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REACTIONS USING MICELLAR SYSTEM : PHOTOCYCLOADDITIONS OF ACENAPHTHYLENE WITH ACRYLONITRILE AND METHYL ACRYLATE

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Photochemical crossed-cycloaddition reaction of acenaphthylene with acrylonitrile in micelle of nonionic surfactant was more effective than in benzene to give better yield of the addition products, especially by adding 1,3,5-heptatriene as quencher. Similarly, acenaphthylene with methyl acrylate in micellar system gave also good yield of the addition products.

In the course of our biomimetic investigation utilizing " reaction in micelle", photodimerization of acenaphthylene(1) has been previously shown to give quantitative yield(>90%) even in the low concentrations where no dimeric products have been obtained in benzene solution.1)

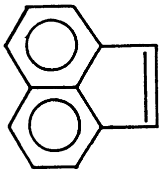
We now report the first photochemical crossed-cycloaddition reaction of acenaphthylene(1) with electron deficient olefins, such as acrylonitrile(2) and methyl acrylate(3) using micellar system. We selected polyoxyethylene-polyoxypropylene cetyl ether(Nikkol PBC-34) as the typical nonionic surfactant and benzene as a typical organic solvent to compare with the micellar system. The reaction conditions for each run were standardized as follows: the solution of (1) with electron deficient olefin in benzene or 5%aq. PBC-34 was irradiated by 100W(or 400W) high pressure mercury arc lamp with Pyrex cell and water cooling through a fine stream of N_2 bubbles at 20-25° for 5h. The results are given in the Table.

For example, irradiation of acenaphthylene(1)[45mg, 14mM]and acrylonitrile(2) [1.85g, 1660mM] in 5%aq. PBC-34[21ml] gave two crossed-cycloaddition products(23.6%), syn(5)[mp. 146-147°, 7.2mg] and anti(6)2),3),4)[mp. 81-82°, 7.1mg] in addition to the dimers of acenaphthylene(60.7%)1), syn(9) and anti(10)[the ratio of 55:45].

As shown in the Table, (1) and (2) in benzene gave no crossed-cycloaddition products, (5) and (6), [Experimental No.1,2,&5], and by adding 1,3,5-heptatriene(4), as triplet quencher, gave (5) and (6) in low yields of 4.2 to 14.3%[Exp. No.3&4].

In contrast, the reaction in micellar system gave the following results: (i) crossed-cycloaddition products (5) and (6) were obtained in the yields of 6.7 to 24.7% even without (4)[Exp.No.6,9,&10], (ii) by adding (4)[5] in the system, the yields of (5) and (6) increased to 77.2%[Exp.No.7,11-13], (iii) the ratios of (5) to (6) were ca. 1:1, (iv) the recovered (1) was not observed in any case(i.e., the reaction went quantitatively)[Exp.No.6-13], (v) power up of lamp, 100 to 400W, was effective to increase the yields of adducts only in the case of (4) present[Exp.No. 3 to 4,& 7 to 11], (vi) the yields of (5) and (6) depend on the relative amount of (2) and (4) against (1)[Exp.No.9 to 10,& 12 to 13], the addition of 1-bromobutane increased the yields of (5) and (6) by the heavy atom effect[6], changing the relative ratio of them to 29:71[Exp.No.8].

Photoreaction of (1) andmethyl acrylate(3) in benzene gave the crossed-cycloaddition products, (7)[mp. 97-98°] and (8)[mp. 66-67°], in low yield(2.6-3.0%) independently of (4)-presence[Exp.No.14&15]. On the other hand, the reaction in micellar system gave better yield of the adducts in the case of (4) absent[14.2%, Exp. No.16] than in the case of (4) present[3.6%, Exp.No.17].



