The Photo-cycloaddition of 3-Cyano-2,4-pentanedione with Cyclohexene and Its Quenching by Enol Ether

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The 1,3-dicarbonyl compound, with an electro-negative substituent, 3-cyano-2,4-pentanedione, gives the photo-addition product with cyclohexane. The adduct must be formed by the retro-aldol reaction of the "2+2" cyclo-addition product and the hemiacetalization of the resulting 1,5-dicarbonyl compound. Enol ether, with a lower ionization potential, does not photoadd to 3-cyano-2,4-pentanedione but quenches the photoaddition between 3-cyano-2,4-pentanedione and cyclohexene. The solvent effect, the ionization potential, and quenching experiments show that the photoaddition follows a process involving a singlet excited complex.

It is well known that 2,4-pentanedione (**1**), a non-cyclic 1,3-dicarbonyl compound, gives a photoaddition product with olefin through its enol form. The classical work by de Mayo *et al.*,[1] however, was not followed by frequent application, even though this type of reaction seems to be a useful method for the preparation of 1,5-diketone and cyclohexenone derivative by the base-catalyzed condensation of the diketone (Eq. 1). To determine the scope and limitation of this type of reaction, we attempted the photocycloaddition of Compounds **2**—**6** with cyclohexene. None of these compounds, however, showed any photo-reactivity. Several factors may influence the reactivity of these compounds such as; a) the electronic configuration of the lowest excited state, nπ^* or $\pi\pi^*$; b) the importance of the enol form in keto-enol equilibrium; c) the fixation of the cyclic *s-cis* conformation by intramolecular hydrogen bonding, and d) the effect of excitation on the intramolecular hydrogen bonding. Non-cyclic 1,3-dicarbonyl compounds with an additional electronegative group, such as methyl 2,4-dioxopentanoate (**7**) or 2-(methoxycarbonyl)-1,3-propanedial (**8**), have been reported to give photo-adducts with olefins.[2,3] This fact strongly suggests the importance of charge transfer interaction between these electronegative dicarbonyl compounds and olefin for the photo-cycloaddition. We selected 3-cyano-2,4-pentanedione (**9**) as a dicarbonyl compound and wish to report on the nature of the photo-cycloaddition of **9** with olefin.

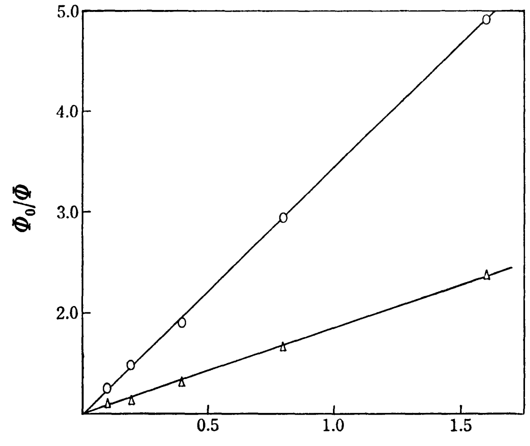
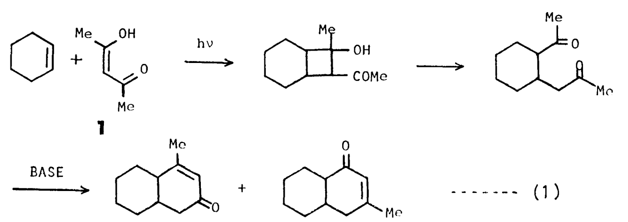
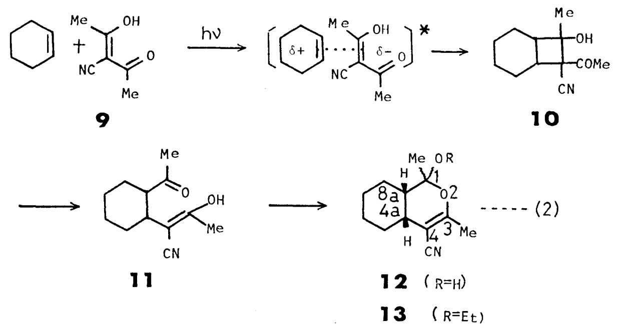
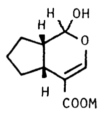


Fig. 1. Quenching of photo-cycloaddition of **9** to cyclohexene by enol ethers.







