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THE *META* PHOTOCYCLOADDITION OF ANISOLE AND BENZONITRILE TO 1,3-DIOXOL-2-ONE

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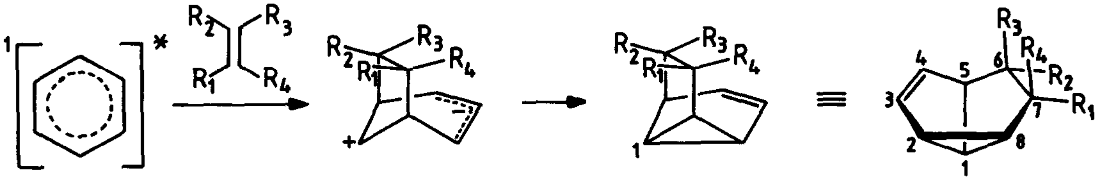
Abstract: The *meta* photocycloadditions of benzonitrile and anisole to 1,3-dioxol-2-one both yield two major products. In both cases the adducts are those which would be expected if some form of polar species were to develop along the reaction pathway. The absence of *exo* adducts in the case of benzonitrile and 1,3-dioxol-2-one is discussed.

In the past twenty years many articles have been published about the *meta* photocycloaddition of arenes to alkenes and several different mechanisms have been proposed for this reaction.[1,2] One which fits all the experimental evidence was first suggested by Bryce-Smith, Gilbert and co-workers[2] in 1980 as one of several possibilities:

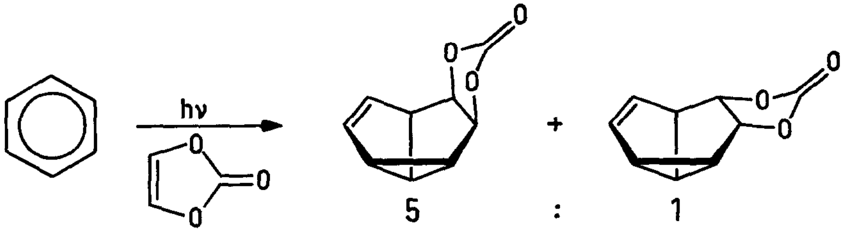


This implies the existence of a discrete zwitterionic intermediate. Although we have not been able to trap such an intermediate and have therefore no evidence for the existence of this species, the results of the irradiations of benzonitrile[3], α,α,α-trifluorotoluene[3] and anisole[4,5] in the presence of cyclopentene do provide a strong indication for the development of some degree of charge separation along the reaction pathway. Electron withdrawing substituents (CN and CF_3) are consistently found at carbon atoms 2 and 4 in the adduct, whereas the methoxy group - being able to stabilize a positive charge - is to be found at carbon atom 1.

The photoaddition of benzonitrile to cyclopentene is, however, unusual in that there is a rather large difference between the ionization potentials of the reactants (10.03 and 9.02 eV, respectively[6]). In agreement with Bryce-Smith and Gilbert's "ionization potential rule"[7] *ortho* addition is the preferred mode and the *meta* adducts are minor products. We therefore decided to investigate the photoaddition of benzonitrile to 1,3-dioxol-2-one (I.P. = 10.08 eV)[6] which could be expected to give a high percentage of *meta* adducts.

Not only does 1,3-dioxol-2-one have a much higher ionization potential than cyclopentene, it also has hetero atoms in the ring and a large dipole moment (3.57 D)[8] in the opposite direction to that of cyclopentene (0.19 D)[8].

Benzene has also been reported to add to 1,3-dioxol-2-one[9], yielding two adducts, one with *endo*, the other with *exo* configuration, in a ratio of 5 : 1.



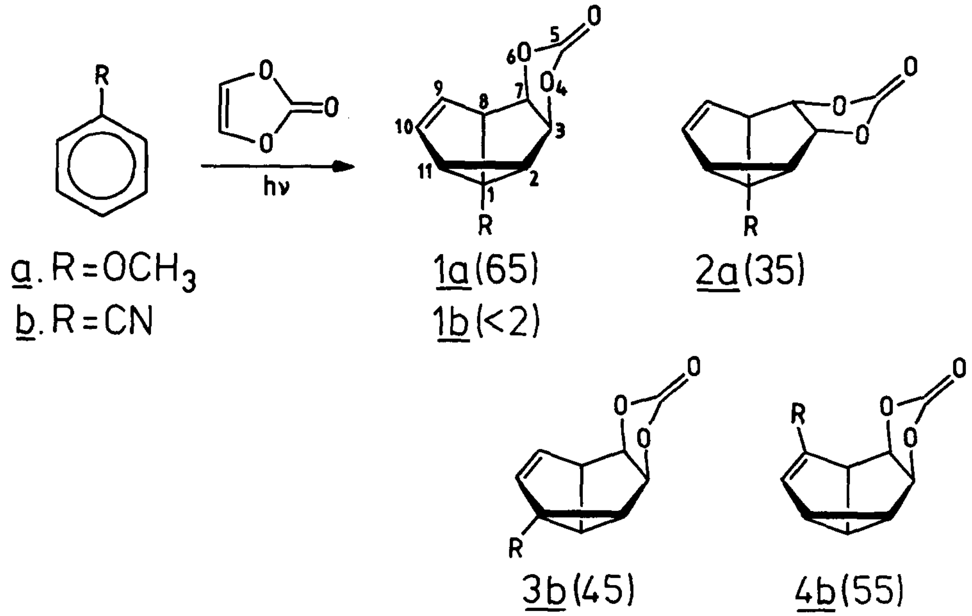
5 : 1

We hoped that a study of the reactions of anisole and benzonitrile with this alkene would provide us with further information about the charge distribution along the reaction pathway.

