Biphasic Photochemistry: Micellar Regioselectivity in Enone Dimerisation

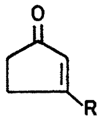
By KONG-HUNG LEE and PAUL de MAYO*

(*Photochemistry Unit, Department of Chemistry, University of Western Ontario, London, Ontario* N6A 5B7, *Canada*)

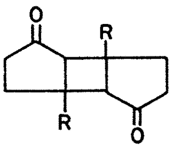
Summary Irradiation of 3-alkylcyclopentenones in potassium dodecanoate micelles leads to greatly increased efficiency of dimerisation over that in homogeneous solution and regiospecific head-to-head control far beyond that possible by solvent variation.

THE intermolecular photocycloadditions of $\alpha\beta$-unsaturated ketones, of which dimerisation is a special case, have been extensively used for the formation of carbocyclic rings.[1] It is known that the regiospecificity is controlled by substitution[2] and by dipole–dipole interactions and that the solvent dielectric constant strongly affects the latter.[3] We now show that irradiation in micellar solution provides another and powerful way of controlling regiospecificity and of increasing efficiency.

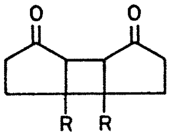
The 3-alkyl cyclopentenones† (**1a**) and (**1b**) were irradiated under the conditions indicated in the Table in potassium dodecanoate (KDC) micelles. Assuming a Poisson distribution[4] there were, at the highest enone concentration, no more than 10% of the micelles with more than 7 enone molecules per micelle and the critical micelle concentration (C.M.C.; 0·024 M) was unchanged. The irradiations gave three cyclobutane dimers [head-to-tail, HT, (**2**) *syn* and *anti*, and head-to-head, HH, (**3**) *anti*].‡ The 4-butyl derivative gives an overwhelming preponderance of the (HH) (**3a**) derivative as compared with irradiation in homogeneous solution in benzene and cyclohexane (see Table). The ratio is, in fact, strongly reversed, and the effect is even more dramatic for the 4-decyl derivative (**1b**). In addition, the efficiency, at the same bulk concentration, is greatly increased in KDC (compare, for instance, lines 1, 3, and 5 in the Table).§



(1)



(2)



(3)

a; R = n-butyl
b; R = n-decyl

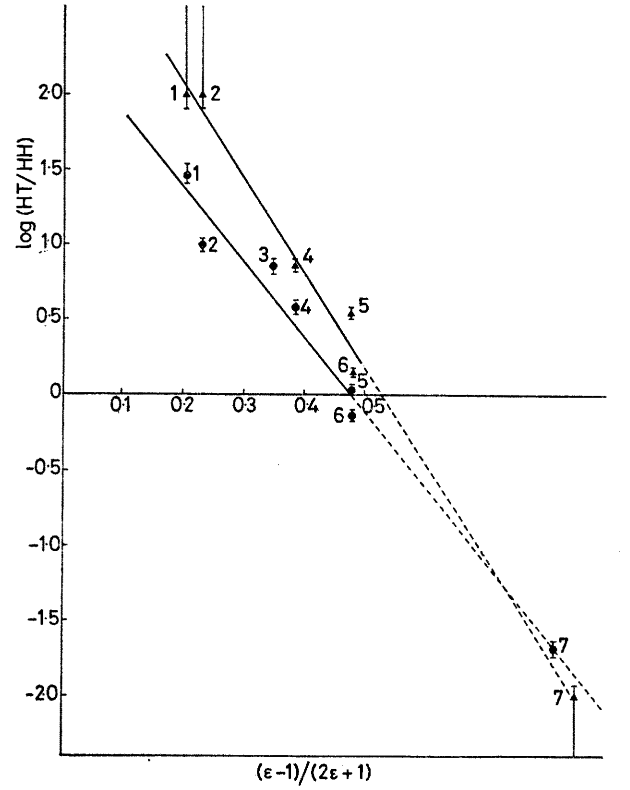


Figure. Variation of dimer ratios with solvent dielectric constant (ε); (**1a**) (●) and (**1b**) (▲): cyclohexane (1), benzene (2), diethyl ether (3), ethyl acetate (4), methanol (5), acetonitrile (6), and KDC (7).

