Substituent Directed *meta* Photocycloaddition of *trans*-1,2-Dichloroethene to Benzonitrile

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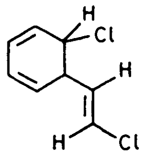
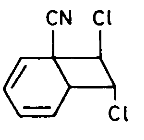
trans-1,2-Dichloroethene undergoes 2,4-photocycloaddition to benzonitrile to yield 4-cyano-6-*exo*,7-*endo*-dichlorotricyclo[3.3.0.0^{2,8}]oct-3-ene (**3**) as the major product, the structure of which has been determined by *X*-ray crystallography; steric and radical stabilisation factors of the addend substituents are considered to direct the reaction to this specific mode of *meta* attack.

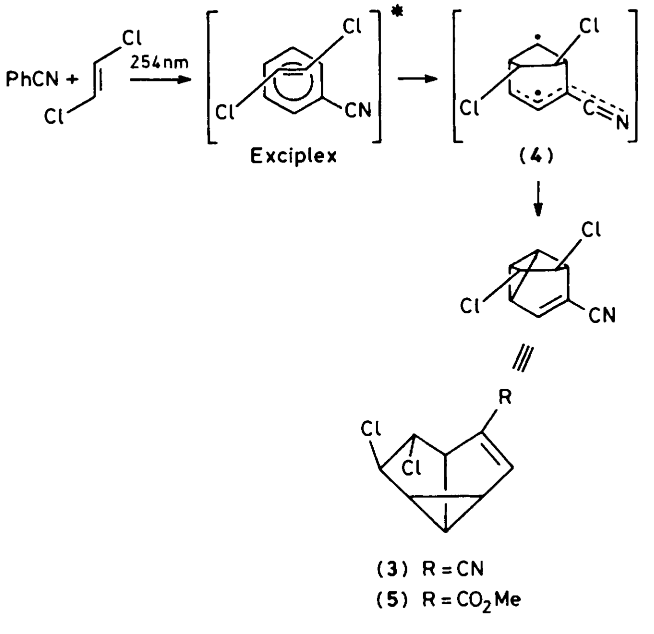
Hydrocarbon ethenes, ethenyl ethers, and vinyl acetate undergo *meta* and/or *ortho* photocycloaddition to benzene and simple benzenoid compounds.[1,2] 1,2-Dichloroethenes behave anomalously and give with benzene, for example, the ethene dimers and a mixture of photoproducts which may be rationalised in terms of the C–Cl insertion intermediate (**1**):[1,3] exception to this type of behaviour is the reported formation of (**2**) from irradiation of *trans*-1,2-dichloroethene and benzonitrile, an arene which typically yields such 1,2-adducts and products derived from reaction of the ethene at the cyano group.[4] We now report that, in marked contrast to the numerous previously reported examples of arene–ethene photoreactions, *trans*-1,2-dichloroethene undergoes 2,4-photocycloaddition to benzonitrile to give 4-cyano-6-*exo*,7-*endo*-dichlorotricyclo[3.3.0.0^{2,8}]oct-3-ene (**3**) (m.p. 102—103 °C) as the major mode (> 50%) of reaction; (**2**) (*ca.* 25%)[4] and products derived from addition at the nitrile function were observed but (**3**) is readily freed from these by crystallisation of the distilled product mixture.† The structure of this *meta* adduct was assigned on the basis of spectroscopic analysis but confirmation by *X*-ray crystallographic determination of a single crystal was necessary as the former data did not produce a totally unambiguous assignment of the stereochemistry, which is essential for mechanistic considerations. The data were as follows: ^{1}H n.m.r. spectrum (CDCl$_3$), δ values: 6.74 (d, H-3, $J_{3,2}$ 2.7 Hz), 4.82—4.89 (d of d, H-7, $J_{7,8}$ 7.0, $J_{7,5}$ 2.5 Hz), 4.36 (br. s, H-6, $J_{6,5}$ 0.1, $J_{6,2}$ 1.0, $J_{6,8}$ 0.01 Hz), 3.54—3.64 (d of d, H-5, $J_{5,1}$ 7.0 Hz), 3.25—3.43 (q, H-1, $J_{1,8} = J_{1,2} =$ 7.0 Hz), 2.50—2.70 (m, H-8, $J_{8,2}$ 8.0 Hz), and 2.18—2.34 (m, H-2); i.r. (Nujol) ν_{max} 2220, 1605, and 942 cm^{-1}; M^+, m/z 198.9952 (17.15%) and 200.9923 (10.76%), pure by t.l.c. and g.l.c.; calc. 198.9956 and 200.9926. The crystals are monoclinic, space group $P2_1/a$, $Z = 4$, $a = 6.430(8)$, $b = 11.81(1)$, $c = 11.99(1)$ Å, $\beta = 102.2(1)°$, $U = 889.5$ Å^3, $D_m = 1.46(2)$, $D_c = 1.49$ g cm^{-3}.