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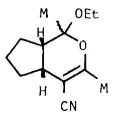

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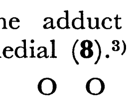
The irradiation of 3-cyano-2,4-pentanedione (**9**) in the presence of excess cyclohexene in variety of solvents gave the photoadduct **12** in variable yields; a cyclic ethyl acetal, **13**, was obtained when absolute ethanol was used as the solvent. The structure of **12** was deduced from the spectral data and by analogy with the structure of the adduct between 2-(methoxycarbonyl)-1,3-propanedial (**8**).[3]



	R_1	R_2	R_3
1	Me	H	Me
2	Me	Me	Me
3	Me	Ph	Me
4	Me	H	Ph
5	Me	H	OMe
6	Ph	H	OEt
7	Me	H	COOMe
8	H	COOMe	H
9	Me	CN	Me

As a precedent, the photoadduct **12** must be derived from the 2+2 adduct, **10**, of 3-cyano-2,4-pentanedione and cyclohexene, which opens the cyclobutane ring by means of retro-aldol-type cleavage, giving the 1,5-dicarbonyl compound, **11**, followed by the hemiacetalization (Eq. 2). The sharp IR absorptions at 3420, 2210, and 1617 cm^{-1} show the presence of hydroxyl, conjugate cyano, and conjugate enol ether groups respectively. The NMR signals at $\delta=1.53$ (singlet) and 2.10 ppm (doublet, $J=2$ Hz) are due to the methyls at the hemiacetal carbon (C_1) and enol ether moieties. The long-range coupling of the latter signal with the hydrogen at C_{4a} (2.96 ppm) has been evidenced by a decoupling experiment.[4] The NMR signal at $\delta=2.96$ due to the hydrogen at C_{4a} is a multiplet with the half-band width of 10 Hz, which shows the lack of vicinal diaxial coupling and the equatorial nature of the H_{4a} on the cyclohexane ring. The observation of Dreiding molecular models indicates that H_{4a} bisects the methylene at C_5 and that the dihedral angle between H_{4a} and H_{8a} is *ca.* 50°. The vicinal couplings between these hydrogens, in addition to the long-range coupling between H_{4a} and C_3-methyl, meet the requirements for H_{4a} being equatorial. These aspects of the NMR spectrum lead us to deduce that the stereochemistry of the ring junction of the adduct is *cis*.

The photoreaction between 3-cyano-2,4-pentanedione (**9**) and cyclopentene in absolute ethanol gave a similar product, **15**, with *cis*-ring fusion, this is completely parallel to the photoreaction of 2-(methoxycarbonyl)-1,3-propanedial to cyclopentene to give the adduct **14**. The photoreaction of **9** was carried out in a variety of solvents, such as hexane, benzene, ether, THF, ethanol, methanol, and methanol–acetonitrile (1 : 1); the yield of the adduct **12** is generally better in alcoholic solvents than in non-polar solvents or in acetonitrile. Casal *et al.*[5] reported that an aromatic 1,3-dicarbonyl compound, **4**, adds photochemically to styrenes or stilbens, though in our trial **4** failed to enter the photo-addition to cyclohexene. From the discussion above, the 1,3-dicarbonyl system with an electronegative group or the conjugated olefin with an aromatic system seems to be required for the photo-addition. The UV spectrum of mixture of **9** and cyclohexene does not show any evidence for the formation of a CT complex, at least in dilute concentrations, in the ground state. These results, in conjunction with the solvent effect, suggest that the photo-addition takes an excited complex process of charge transfer. The attempted photoreaction of **9** with an olefin having a lower ionization potential, such as ethyl vinyl ether (I_p: 8.6 eV),[6] 2,3-dihydro-1,4-dioxin (I_p: *ca.* 7.6 eV),[7] or *cis*-1,2-dimethoxyethylene (I_p: 8.0 eV)[6] in ether, does not give any photoadduct, but the starting material is recovered. On the other hand, cyclohexene (I_p: 8.9 eV), with higher ionization potential, shows photoreactivity in the same solvent; hence, the excited complexes with olefins having lower ionization potentials are considered to be dissociated into radical-ion pairs by electron transfer in ether. Since the excited complex formation is favored with such olefins, enol ethers are expected to quench the photo-addition between **9** and cyclohexene. Such was found to be true in the photo-addition of 2-buten-4-olide with olefins and its quenching by 1,1-dimethoxyethylene.[9] Stern-Volmer plots of the quenching experiments on the photo-addition of **9** indeed show a straight line with the slopes of 2.46 and 0.85 M^{-1} for 2,3-dihydro-1,4-dioxin and ethyl vinyl ether respectively (Fig. 1). The importance of charge transfer and electron transfer for this quenching is evident from the quenching-rate constants being dependent upon the ionization potential of the quencher. 1,3-Pentadiene (I_p: 8.7 eV)[8] and oxygen do not quench the photo-addition of **9** in a normal manner for a triplet quenching, but a higher concentration of 1,3-pentadiene quenches the reaction and gives the 1 : 1 adduct, in a poor yield, from the excited complex between **9** and 1,3-pentadiene.

