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EFFECT OF MICELLAR MEDIUM ON PHOTOANNELATION Vs ENERGY TRANSFER IN THE SYSTEM EXCITED CYCLOHEX-2-EN-1-ONE-CYCLOPENTADIENE

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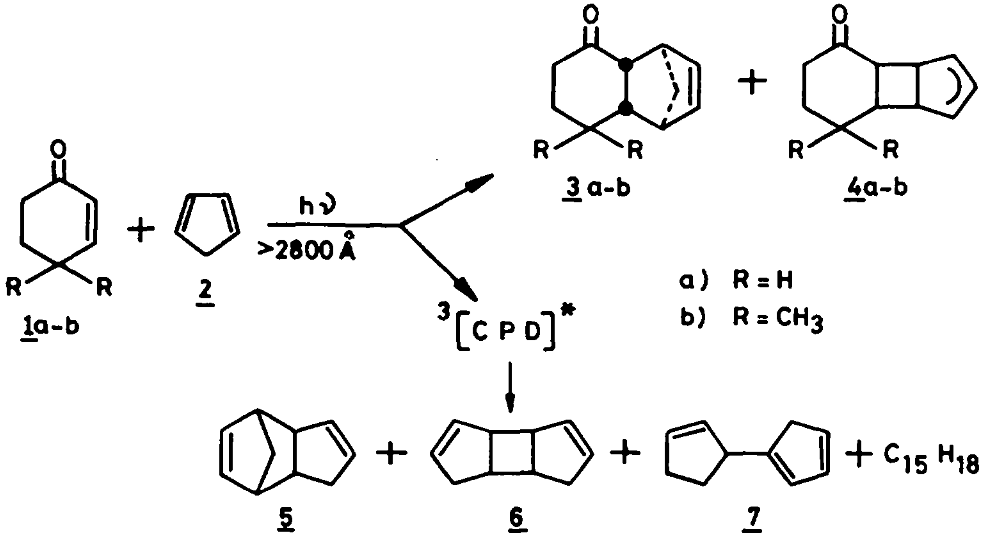
Abstract : The relative ratio of enone-CPD adducts and $C_{15}H_{18}$ formed in the photochemical reaction between cyclohex-2-en-1-one and its 4,4-dimethyl derivative and CPD in different media suggest that an exciplex is responsible for 2+2 photoannelation and energy transfer and a transoid or twisted enone for photo Diels-Alder reaction.

Conjugated dienes are known to act as efficient quenchers[1,2] for enone triplet and the mechanism involves both energy transfer and chemical reaction. The energy transfer produces triplet diene which are known to give different dimeric products[3,4] (2+2, 4+2 and 4+4 cycloadditions). Cantrell[5] studied the photoannelation reaction between different enones and conjugated dienes and reported the formation of both enone-diene 2+2 and 4+2 adducts. No further attempts were made to distinguish between the different photochemical and photophysical process in the system excited enone-diene. We looked for a clue to their relative importance by studying the reaction of cyclohex-2-en-1-one 1a and its 4,4-dimethyl derivative 1b with CPD 2 in different media like cyclohexane, micelles and microemulsions.

PHOTOPRODUCTS



Scheme 1

The GC-MS analysis of the product mixture from the reaction between n-π^* excited enone 1a and CPD showed the presence of the already known[5] enone-CPD photo Diels-Alder

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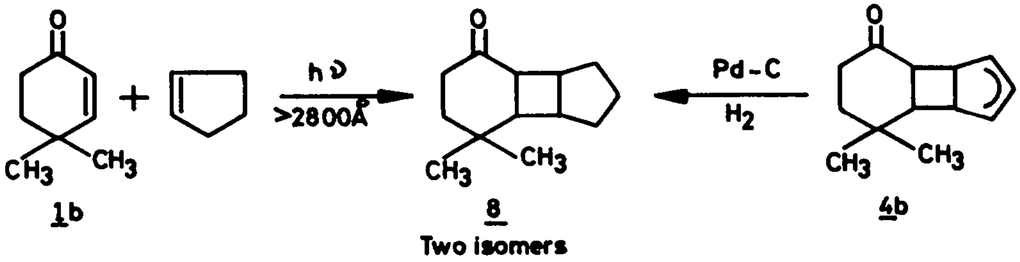
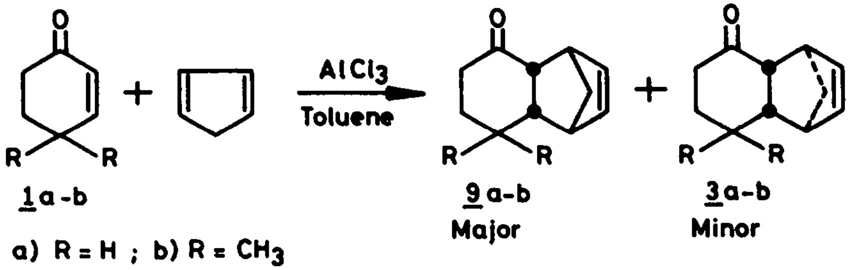
adduct 3a and a mixture of isomeric 2+2 adducts represented as 4a and a new hydrocarbon $C_{15}H_{18}$ in addition to isomeric $C_{10}H_{12}$ hydrocarbons 5-7 known to be formed in the photochemical reactions of CPD sensitized by ketones with different triplet energy[3,4,6]. The system enone 1b and CPD gave the corresponding products all of which are shown in Scheme 1.

