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THE *META* PHOTOCYCLOADDITION OF BENZONITRILE AND α,α,α-TRIFLUOROTOLUENE TO CYCLOPENTENE

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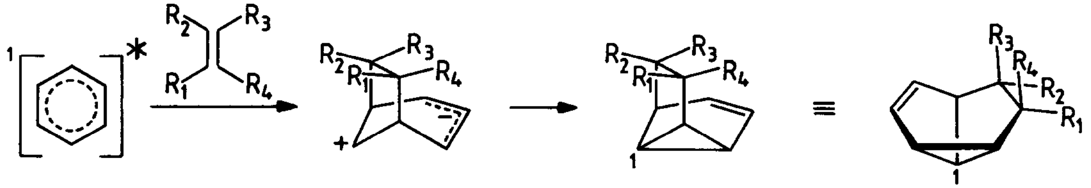
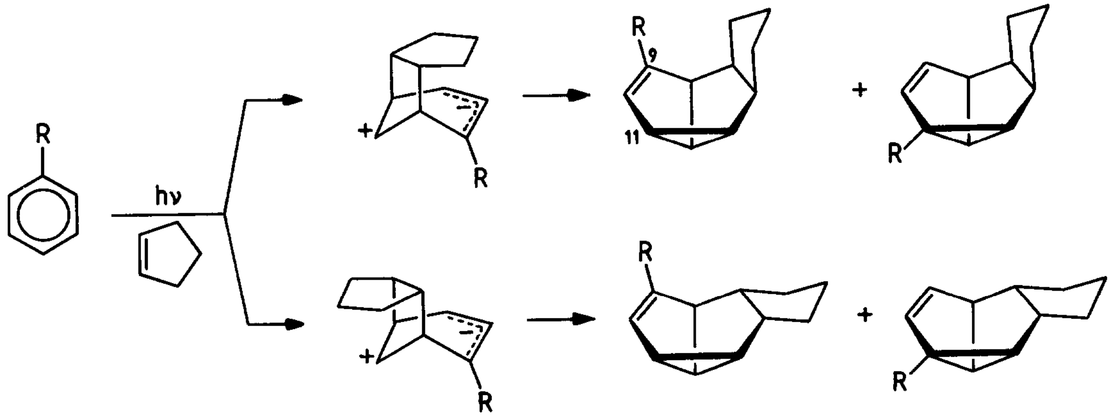
Abstract: The photocycloaddition of benzonitrile to cyclopentene yields four major cyano-substituted tetracyclo[$6.3.0.0^{2,11}.0^{3,7}$]undec-9-enes, all with the cyano group at positions 9 or 11. This is in agreement with a reaction pathway involving polarized structures as are the results of the irradiation of α,α,α-trifluorotoluene in the presence of cyclopentene.

Several mechanisms have been proposed for the *meta* photocycloaddition of aromatic compounds to alkenes.[1,2] Although Bryce-Smith, Gilbert and co-workers mentioned the possibility of a zwitterionic intermediate already in 1980[2], this suggestion does not seem to have been considered seriously until quite recently.[3]



Experimental evidence for a pathway via dipolar structures was found in the irradiation of cyclopropylbenzene[4] and anisole[5,6] in the presence of various olefins. Both substituents, being able to stabilize a positive charge, were consistently found at position 1 in the adduct.

In order to obtain further information we investigated the photocycloadditions of aromatic compounds bearing electron withdrawing substituents. In the case of a reaction mechanism in which charge separation plays a role, the electron withdrawing groups would stabilize the negative charge, thus forming products substituted at carbon atoms 9 and 11. On this basis one would expect the formation of four *meta* adducts, two with *endo* and two with *exo* configuration.