(**1**)



(**2**)



(**3**) R = CN
(**5**) R = CO$_2$Me

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† Irradiation (30 W at 254 nm) of 100 ml of an equivolume mixture of the reactants for 16 h with periodic cleaning of the quartz surface produces 1 g of (**3**) following distillation and crystallisation of the crude product. Photoproduct (**3**) was recrystallised from 10% diethyl ether in hexane.

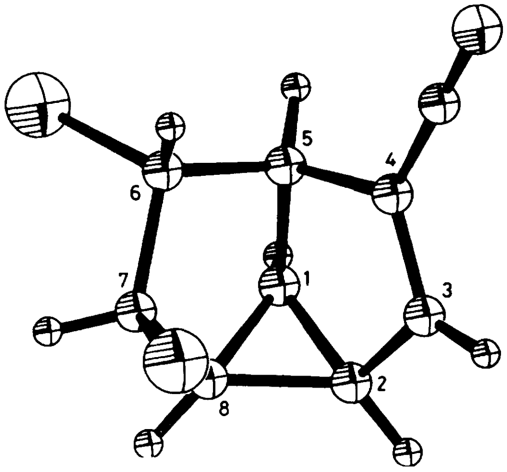

Figure 1. *X*-Ray structure of the adduct (**3**).

1137 Independent reflections above background were measured on a diffractometer and the structure was refined by full-matrix least-squares to *R* 0.072.‡ The asymmetric unit contains discrete molecules of (**3**) (see Figure 1). The Cl–C–C–Cl torsion angle is $-140.6(7)°$.

Specific formation of this particular *meta* cycloadduct (12 possible *meta* adduct isomers) has important mechanistic and synthetic implications. The 2,4-attack of the ethene onto benzonitrile provides the first example of *meta* cycloaddition of this arene and is without precedence in arene photochemistry, as the numerous previously reported examples of the *meta* cycloaddition reaction result in the arene substituent residing preferentially on the 1- and occasionally on the 3-position in the product;[5] also rarely is only one stereoisomer formed. We rationalise the present observations in terms of substituent steric and radical stabilisation factors favouring the specific formation of the intermediate (**4**) which possibly results from collapse of the suitably addend oriented exciplex. By this argument, other benzenoid compounds with conjugative substituents and similar ionisation potentials to this ethene (9.64 eV)§ should behave analogously to benzonitrile and indeed methyl benzoate does yield (**5**), although with higher proportions of by-products than (**3**).

Previously it has not proved possible to functionalise the dihydrosemibullvalene skeleton (*meta* cycloadduct) by irradiation of arenes and ethenes bearing the functionality: the *ortho* cycloaddition mode tends to dominate in such cases.[1] Formation of (**3**), therefore, illustrates the synthetic potential of the *meta* reaction from arene–ethene systems having similar addend ionisation potentials and in which the functionalising substituents provide the necessary orienting factors for the addends in the reaction intermediate to render the process regio- and stereo-specific.

Received, 23rd March 1983; Com. 376

References

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‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

§ It has been previously noted that the quantum yield for *meta* cycloaddition is greater than that of the *ortho* process when the ionisation potential difference between the addends is 'small'; 'large' differences caused by the introduction of functional groups into either or both of the addends results in the *ortho* photocycloaddition being the preferred or sole mode of reaction.[1]