Enone-CPD 2+2 adducts 4a-b : Cantrell[5] identified three isomeric 2+2 adducts represented as 4a from 1a and CPD and our results agree with this finding. The system excited enone 1b-CPD gave an inseparable mixture of two isomeric adducts represented as 4b and their identity was established by catalytic hydrogenation to 8 and comparison with the isomeric mixture obtained from the photoannelation of 1b to cyclopentene as shown in Scheme 2.



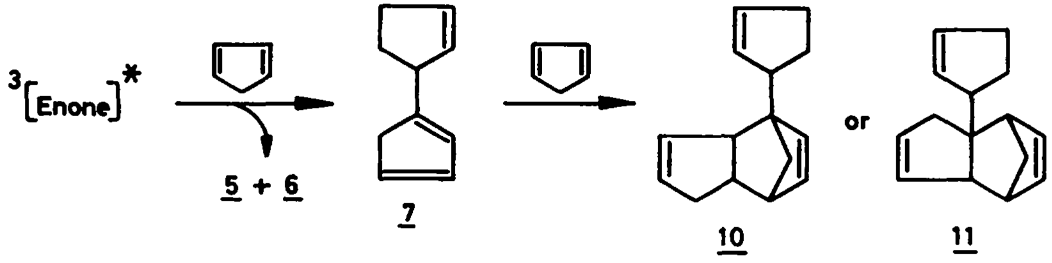
Scheme 2



Scheme 3

Enone-CPD 4+2 adducts : The photo Diels-Alder adduct 3a was presumed[5] to be one of the two trans fused exo or endo isomers which could have been formed via a radical route or by concerted addition to a strained photochemically produced trans enone. Although spectroscopic studies[7] gave no evidence for the formation of an excited transoid enone, the formation of trans fused[8] enone-olefin 2+2 adducts has been interpreted on the basis of a transient transoid enone. On this basis the photo Diels-Alder adduct 3 could have trans fused ring system. Molecular models have shown that a trans ring junction in 3 is highly strained and base treatment should give the cis fused isomer. Treatment of 3a or 3b with base did not result in any change as revealed by ^{1}H-NMR spectrum. The spectral data of 3a and 3b agree with the exo isomer formed as a minor product in $AlCl_3$ catalysed thermal reaction reported in literature[9] (see Scheme 3). On this basis the photo Diels-Alder adduct were identified as cis fused exo isomers 3a and 3b respectively.

$C_{15}H_{18}$ Hydrocarbon : The IR spectrum showed characteristic -C=C- absorption bands at ν_{max} 1615 and 1575 cm^{-1} for the presence of a cyclopentene and norbornene ring system[10] like in DCPD 5. In order to test if the trimer is formed from DCPD, separate experiments were conducted with enone 1a and CPD in the presence of varying amounts of DCPD. This did not increase the relative yield of $C_{15}H_{18}$ thus excluding its formation by reaction of DCPD with CPD. The ^{1}H-NMR spectrum of $C_{15}H_{18}$ revealed the presence of protons on sp^{2}and sp^3 carbons in the ratio of 1:2. The UV spectrum showed λ_{max} at 212 nm excluding the presence of a conjugated diene function. We arrived at two possible structures 10 or 11 for $C_{15}H_{18}$ based on the reported[6] formation of 1-(cyclopenten-3-yl)-cyclopentadien-1,3 7 as one of the products from the sensitized dimerisation of CPD. A photo Diels-Alder reaction between the dimer 7 and CPD can give the trimer which can have either structure 10 or 11.



