Tetrahedron Letters,Vol.23,No.44,pp 4611-4614,1982 0040-4039/82/444611-04$03.00/0
Printed in Great Britain

MECHANISMS AND SELECTIVITIES IN THE ORTHO PHOTOCYCLOADDITION OF ETHENES TO THE BENZENE RING

by Andrew Gilbert and Paul Yianni

Chemistry Department, University of Reading, Whiteknights, Reading, Berkshire, RG6 2AD.

Summary: Mechanisms for the *ortho* photocycloaddition of ethenes to arenes are considered in the light of new observations concerning the addition reactions of benzonitrile to dienophilic ethenes.

Formation of [2+2] cycloadducts by ultraviolet irradiation of arene-ethene donor-acceptor systems is a common reaction with synthetic potential which also has mechanistic features of general interest in photochemistry.[1-7] The regioselectivity of the process can be markedly increased by increase in the relative electron donor-acceptor properties of the addends and solvent polarity,[6,7] and for aryl nitriles attack of the ethene at the nitrile function can be the preferred mode of reaction.[4,8] The intermediacy of excited-state complexes and preferred addend orientations in such species are considered to account for the general features of the reaction. In benzene-ethene systems which have no obvious electron donor-acceptor relationship, *meta* photocycloaddition leading to tricyclo($3,3,0,0^{2,8}$) oct-3-ene derivatives (1) is a competing and frequently the sole reaction.[9-11] Thus *meta* cycloaddition is favoured for benzene-alkene and phenyl ether-nucleophilic ethene systems but in contrast no photoreactions have been described for cases in which both addends may be considered as electron acceptor species and in particular benzonitrile-acrylonitrile is reported not to yield photoadducts.[7] The *meta* process arises from the arene S_1 state[12] from which it is a symmetry allowed reaction[13,14] but a concerted [2+2] process requires either a species in which there is a measure of charge-transfer between the addends (as above) or by attack of the S_1 ethene directly onto the S_0 arene.[13] It is thus of mechanistic importance to examine this latter route to [2+2] cycloaddition of ethenes and arenes and to accomplish this we have studied the photoreactions of benzonitrile with dienophilic ethenes under conditions such that the latter may be electronically excited.

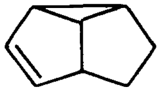
Solutions of benzonitrile in methyl acrylate, methyl methacrylate, acrylonitrile or methacrylonitrile were exposed to 254 nm radiation both in the absence and presence of cyclohexane and acetonitrile as solvent. Relative concentrations were such that the ethene absorbed approximately 60% of the incident radiation. Combined m.s./g.l.c. analysis (WCOT Carbowax 20M) of the viscous oil remaining after removal of the reactants and solvents showed that all systems produced very complex mixtures of 1:1 adducts and ethene dimers. Fragmentation of all 1:1 adducts to starting materials was facile and indicates the absence of *meta* adduct structures for any of the photoproducts.[15] The ratio of the two types of products varied with the system and relative reactant concentrations as noted previously.[16] Chemical yields of the adducts were low (ca. 0.5g from 100 ml of neat reactants irradiated for 25 hrs) reflecting the variable thermal and photolabilities of the isomers, and quantum efficiencies were only approximately 0.1 of those for these ethenes with electron donor arenes (e.g. anisole) under similar experimental conditions. In view of the low yields of complex mixtures, it proved impractical to separate individual components but by flash chromatography the photoproducts were fractionated into ethene dimers and 1:1 adduct regio-isomers with respect to the arene. For example irradiation of an equimolar mixture of benzonitrile and methyl acrylate produced a 6:1 ratio of 1:1 adducts and dimers respectively. The adducts were separated into two fractions which, from their spectroscopic properties and their comparison with those of bicyclo[4.2.0]octa-2,4-diene derivatives, were shown to be the 1-cyano and 3-cyano regio isomers (2a) and (3a) respectively and which had been formed in a ratio of 2:3; component (2a) comprised two and (3a) four isomers.* These and the results from the other ethenes are summarised in the Table and are of significance as they represent examples of cycloaddition of an ethene to a benzenoid compound in which both have electron acceptor properties. Only the 1-cyano ortho cycloadducts in the present series reacted (refluxing ethanol for 24 hrs) to any detectable extent with N-phenylmaleimide. In some cases pure 1:1:1 adduct isomers were isolated; for example the 1-cyano-8-methyl-8-carbomethoxy ortho cycloadduct mixture yielded a Diels-Alder derivative (m.p. 222-224°C) which from analytical and spectroscopic data was assigned structure (5).

Table. Products from 254 nm Irradiation of Benzonitrile with Dienophilic Ethers

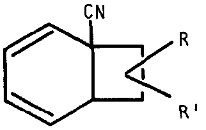
Ethene	Ratio of 1:1 adducts: ethene dimers	Ratios of ortho cycloadducts*		
		1-CN(2)	2-CN(4)	3-CN(3)
Methyl acrylate	6:1	2(2 isomers)(2a)	-	3(4 isomers)(3a)
Methyl methacrylate	1:1	1 (3 isomers)(2b)	-	1 (3 isomers)(3b)
Acrylonitrile	No dimers detected	3(3 isomers)(2c)	-	2(2 isomers)(3c)
Methacrylonitrile	1:2	1 (1 isomer)(2d)	-	3 (3 isomers)(3d)

* Adducts reported were >10% concentration of the total adduct mixture.