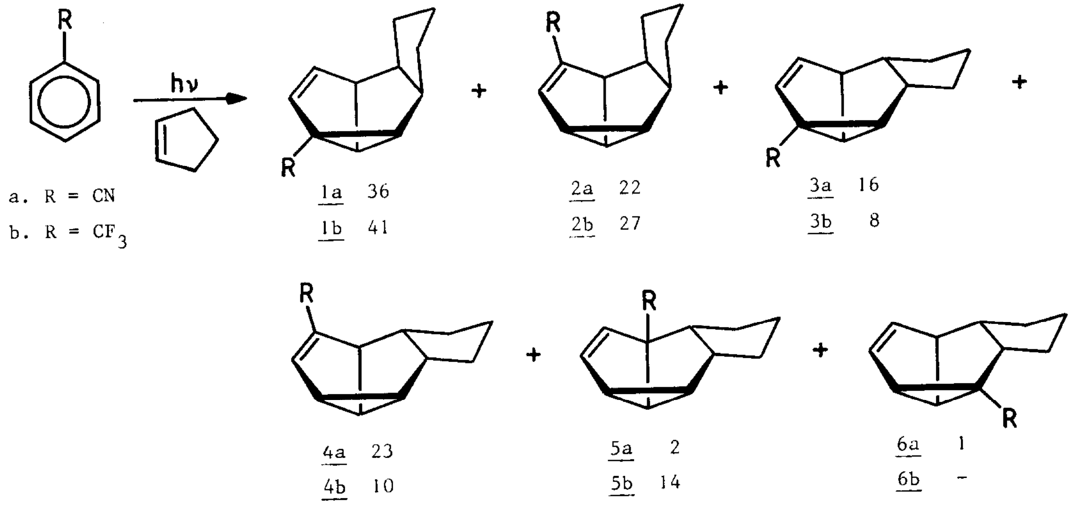
The aromatic compounds (benzonitrile and α,α,α-trifluorotoluene) were irradiated at 254 nm (Rayonet Photochemical Reactor RPR 200 fitted with eight lamps) in cyclohexane (200 ml) in the presence of cyclopentene. The concentrations were: 0.9 M alkene and 0.3 M arene.

After irradiation for 72 hours the solutions were examined by means of GC-MS and the solvent was removed. The remaining arene was recovered (benzonitrile 60 %, α,α,α-trifluorotoluene 40 %) and the products were separated by means of preparative GC (20 % DEGS on Chromosorb 80 - 100 mesh, 6 m × 8 mm, 130^0).

The fractions were analyzed by means of 1D and 2D ^{1}H NMR spectroscopy (Bruker WM 300 spectrometer). All spectra were measured in $CDCl_3$.

The product ratios were determined at low conversions (Merry-go-round, H. Mangels, Bornheim/Roisdorf, Germany; Hanau TNN 15/32 low pressure mercury lamp) by means of capillary GC (OV 101, 30 m, 100^0). This was necessary because several of the photoadducts are photo- and thermolabile and the product ratio changes with the irradiation time.

In the case of benzonitrile the *ortho* adduct formed 70 % of the photoproducts at low conversion. This adduct is very similar to one described in the literature[7] and will not be discussed here. The *meta* adducts formed the remaining 30 %. Under the same conditions a possible *ortho* adduct of cyclopentene and α,α,α-trifluorotoluene constituted less than 10 % of the photoproducts. The *meta* adducts were formed in the following ratios:



a. R = CN

b. R = CF_3

1a	36	2a	22	3a	16	4a	23	5a	2	6a	1
1b	41	2b	27	3b	8	4b	10	5b	14	6b	-

The NMR data of the *meta* photoadducts are presented in Tables 1 and 2.

	1a	2a	3a	4a	5a	6a	1b	2b	3b	4b	5b
H-1	3.39	3.11	3.09	2.68	2.83	3.09	3.01	3.22	2.72	2.72	2.94
H-2	2.39	2.02	2.05	1.57	1.53		2.25	1.94	1.87	1.8	1.84
H-3	3.07	3.11	2.45	2.43	2.36	2.45	3.22	3.08	2.4	2.42	3.07
H-4	1.2	1.2	1.2	1.2	1.4	1.4	1.2	1.3	1.1	1.2	1.2
H-5	|	|	|	|	|	|	|	|	|	|	|
H-6	2.1	2.1	2	2	2.1	2.1	1.9	1.9	1.9	2.0	1.9
H-7	3.22	3.35	2.14	2.43	2.46	2.25	3.22	3.30	2.18	2.46	3.49
H-8	3.11	3.11	3.16	3.23		3.16	3.08	3.09	3.14	3.16	
H-9	5.77		5.59		5.45	5.55	5.83		5.64		5.58
H-10	5.62	6.69	5.46	6.45	5.72	5.66	5.67	6.31	5.52	6.10	5.95
H-11		1.80		1,94	2.00	2.59		1.70		1.84	1.84

Table 1. Chemical shifts (in ppm relative to TMS) of *meta* cycloadducts 1a - 6a and 1b - 5b in $CDCl_3$ at 293 K.