Scheme 4

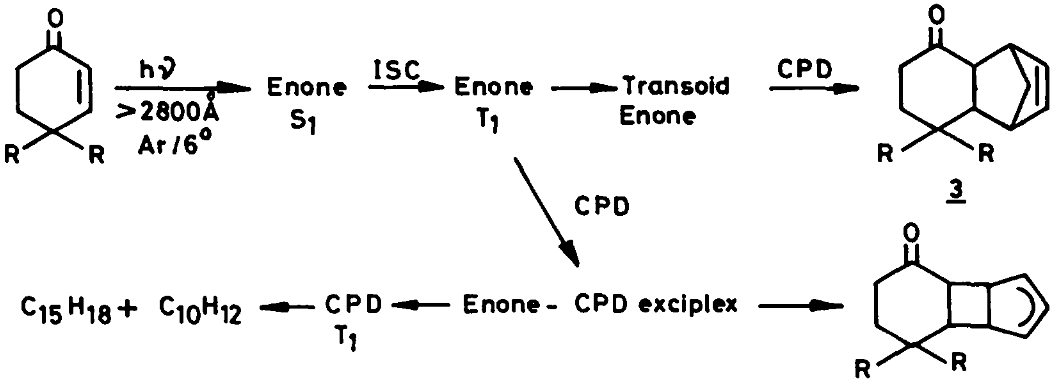
EFFECT OF MEDIUM

The relative ratio of products formed in cyclohexane, cyclohexane + n-butanol, micelles and microemulsions were estimated by gas chromatography and the results are given in Table 1. In this regard the CPD dimers 5-7 are not included because their relative amounts could not be estimated accurately due to the formation of DCPD under the conditions of analysis. It is therefore assumed that the estimation of the trimer $C_{15}H_{18}$ would qualitatively represent the energy transfer process and our interest at the moment is confined to relate the different possible enone transients, with the different photochemical processes. The results show that the relative ratio of photo Diels-Alder adduct 3 to the combined yield of 2+2 adduct 4 and

Table 1 : Medium effects on the product ratio in photoreaction of 1 with CPD

Entry	Medium	Relative ratio of product for 1a + CPD			Relative ratio of product for enone 1b + CPD		
		3a	4a	$C_{15}H_{18}$	3b	4b	$C_{15}H_{18}$
1	Cyclohexane	32	35	33	52	22	26
2	Cyclohexane : n-butanol (97:3)	31	41	28	52	26	22
3	SDS	32	56	12	50	39	11
4	Cetyl trimethylammonium bromide	31	60	9			
5	Lauryl ether	32	50	18			
6	Microemulsion	31	49	20			
7	Cyclohexane + DCPD	32	35	33			

$C_{15}H_{18}$ remains constant irrespective of the medium used. This signifies that the compounds 3 and 4 do not originate from a common transient enone. In micelles the yield of 2+2 adduct 4 shows an increase over that of $C_{15}H_{18}$. This is possible if a common intermediate is visualised for the formation of both these products. The nature of this intermediate can be inferred from the mechanism of enone-olefin photoannelation, where the formation of an exciplex[11] was postulated. The exciplex can collapse into ground state components, or result in the formation of 2+2 adduct, or energy transfer to produce triplet olefin, the latter in turn undergoing typical reactions[3,4]. In the event of the exciplex being a common intermediate for 4 and triplet CPD and hence $C_{15}H_{18}$, it may be expected that in micelles the exciplex would be stabilised to favour the formation of 2+2 adduct over energy transfer. An increase in quantum efficients of intermolecular cycloaddition reactions in micellar solutions over homogeneous solutions was observed in photocycloadditions[12]. The process that leads to the formation of Diels-Alder adduct should involve a different transient. The fact that the enones



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Scheme 5

1a-b do not give Diels-Alder reaction under thermal conditions unless catalysed by a Lewis acid should be taken into consideration[13]. The nature of enone intermediate responsible for Diels-Alder reaction with CPD may be understood from the work of D.I. Schuster et al[14] who proposed a ground state trans-cyclohex-2-en-1-one as responsible for some photochemical reactions. Taking the overall decay processes into consideration and the results obtained in the present study on medium effects, we propose that a transoid or twisted enone is responsible for photo Diels-Alder reaction with CPD. Scheme 5 depicts these pathways.

