Photocycloaddition of Phenanthrene with Olefins

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Summary Phenanthrene undergoes photocycloaddition at the 9,10-positions with certain olefins to afford the corresponding dihydrophenanthrocyclobutenes.

MUCH interest has been shown in photoaddition reactions of the aromatic nucleus with unsaturated compounds.[1] However, little is known of the photochemistry of phenanthrene with olefins except for the reaction with maleic anhydride.[2]

We have investigated the photocycloaddition of phenanthrene with olefins such as *cis*- and *trans*-dichloroethylene, dimethyl maleate, and acrylonitrile, which provide a convenient route for preparation of dihydrophenanthrocyclobutenes.

Irradiation was carried out through Pyrex with a high-pressure mercury arc lamp under nitrogen at room temperature. The photoadducts were obtained in considerable yields and fully characterized by elemental analysis and by their i.r., u.v., n.m.r., and mass spectra.

Excluding *trans*-addition at the 9,10-positions of (I), three stereoisomers (II), (III), and (IV) possible from the cycloaddition were obtained in the reaction of (I) with either *cis*- or *trans*-dichloroethylene. Two isomers, (VI) and (VII), were obtained from the addition of (I) and acrylonitrile. The results, and tentative assignments for these stereoisomers, are shown in the Table.

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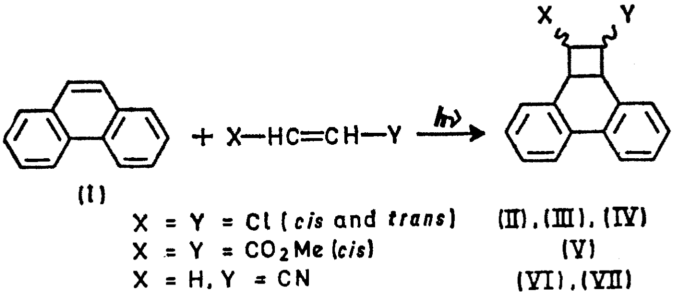
Olefin	Solvent	Irrad. time (h)	Product	Tentative assignment	Yield[a] (%)	M.p.
cis-Dichloroethylene (3·3)[b]	—	36	(II)	*cis,trans,trans*	21·9	145—160° dec.
			(III)	*cis,cis,cis*	7·4	161·5—163°
			(IV)	*cis,trans,cis*	3·0	190° dec.
trans-Dichloroethylene (5·0)	Et_2O	120	(II)		24·9	
			(III)		32·4	
			(IV)		0·6	
Dimethyl maleate (3·0)	Et_2O	120	(V)	[c]	61·8	104—111°
Acrylonitrile (10·0)	EtOH	2	(VI)	*syn*	78·4	118—120°
			(VII)	*anti*	19·6	169—172°

[a] Yield based on reacted phenanthrene.
[b] Figures in parentheses denote molar equivalents of olefin to one of phenanthrene.
[c] No stereochemical assignment was made because the separation of (V) into pure isomers was not performed.



Although the photoreaction of indene or naphthalene with acrylonitrile led to the formation of substituted products along with cycloadducts,[3] no substituted products could be detected at all under our conditions. Furthermore, *cis–trans*-isomerization was observed with both *cis*- and *trans*-dichloroethylene or dimethyl maleate.

(*Received, September* 15*th*, 1970; *Com.* 1570.)

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[2] D. Bryce-Smith and B. Veckery, *Chem. and Ind.*, 1961, 429.
[3] J. J. McCullough and C. W. Huang, *Chem. Comm.*, 1967, 815; J. J. McCullough, C. Calvo, and C. W. Huang, *ibid.*, 1968, 1176; J. J. McCullough and C. W. Huang, *Canad. J. Chem.*, 1969, **47**, 757.