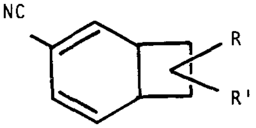
There are several important features of the present results. Thus only ortho cycloaddition reactions between the addends are observed and this is consistent with predictions[13] from orbital symmetry considerations for systems in which the ethene is the excited species. Under conditions which allow excitation of the acrylonitriles then in modification of our earlier report[7] even these dienophiles photoadd to benzonitrile albeit in low yield. No system shows any evidence for complexation between the addends and formation of excited-state complexes is not considered favourable. Overall the formation of these ortho cycloadducts shows little selectivity between 1,2- and 3,4-attack of the ethene onto the arene but with electron donor-acceptor systems (e.g. benzonitrile-nucleophilic ethenes,[4] anisole-dienophiles[1,6,7]) selectivity towards 1,2-attack is observed and in the latter case the selectivity is further increased with increase in solvent polarity.[6] In contrast change of solvent from cyclohexane to acetonitrile had no signifi-



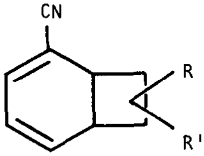
(1)



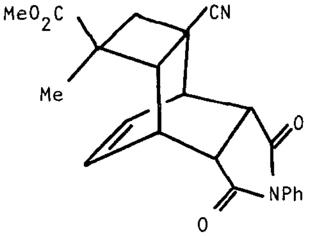
(2) a, R=CO$_2$Me, R'=H
b, R=CO$_2$Me, R'=Me
c, R=CN, R'=H
d, R=CN, R'=Me



(3) a, R=CO$_2$Me, R'=H
b, R=CO$_2$Me, R'=Me
c, R=CN, R'=H
d, R=CN, R'=Me



(4)



(5)

cant effect on the selectivity of the present ortho cycloadditions although the overall yield of that of methyl acrylate was exceptionally increased by a factor of two. It is convenient to rationalise the present results with those observed with these ethenes and anisole in terms of attack by S_1 ethene onto S_0 arene in the former case and, for the latter systems, the involvement of an exciplex in which the addends have preferred orientations. But the absence or very low yields (<10%) of formation of 2-substituted isomers from both series of systems is not readily explained by such mechanisms and is indeed most remarkable. We have recently observed that the exo and endo stereoisomers of 7-cyanobicyclo[4.2.0]octa-2.4-diene are readily interconverted thermally and photochemically and should this arise via 6-7 bond fission and recombination at the 2-position then a similar pathway would interconvert pairs of the disubstituted derivatives under consideration (e.g. 2,8-↔3.7-isomers although the process with the 1,7- and 3,8-derivative yields the same isomers). To account for the present observations by such a feature, however, it is necessary to consider that the 1,7-, 1,8-, 3,7- and 3,8-disubstituted isomers of bicyclo[4.2.0]octa-2,4-diene are more stable than the 2,7- and 2,8 isomers and there appears no obvious reason for this: further the absence of detectable amounts of bicyclo[2.2.2] octadienes, expected as byproducts in this mechanism, is disconcerting. At present the most likely mode of interconversion between the 7-cyano stereoisomers involves 1,6-bond cleavage and reformation. These lability studies continue.

Consistent with the present ortho photocycloadditions arising from excitation of the dienophile, irradiation at wavelengths greater than 290 nm of N-butylmaleimide in benzonitrile produced small amounts of a 2:1 adduct together with much ethene dimer.[17] With exciting radiation of both 254 nm and > 290 nm no trace of cycloadducts were observed from the benzonitrile-maleic anhydride system simply because there is no ground state complex between the addends and uncomplexed maleic anhydride cannot be directly excited under such conditions.

References

1. M.Ohashi, Y.Tanaka, and S.Yamada, J.Chem.Soc.Chem.Comm., 1976, 800, and Tetrahedron Letters, 1977, 3629.
2. R.A.Caldwell and D.Creed, Acc.Chem.Res., 1980, 13, 45.
3. M.Yasuda, C.Pac, and H.Sakurai, Bull.Chem.Soc.Jap., 1980, 55, 502.
4. T.S.Cantrell, J.Org.Chem., 1977, 42, 4238.
5. S.L.Mattes and S.Farid, Acc.Chem.Res., 1982, 15, 80.
6. A.Gilbert and P.Yianni, Tetrahedron Letters, 1982, 255.
7. A.Gilbert and P.Yianni, Tetrahedron, 1981, 3275.
8. N.C.Yang, B.Kim, W.Chiang, and T.Hamada, J.Chem.Soc.Chem.Comm., 1976, 729; J.J.McCullough, R.C.Miller, D.Fung, and W.S.Wu, J.Amer.Chem.Soc., 1975, 97, 5942.
9. A.Gilbert, Pure Appl.Chem., 1980, 52, 2669, and references therein.
10. J.A.Ors and R.Srinivasan, J.Org.Chem., 1977, 42, 1321.
11. R.S.Sheridan, Tetrahedron Letters, 1982, 267; D.Bryce-Smith, G.A.Fenton, and A.Gilbert, ibid., 2697.
12. A.Morikawa and R.J.Cvetanovic, J.Phys.Chem., 1968, 49, 1214.
13. D.Bryce-Smith, Chem.Comm., 1969, 806.
14. The *meta* process is also allowed from the S_1 ethene[13] but such ethenes that undergo the reaction have very weak absorbances at the excitation wavelength (254 nm).
15. K.E.Wilzbach and L.Kaplan, J.Amer.Chem.Soc., 1971, 93, 2073.
16. D.Bryce-Smith, B.E.Foulger, J.Forrester, A.Gilbert, B.H.Orger, and H.M.Tyrrell, J.Chem.Soc., 1980, 55.
17. C.E.Rees, Ph.D. Thesis, Reading, 1973.

(Received in UK 26 August 1982)