EXPERIMENTAL

General : The ^{1}H-NMR spectra were recorded on Varian FX-80A FT instrument in chloroform-d using TMS as internal standard. The IR and mass spectra were recorded on a Beckman IR and a VG micromass 70-70H spectrometers respectively. Cyclopentadiene prepared afresh by the cracking[15] of commercially available DCPD was used in all experiments. The DCPD used in the irradiation experiments was prepared by the dimerisation[16] of freshly prepared CPD at low temperature. Enone 1b was prepared by a reported method[17].

Irradiation : All irradiations were carried out in a 500 ml capacity jacketed reactor with a Pyrex immersion well using a Hanovia 450 Watt medium pressure Hg-arc lamp under continuous purging with Ar. The temperature of irradiated mixture was maintained constant at 6° ± 1 by chilled water circulation using a thermostat. The concentrations of the enone and CPD were 0.1M and 0.4M respectively. The solutions in micelles were prepared by dissolving SDS (9×10^{-3}M) or cetyl trimethyl ammonium bromide (9.2×10^{-4}M) or lauryl ether (1×10^{-3}M) in double distilled water mixing the enone and CPD and irradiated after sonication. The microemulsions were made by mixing SDS, H_2O cyclohexane and n-butanol in weight ratio 13:44:21:22 respectively.

GC analysis of photo products : The irradiated mixture obtained from reactions in organic solvent or the organic extract of the sodium chloride treated micellar medium was concentrated in vacuum at room temperature to remove the volatile components and the residue was analysed on a H.P. 5880 gas chromatograph using FID detector. In the case of enone 1a the analysis was done using a 8' x 1/8" S.S. column packed with 10% carbowax 20M on chromosorb WHP (100-200 mesh) with temperature programming (80°-5 min-10°/min.-220°). The retention times are $C_{15}H_{18}$-14.4 min, 3a-16.2 min and for the isomeric mixture 4a-16.9 min and 17.1 min. In the case of enone 1b a 8'x1/8"SS column packed with 10% carbowax 20M on DMCS treated and acid washed chromosorb W (80-100 mesh) with two ramp temperature programming (80°-5°/min-120°-2 min-10°/min-200°) was used. The retention times are $C_{15}H_{18}$-19.5min, 3b-25min and 4b-26 min.

1. **Isolation and identification of photo products :** The crude reaction mixture obtained after the removal of volatile compounds in high vacuum, was subjected to C.C. over silica gel using first hexane as eluent to obtain the CPD trimer. Subsequent elution with benzene gave fractions rich in 4+2 and 2+2 adduct. A repeat column chromatography gave analytically pure compounds. The 4+2 adduct[9] 3a and 3b and the isomeric mixture of 2+2 adducts[5] 4a were

known compounds and the spectral data agreed with those reported in literature. The data for the new compounds are given below.

a) **CPD trimer $C_{15}H_{18}$ 10 or 11** : IR (neat)ν_{max} : 1615 and 1575 cm^{-1}; UV (EtOH):λ_{max} at 212 nm (ε 19,700). ^{1}H-NMR ($CDCl_3$) δ ppm:5.4-6.1 (over lapping m,6H),3.0(m,1H), 1.7-2.8 (m,11H); High resolution mass spectrum : M^+ at m/z 198.1409, calculated for $C_{15}H_{18}$ 198.1409.

b) **Tricyclo[6.3.0^{2,7}0]-undeca-(9 or 10)en-3-one 4b** : IR (neat)ν_{max} : 3047, 1715 and 1603 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δppm:5.76 (d,2H); High resolution mass spectrum : found M^+ at m/z 190.1354 calculated for $C_{13}H_{18}O$ 190.1358.

c) **Tricyclo[6.3.0^{2,7}0]-undecan-3-one 8** : Compound 4b (342.5 mg 1.8 mmol) was hydrogenated over 10% Pd-C (50 mg) in 25 ml of ethanol at atmospheric pressure and RT and results in the consumption of 43 ml of hydrogen. The reaction mixture was filtered and the product is freed from solvent in high vacuum. GC analysis showed the presence of two components the reduced product which are identical with the isomers prepared from the photoannealation of enone 1b with cyclopentene in cyclohexane. The irradiation was done as described above and the product which contains two isomers was isolated by CC over SiO_2. IR (neat)ν_{max} : 1700 cm^{-1}; High resolution mass spectrum : M^+ at m/z 192.1514. Calculated for $C_{13}H_{20}O$ 192.1515.

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