The aromatic compounds were irradiated at 254 nm (Rayonet Photochemical Reactor RPR 200 fitted with eight lamps) in methanol in the presence of the alkene. The concentrations used were 1 M arene and 3.5 M alkene. The solvent was removed, polymers were removed by means of silica gel chromatography (25 % ethyl acetate in hexane) and the products were separated by means of HPLC (17 % EtOAc in n-hexane; 60 atm.; 17 ml/min.). The products were identified by means of 1D and 2D NMR spectroscopy at 300 MHz (Bruker WM 300 spectrometer) in $CDCl_3$.

The product ratios were determined by means of NMR spectroscopy of the crude mixture at low conversion (2 - 5 %) (Merry-go-round, H. Mangels, Bornheim/Roisdorf, Germany; Hanau TNN 15/32 low pressure mercury lamp). As expected, the photoaddition of benzonitrile to 1,3-dioxol-2-one yields only *meta* adducts. In the case of anisole (I.P. = 8.54 eV)[6] some 30 % of the reaction products were *ortho* adducts as determined by NMR.

The following *meta* adducts were formed (product ratios in parentheses):



a. R = OCH_3
b. R = CN

1a(65)
1b(<2)

2a(35)

3b(45)

4b(55)

The proton chemical shifts and the proton-proton coupling constants of products 1a, 2a, 1b, 3b and 4b are presented in Tables 1 and 2.

Adduct 4b is photolabile and cannot be detected at higher conversions. The *exo* adduct 2a is also photolabile and the *endo*/*exo* ratio slowly increases with the time of irradiation. This agrees with Heine and Hartmann's observation of an *endo*/*exo* ratio of 5 : 1 at 70 % conversion for benzene and 1,3-dioxol-2-one.[9]

protons	1a	2a	1b	3b	4b
1				3.86	3.12
2	2.38	2.40	2.38	3.25	2.31
3	5.37	4.73	5.37	5.51	5.48
7	5.37	4.73	5.37	5.35	5.34
8	3.77	3.70	3.77	4.17	3.82
9	5.70	5.58	5.70	5.81	
10	6.00	5.80	6.01	5.94	6.83
11	2.48	2.47	2.49		2.36
OCH_3	3.39	3.39			

Table 1. Proton chemical shifts (ppm relative to TMS) of compounds 1a, 2a, 1b, 3b and 4b in $CDCl_3$ (300 MHz) at 298 K.

J	1a	2a	1b	3b	4b
1,2				6.9	6.1
2,3	5.5		5.2	6.9	6.0
3,7				8.8	6
7,8	5.9		5.9	6.4	7
8,9	2.7	2.8	2.7	2.7	
9,10	5.7	5.7	5.8	5.5	
10,11	2.2	2.4	2.3		2.6
1,11					6.1
1,8				5.6	
2,11	8.7	9.2	9.0		
3,8	2.6			1.5	1.5
9,11		1.2			

Table 2. Proton-proton coupling constants (Hz) of compounds 1a, 2a, 1b, 3b and 4b in $CDCl_3$ (300 MHz) at 298 K.

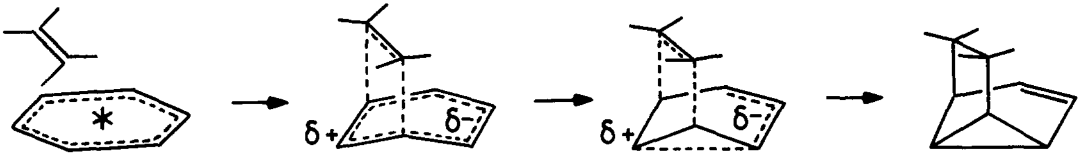
The product substitution pattern is in agreement with that of the adducts resulting from the irradiations of benzonitrile and anisole in the presence of cyclopentene. It seems likely that in this case again there is some degree of charge separation along the reaction pathway.

The *endo*/*exo* ratios are interesting. Even at very low conversion we could not detect any benzonitrile adducts with the *exo* configuration. The irradiation of α,α,α-trifluorotoluene in the presence of 1,3-dioxol-2-one (which was simultaneously and independently investigated by J. Mattay et al.[10] and by us) yielded also only adducts with the *endo* configuration and a similar substitution pattern.

Ultraviolet absorption spectra of the solutions of the reactants (1 M and diluted to 10^{-5} M) do not betray the existence of a ground state charge transfer complex and we are forced to conclude that the electron withdrawing substituents enhance the degree of charge separation along the reaction pathway and that the oxygen atoms in the five membered ring (which are electron deficient due to the effect of the carbonyl group[11]) are able to enjoy an electronic interaction with the negatively charged allylic moiety of the six membered ring. This would naturally result in a preference for the *endo* configuration. Although the directing and stabilizing effect of the methoxy group is certainly no less than that of the cyano group[12], the preference for formation of the *endo* adduct is less pronounced in the case of anisole. The methoxy group of the electron rich anisole stabilizes the positive charge that develops during the addition and the negative charge may flow in the direction of the electron deficient alkene. This would result in a less strong preference for the *endo* configuration than in the case of benzonitrile.

In the light of these results it is important to review the results of the irradiation of benzene and anisole in the presence of 1,3-dioxole.[13,14,15] In this alkene the oxygen atoms are comparatively electron rich and the *endo*/*exo* ratios are 18 : 82 for benzene and 25 : 75 for anisole (the latter ratio was determined at high conversion; at low conversion the percentage of *exo* adduct will be even higher), showing a preference for the *exo* configuration supposedly due to electronic repulsion.

The reaction pathway that we therefore propose is one proceeding via a species with a certain amount of charge separation in which the degree of polarization can be accentuated by the substituents on the aromatic ring.



We are presently investigating the effect of solvent polarity on the reaction rate.

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