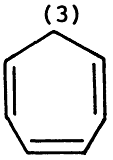
(1)

$CH_2=CH-CN$

(2)

$CH_2=CH-COOCH_3$

(3)



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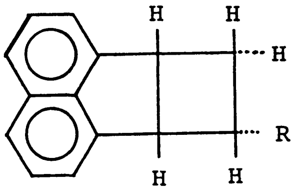
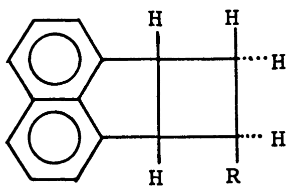


syn

(5) R=-CN

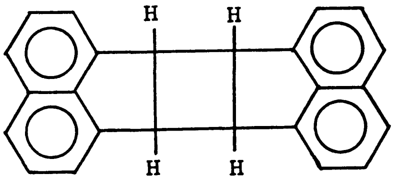
(7) R=-COOCH$_3$



anti

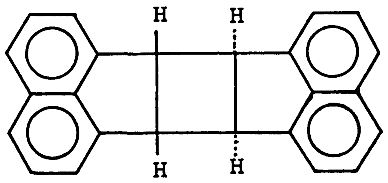
(6) R=-CN

(8) R=-COOCH$_3$



syn

(9)



anti

(10)

Table Reactions of Acenaphthylene(1) with Acrylonitrile(2) and Methyl Acrylate(3) in Benzene and Micelle

Experimental No.	Solvent	(1) mM	(2) mM	(4) mM	Recovered (1) %	Yield of adducts % (ratio of (5) : (6))	Yield of dimers % (ratio of (9) : (10))
1	benzene	741	1450	0	90	0	7.8 (93: 7)
2	benzene	741[a]	1460	0	71	0	26.9 (95: 5)
3	benzene	8	1450	24	86	4.2	8.3 (62:38)
4	benzene	8[a]	1450	23	72	14.3	2.0 (57:43)
5	benzene	11[a]	390	0	68	0	18.5 (90:10)
6	5%PBC-34	12	1470	0	0	24.7(49:51)	71.7 (67:33)
7	5%PBC-34	8	1450	19	0	37.6	58.0[d](100:0)
8	5%PBC-34	30	1240	0[b]	0	40.0(29:71)	57.7 (42:58)
9	5%PBC-34	13[a]	390	0	0	6.7	92.2 (67:33)
10	5%PBC-34	14[a]	1660	0	0	23.6(50:50)	60.7 (55:45)
11	5%PBC-34	8[a]	1460	23	0	77.2(47:53)	16.0[d](100:0)
12	5%PBC-34	12[a]	1450	18	0	73.1(50:50)	22.2 (86:14)
13	5%PBC-34	12[a]	1450	45[c]	0	34.9	60.8[d](100:0)
		(1)	(3)	(4)		((7):(8))	
14	benzene	7.2	490	0	86	2.6	5.9 (29:71)
15	benzene	7.2	490	12	87	3.0	5.1 (83:13)
16	5%PBC-34	7.1	490	0	0	14.2(18:82)	80.0 (29:71)
17	5%PBC-34	7.2	490	9.6	0	3.6	95.2 (87:13)

[a] Used 400W high pressure lamp

[b] Added 1-bromobutane (1540mM)

[c] Saturated

[d] Only (9) was obtained

References and Footnotes

1) Y. Nakamura, Y. Imakura, T. Kato, and Y. Morita, J. Chem. Soc., Chem. Commun., 887 (1977).

2) B.F. Plummer and R.A. Hall, J. Chem. Soc., Chem. Commun.,44 (1970).

3) Regarding the stereochemistry of adducts (5) and (6), Plummer and Hall(2) have reported as (5) mp. 139-141° to be anti and (6) mp. 80-82° to be syn. However, we have concluded that they have to be reversed their stereochemistry, i.e., (5) to syn and (6) to anti, from the chemical correlations and the proton magnetic resonance spectral data. We will report about these in the subsequent article.(4)

4) Y. Nakamura, Y. Imakura, and Y. Morita, Chem. Lett., 969 (1978).

5) We found that polymerization of acrylonitrile(2) was promoted by acenaphthylene (1) in micelle, but prevented by adding 1,3,5-heptatriene(4) as the quencher in the system. Neither acrylonitrile only nor acrylonitrile with acetone in micelle under the same condition did give polymerization product.

6) D.O. Cowan and R.L. Drisko, Tetrahedron Lett., 1255 (1967).

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