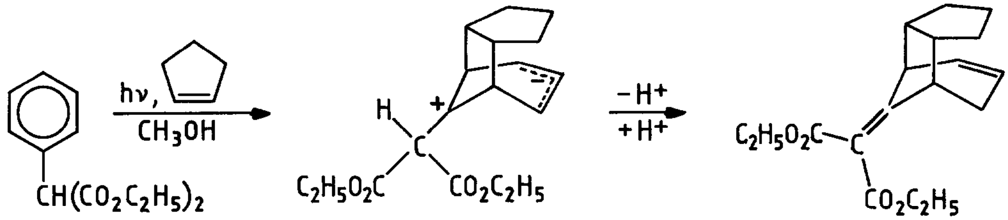
	1a	2a	3a	4a	5a	6a	1b	2b	3b	4b	5b
J(1,2)	7.0	7.5	6.8	6.0	7.3	-	7.3	7.2	7.3	6.8	6.8
J(2,3)	7.1	7.5	*	*	*	-	7.3	7.2	*	*	*
J(3.7)	+	+	6.7		8.0	6.7	+	+	8.2	+	7.5
J(7,8)	+	+	*	*	-	*	6.0	+	*	*	-
J(8,9)	2.5	-	2.5	-	-	1.9	2.4	-	2.5	-	-
J(9,10)	5.5	-	5.4	-	5.3	5.2	5.6	-	5.5	-	5.5
J(10,11)	-	2.8	-	2.7	2.4	2.1	-	1.9	-	+	0.8
J(11,1)	-	6.4	-	6.2	6.7	6.9	-	7.6	-	6.3	6.8
J(1,8)	5.9		5.5	5.7	-	6.0	7.5	6.2	5.6	5.7	-
J(2,11)	-	7.5	-	7.9	7.3	-	-	8.9	-	+	
J(3,8)	*	*	*	*	-	*	*	+	*	*	-

Table 2. Coupling constants (Hz) of *meta* cycloadducts 1a - 6a and 1b - 5b in $CDCl_3$ at 293 K. (* = too small to be detected; + = coupling proved to be present by 1D and 2D decoupling experiments but cannot be determined accurately due to high multiplicity of the signal).

It is interesting to compare the results to those of the irradiation of anisole and cyclopropylbenzene. The methoxy, cyclopropyl and cyano substituents are all able to stabilize a radical, whereas the methoxy and cyclopropyl substituents are the only ones capable of stabilizing a positive charge. The trifluoromethyl group is only able to stabilize a radical to a very slight extent.[8] The dissimilarity of the reaction of benzonitrile and anisole and the similarity of the reaction modes of benzonitrile and trifluorotoluene provide a strong indication for the existence of some charge separation along the reaction pathway.

We tried to intercept a hypothetical zwitterionic intermediate with various methods:

1. In the irradiation mixture of diethyl phenylmalonate we had hoped to but failed to find the following tricyclic product:



2. In the case of *meta*-(α-bromoethyl)anisole with cyclopentene a bromide ion could have been expelled from the anionic half of the zwitterionic intermediate resulting, after reaction of the positive part with a nucleophilic solvent molecule, in a tricyclic diene. Such a product could however not be detected.
3. We could not detect any tricyclic adducts resulting from the irradiation of toluene and cyclopentene in acidic methanol.
4. In the irradiation mixture of anisole with cyclopentene in ethanol we were unable to detect the presence of the alkoxy exchanged adduct, the 1-ethoxytetracyclo[6.3.0.0^{2,11}.0^{3,7}]undec-9-ene.

Although we therefore have no evidence for the existence of a discrete zwitterionic intermediate as referred to above, it does seem likely that the reaction should proceed with a certain degree of charge separation, the negative charge residing on the allylic moiety of the six membered ring. In the light of this proposed reaction pathway it is interesting to take a closer look at the product ratio for benzonitrile and trifluorotoluene with cyclopentene. The ratio of 9- to 11-substituted adducts is very similar for both substituents. In both cases carbon atom 11 is the preferred substitution position due to the electron withdrawing effect of the substituent. Although the trifluoromethyl group is rather less selective than the cyano group it is noticeable that no 1-substituted adduct could be detected in either case. This is in agreement with the proposed mechanism. Calculations[9] of the distribution of charge which develops in the course of the reaction indicate that there is a slight positive charge on carbon atom 10 which is in agreement with the absence of 10-substituted adducts.

We are now investigating the effect of the solvent on the product formation rate.

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