Biphasic Photochemistry: Micellar Control of Regioselectivity in Enone Photoannelations

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Summary Photocycloadditions of 3-butylcyclopent-2-enone to alkenes and alkenyl acetates in potassium dodecanoate micelles give [2 + 2] cycloadducts the regioselectivity of the addition is different from that obtained in homogeneous solution in organic solvents

PHOTOCHEMICAL cycloaddition is a useful synthetic tool which has been frequently exploited, but to extend its usefulness the regiospecificity must be controlled At present some control may be achieved by substitution in the reactants or by variation of the solvent polarity, further means of control are highly desirable

Recently, it was observed that $\alpha\beta$-unsaturated cyclic enones will dimerise photochemically in sodium and potassium dodecanoate micelle solutions and that they give products of a predominant head-to-head cycloaddition,[1,2] isomers not otherwise easily obtainable We report here that mixed additions† can be achieved and that a significant control of regioselectivity can also be obtained in photo-

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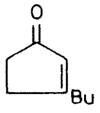
† A mixed addition in a neutral 2 phase system has already been reported (Y Nakamura Y Imakura, and Y Morita *Chem Lett* 1978 965) but its synthetic utility is dubious since one of the substrates needed to be >1 2 M in order to reduce but not eliminate the competing dimerisation of the other

annelations when the reaction is performed in micellar potassium dodecanoate (KDC).

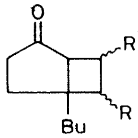
3-Butylcyclopent-2-enone (**1**), when irradiated in KDC micelles or in organic solvents in the presence of the olefins (10^{-2}—10^{-1} M) (**2**), gave the corresponding [2 + 2] cycloadducts‡ in good to excellent yields as mixtures of the isomers



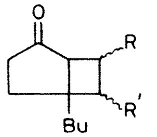
(1)

RCH=CHR′

(2)



(3)



(4)

a; R = Bu^n, R′ = H
b; R = n-C_6H_{13}, R′ = H
c; R = Bu^n, R′ = OAc
d; R = n-C_5H_{11}, R′ = OAc

(**3**) and (**4**). The olefins were normally employed in a 5—30-fold molar excess, but lower ratios were also satisfactory, thus reducing the amount of olefin required; the regioselectivity was not, as shown by g.l.c. analysis, sensitive to the olefin: enone ratio. Photocycloadditions of (**1**) to (**2a**) and (**2b**) in any of the reaction media used gave reaction mixtures wherein isomers (**3a**) and (**3b**), respectively, were in excess. When the reactions were performed in KDC micelles the yields of these isomers were much higher than those obtained in polar solvents (Table). The effect was accentuated when (**1**) was irradiated in the presence of (**2c**) or (**2d**); the ratios [(**3c**) or (**3d**)]: [(**4c**) or (**4d**)] increased by at least 2 orders of magnitude when the reaction medium was changed from an organic solvent to micellar KDC.

TABLE. Product distribution from the photocycloadditi ons of (**1**) to (**2**).[a]

Olefin	Medium	Yield[b]/%	(**3**)[c]/%	(**4**)[c]/%
(**2a**)	KDC[d]	98	78	22
	Diethyl ether	97[e]	57	43
	Cyclohexane	95	51	49
(**2b**)	KDC[d]	99	88	12
	Acetonitrile	92	63	37
	Methanol	96	62	38
	Diethyl ether	99[e]	57	43
	Cyclohexane	92	53	47
(**2c**)	KDC[d]	95	70	30
	Methanol	65	0	100
	Diethyl ether	85[e]	0	100
(**2d**)	KDC	68[c]	70	30
	Methanol	65	0	100
	Cyclohexane	53[e]	0	100

[a] All reactions were performed at room temperature by irradiating degassed solutions with Pyrex-filtered light from a 450 W medium-pressure lamp. [b] Unless otherwise stated the yields are determined by g.l.c. analysis and are based on the unrecovered enone. [c] The (**3**) : (**4**) ratios were determined by g.l.c. analysis of the reaction mixtures in the cases of (**2a**) and (**2b**). In the cases of (**2c**) and (**2d**) the ratios were determined by g.l.c. analysis of the product mixtures, obtained by hydrolysing and subsequently oxidising the cycloadduct mixtures. [d] The mean number of enone molecules per micelle varied from 0·15 to 1·0. [e] Isolated yield.

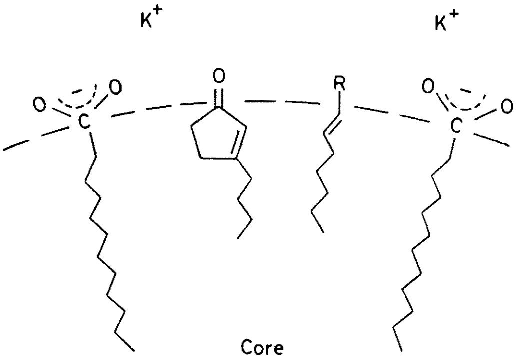


FIGURE. Schematic presentation of the most favourable orientations of (**1**) and (**2**) with KDC micelles.

We believe that these changes in regioselectivity are due to a specifically micellar effect and are not a function of the medium polarity. In the micelle (Figure) enone (**1**) will be oriented mainly with the carbonyl group in the Stern layer and the butyl group in the core.[1,3] The olefins, and particularly (**2c**) and (**2d**) because of the polar acetoxy-group, will be incorporated mainly into the micelle as shown in the Figure. Consequently, the yield of the regioisomers with alkyl groups attached to C-5 and C-6 increases relative to that obtained on irradiation in organic solvents.

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‡ All new compounds were characterized spectroscopically and, except (**3d**) and (**4d**), with a precise mass determination or an elemental analysis.

[1] K. H. Lee and P. de Mayo, *J. Chem. Soc., Chem. Commun.*, 1979, 493 and references therein.
[2] R. Fargues, M. T. Maurette, E. Oliveros, M. Riviere, and A. Lattes, *Nouv. J. Chim.*, 1979, **3**, 487; Y. Nakamura, T. Kato, and Y. Morita, presented at the American Chemical Society National Meeting in Hawaii, April 1979.
[3] K. H. Lee and P. de Mayo, *Photochem. Photobiol.*, 1980, **31**, 311.