Table. Product distribution in the dimerisation of (**1**)[a]

Medium	Concentration (× 10³ M) (Compound)	HT/%	HH/%	% Enone recovered	Yield/%[b]
KDC[c]	5·6 (**1a**)	2	98	12	100
c-C_6H_{12}	23·0 (**1a**)	96	4	None	37
c-C_6H_{12}	5·7 (**1a**)	96	4	None	*ca.* 1
C_6H_6	60·0 (**1a**)	91	9	63	6
C_6H_6	5·9 (**1a**)	91	9	62	*ca.* 1
KDC	4·76 (**1b**)	1	99	—[d]	—[d]
c-C_6H_{12}	24·0 (**1b**)	100	0	—	—
C_6H_6	35·0 (**1b**)	100	0	—	—

[a] The solutions were irradiated for 10 h with a 450 W medium pressure mercury arc with a Pyrex filter. [b] Error in g.l.c. analysis ±3%. The yield is based on recovered enone. [c] KDC 0·08 M, C.M.C. = 0·024 M. [d] Not determined.

It was possible that this regioselective effect was the equivalent of that already described[3] and the results should then be correlated using the Kirkwood–Onsager equation. Under these conditions the dimerisation in the micelle might be considered as occurring in the Stern layer, effectively in a medium with a dielectric constant greater than that of water. The logarithm of the HT/HH ratio was plotted (see Figure) against the Kirkwood–Onsager func-

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† All new compounds were characterised spectroscopically and with precise mass determinations except that (**2a**) was isolated as a mixture of *syn*- and *anti*-isomers.

‡ The structures are based on physical data (see footnote †) and by close analogy with the detailed study of the dimerisation of other 3-alkylcyclopent-2-enones.[5]

§ In the presence of surfactants there have been two other studies of photodimerisation. In that of uracil[6] the effects of the micelle are obscure. A local concentration effect has been observed, however, with acenaphthylene dimerisation;[7] the addition of acenaphthylene to acrylate on the other hand was clearly under non-micellar, possibly bilayer, conditions.[8]

tion.¶ In cyclohexane and benzene the concentrations of enone were extrapolated to infinite dilution. In these solvents HT dimers preponderate (>10:1). Reasonable linearity is obtained for the solvents used and the maximum value of this function (0·5) is reached with (**1**) in methanol and acetonitrile. The HT:HH ratio then approximates to a limit of 1:1. However, the ratio found in the micelle is far greater, 1: *ca.* 30, and cannot, therefore, be dictated by the dielectric constant, even allowing for the crudity of the function.¶ Nor can hydrogen bonding *per se* be responsible since methanol and acetonitrile solutions yield similar ratios. We conclude that the enones are incorporated into the micelle and their orientation is directed by it. With the use of micelles the ratio of products (**1a**):(**1b**) differs from that obtained in hydrocarbon solvents by 2—3 orders of magnitude, and the technique has obvious synthetic utility.

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¶ In some treatments (J. G. Kirkwood, *J. Chem. Phys.*, 1934, **2**, 351; 1937, **7**, 911; L. Onsager, *J. Amer. Chem. Soc.*, 1936, **58**, 1486) the cavity radius has been identified with that of the solute (*cf.* K. Laidler and H. Eyring, *Ann. New York Acad. Sci.*, 1940, **39**, 303). We have used this and omitted the molar volume term since it is then a constant. Other treatments have, however, used the molar volume of the solvent (see J. A. Berson, Z. Hamlet, and W. A. Mueller, *J. Amer. Chem. Soc.*, 1962, **84**, 297; J. Powling and H. J. Bernstein, *ibid.*, 1951, **73**, 4353). The function is, in any event, an approximation which deteriorates with high polarity, and includes only electrostatic effects and not any specific solute–solvent interactions; it is therefore surprising that it has served so well.

[1] P. Eaton, *Accounts Chem. Res.*, 1968, **1**, 50; P. de Mayo, *ibid.*, 1971, **4**, 41.

[2] E. J. Corey, J. D. Bass, R. LeMahieu, and R. B. Mitra, *J. Amer. Chem. Soc.*, 1964, **86**, 5570.

[3] See, for instance, B. D. Challand and P. de Mayo, *Chem. Comm.*, 1968, 946; G. Mark, F. Mark, and O. E. Polansky, *Annalen*, 1968, **719**, 151; P. Margaretha, *Chimia*, 1975, **29**, 203.

[4] L. G. Parrott, 'Probability and Experimental Errors in Science,' Dover, New York, 1961.

[5] R. Reinfried, D. Bellus, and K. Schaffner, *Helv. Chim. Acta*, 1971, **54**, 1517.

[6] J. F. Fendler and G. Bogan, *Photochem. Photobiol.*, 1974, **20**, 323.

[7] Y. Nakamura, Y. Imakura, T. Kato, and Y. Morita, *J.C.S. Chem. Comm.*, 1977, 887.

[8] Y. Makamura, Y. Imakura, and Y. Morita, *Chem. Letters*, 1978, 965.