6·61 (3H, s, OCH$_3$), 7·4–8·7 (8H, m), 8·76 (3H, t, J = 6·8), 8·80 (3H, d, J = 7·0, CH$_3$CH); mass spectrum, m/e 202 (P).

Photoaddition of 3-methoxycyclohexenone to 1,1-dimethoxyethylene. A soln of 3-methoxycyclohexenone (2·4 g, 0·02 mole) and 1,1-dimethoxyethylene (44 g, 0·50 mole) in dry benzene (150 ml) was irradiated under the standard conditions for 36 hr. Distillation of the solvent and unchanged dimethoxyethylene, followed by evaporative distillation of the residue in a modified Hickman still gave first, unchanged 3 (1·1 g) and then crude adduct **19**, 6,7,7-trimethoxybicyclo[4.2.0]octan-2-one (0·68 g, 90% pure by GC; 30%) as a colorless oil, 100–110° (bath)/0·2 mm; UV: end absorption; IR (film): 1704 (C=O) and 1050–1210 (C—O) cm^{-1}; NMR (CCl$_4$): τ 6·76, 6·84, and 6·86 (3H each, singlets, Me); 7·8 (1H, m, H-1), and 7·6–8·6 (8H, m); m/e 214 (P). Because of the thermal instability of **19** we were unable to obtain a pure sample (and accurate analytical data).

Pyrolysis of adduct 19; *isolation of* 23. Compound 23 could be obtained from 19 by distillation from a flask preheated to 220–240° at 30 mm, or more simply by preparative scale gas chromatography of 19 on column E at 210° (injector block temp, 250°). The latter method gave a clean conversion to a pale yellow oil which was redistilled (bp 50° (bath)/0·3 mm) to give pure 23; (IR (film) 1767 (C=O) and 1628 (C=C)cm⁻¹; NMR (CCl₄) τ 5·04 (1H, d, $J = 3·3$, —C$\underline{H}$—O—), 6·23 and 6·62 (3H each, singlets, Me) 7·08 (1H, m, —C$\underline{H}$—CH—O), and 8·35–8·55 (6H, m); mass spectrum : m/e (182 (1·0, P), 154 (11·5), 139 (5·0), 122 (2·9) and 111 (6·5). (Found: C, 65·09; H, 8·70. Calcd. for $C_{10}H_{16}O_3$: C, 65·38; H, 8·79%). A 2,4-DNP isolated after the usual treatment was recrystallized from EtOAc to give tiny yellow prisms, mp 236–238°, which analyzed for a *bis*-DNP derivative of a diketone obtained from hydrolysis of a keto-enol ether. (Found: N, 21·0. Calcd. for $C_{21}H_{17}N_8O_9$: N, 21·3%). Stirring a sample of 19 (0·1 g) with 2:1 THF-6N HCl for 6 hrs, pouring into water, extraction with ether, drying and evaporation of the ether extracts gave a pale yellow oil, (bp 80–90°/0·3 mm), [IR (film) 1779 and 1702 cm⁻¹; m/e (P) 152], dione 20.

Photolysis of 3 *in tetrahydrofuran.* Irradiation of a soln of 3 (1·25 g) in THF for 60 hr and workup as before gave, besides recovered 3 (0·7 g), a fraction (0·8 g, bp 110–210°/0·3 mm) whose IR (v_{max} 1709 cm⁻¹) and NMR spectra [τ 3·9 (1H, S), 6·0 (1H, m) and 7·9–8·7 (m)] and mass spectrum (m/e 166) indicated it to be 3-(2-tetrahydrofuryl)2-cyclohexenone.

Irradiation of vinylogous amides. Compounds 4,[16] 5a,[17] and 5b were irradiated through Corex or Pyrex in CH_2Cl_2 or THF in the presence of cyclopentene and acrylonitrile (20-fold excess). Compound 4 was destroyed after 24 hr exposure to Pyrex-filtered light. The bicyclic compounds 5a and 5b were unchanged after several days exposure to Pyrex-filtered light, but underwent slow decomposition when a Corex filter was used. In no case was the formation of any adduct detected.

Photoaddition of 24 *to cyclopentene.* A soln of 24,[18] (0·50 g, 2·8 mmole) and cyclopentene (23 g, 0·33 mole) in acetonitrile (150 ml) was irradiated for 6 hr. Evaporation of the solvent and excess olefin gave a viscous pale-yellow syrup which was chromatographed on silica gel. Elution with CH_2Cl_2 EtOAc (9:1) gave adduct 25 as an almost colorless viscous oil, v_{max} (film) 1717 and 1652 cm⁻¹; NMR (CDCl₃) τ 6·1 (1H, br, NH) 7·3–7·9 (7H. m) 8·0–8·6 (10H); m/e (P) 247.

Quantum yields. Quantum yields were estimated by following the extent of the reaction using filter solutions to isolate the 313 nm line from the mercury lamp. The benzophenone-benzhydrol system was used as actinometer.

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