In conclusion, the photo-cycloaddition of 3-cyano-2,4-pentenedione (**9**) to olefin takes a singlet excited complex process, and the cyclization competes with the electron-transfer process, employing **9** as an electron accepter (A) and olefin as a donor (D).

$$\begin{tikzcd}
\text{``A''} \arrow[r, "h\nu"] & {[A]^{*1}} \arrow[r, "\text{``D''}"] & {[A\cdots\cdots D]^{*}} \arrow[r] \arrow[d, "\text{solvent}"] & \text{Adduct} \\
 & & {[A(\text{solvent})]^{-} + [D(\text{solvent})]^{\dot{+}}} &
\end{tikzcd}$$

Experimental

Preparation of Materials. The 3-cyano-2,4-pentanedione (**9**) (mp 51 °C, UV: $\lambda_{\max}^{\mathrm{EtOH}}$ 276 nm (10300)), was synthesized by the method of Traub[10] from 2,4-pentanedione and cyanogen generated by the addition of a sodium cyanide solution to a solution of copper(II) sulfate.[11] The cyclohexene was prepared by the acid-catalyzed dehydration of cyclohexanol and was distilled before use. Commercially available ethyl vinyl ether was distilled (bp 36—37 °C) immediately before use to remove the stabilizer. The 2,3-dihydro-1,4-dioxin (bp 94—95 °C) was prepared by the method of Sammerbell *et al.*[12,13] by the dechlorination of *trans*-2,3-dichloro-1,4-dioxane. The *cis*-1,2-dimethoxyethylene (bp 97 °C) was prepared by the method of Shostakoviskii *et al.*[14] by the gas-phase elimination of methanol from 1,1,2-trimethoxyethane[15] catalyzed by silica gel–BaO at 350—370 °C. The collection of the fraction boiling at 97 °C by repeated distillations gave *cis*-1,2-dimethoxyethylene.

*Photo-cycloaddition of 3-Cyano-2,4-pentanedione(**9**) with Cyclohexene.* To **9** (125 mg, 1 mmol) and cyclohexene (5 g, 60 mmol) we added one of the solvents, and the total volume was adjusted to 10 ml. The solution, placed in a Pyrex tube was sealed by means of a rubber septum and the solution was bubbled by argon for several minutes through a syringe needle. Irradiation was carried out externally with a 450-W high-pressure mercury lamp mounted in the center of a rotary irradiation apparatus (Rikosha Merry-go-round type; the distance between the lamp and the tube is *ca.* 5 cm) for 50—60 h, the reaction being monitored by TLC analyses. In the case of the methanol solution, the starting **9** disappeared after 55 hs' irradiation, at this time the solution was condensed *in vacuo*. The chromatography of the residue on alumina (Merck act. II-III) eluted with 1) benzene, 2) benzene–ether (1:1), and 3) ether gave a crystal of the adduct **12** from the benzene–ether eluate (125 mg, 60%). **12**, mp 113.8—114.3

°C(recrystalyzed from ether). Found: C, 70.01; H, 8.37; N, 6.98%. Calcd for $C_{12}H_{17}NO_2$: C, 69.54; H, 8.27; N, 6.76%. MS (80 eV): m/e(%) 207(M^+, 10), 189(7), 165(50), 164(39), 149(19), 136(53), 125(100), 122(75), 81(72), 71(66), and 43(92). UV: λ_{max}^{EtOH} 236 nm (16900). IR(Nujol): 3420, 2210, 1617, 1275, 1155, and 1065 cm^{-1}. NMR($CDCl_3$): (δ) 4.00(3H, s), 2.96(1H, diff. s $W_{1/2}$: 10 Hz), 2.10(3H, d, J=2 Hz), 1.53(3H, s), and 2.1—0.8 ppm(10H). The yield of the adduct **12** was best in methanol or ethanol (60—70%), and worse in a non-polar solvent or in acetonitrile. Ethyl acetal was obtained when absolute ethanol was used as a solvent. The refluxing of the methanol solution of **9** without irradiation as a dark reference gave no adduct at all.

Quenching Experiments. *a) Quenching by Enol Ether or 1,3-Pentadiene*: A solution of 3-cyano-2,4-pentenedione (**9**) (0.05 mol/l), cyclohexene (1.5 mol/l), and 0—0.6 mol/l of a quencher (2,3-dihydro-1,4-dioxin, ethyl vinyl ether, or 1,3-pentadiene) in ether was placed in Pyrex tubes and irradiated by using a rotary irradiation apparatus after the deoxygenation of the system. After irradiation for 17 h, GLC analyses showed that the starting material was still a major component in the reaction mixture; to each reaction mixture we added the same amount of 1,2-di-*m*-tolylethane as an internal reference. Stern-Volmer plots obtained by GLC analyses of the adduct in each reaction mixture gave the straight lines with the slopes of 2.46 and 0.85 M^{-1} for 2,3-dihydro-1,4-dioxin and ethyl vinyl ether respectively.

b) Quenching by Oxygen: The mixture of **9** (0.05 mol/l) and cyclohexene (1.5 mol/l) in ether was placed in two Pyrex tubes; one of the solutions was bubbled by oxygen under cooling in an ice-salt bath, while the other was purged with argon. Irradiation of both solutions for 15 h and GLC analyses did not show any distinct difference in the photoreactivity.

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