Tetrahedron Letters,Vol.24,No.35,pp 3745-3748,1983 0040-4039/83 $3.00 + .00
Printed in Great Britain

SUBSTITUENT AND WAVELENGTH EFFECTS IN THE PHOTOCHEMISTRY OF 5,6,7,8-TETRACHLORO-3a,9a-DIHYDRO-2,3,9a-TRIARYLFURO(2,3-b)(1,4)BENZODIOXIN DERIVATIVES

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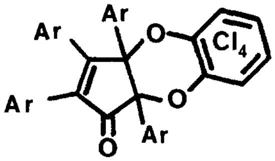
Summary: A study of the photoreactions of some triarylfurobenzodioxin derivatives has shown that the outcome is dependent on the type and position of the substitution on the 9a-aryl group. A wavelength dependence is also reported.

Some years ago we reported the synthesis of the adducts (1) and (2) by thermal reaction of tetraarylcyclopentadienones[1] and arylfurans[2] with tetrachloro-1,2-benzoquinone. The photoreactions of these adducts were shown in all cases to be clean and efficient yielding cyclopentaphenanthrenones (3)[3] and phenanthrofurans (4)[4] respectively. The rationalisation of the process was based on the assumption, under the conditions of the irradiation[5], that the oxygen-substituted cis-stilbene system was preferentially excited and led to a dihydrophenanthrene[6]. Subsequent elimination, by a thermal process, of tetrachlorocatechol led to the isolated products No data was collected at that time to suggest that alternative reaction paths were available to the molecule. In recent work we have shown that the photoreactions of the triarylfurobenzodioxins are subject to substituent and wavelength effects which were not detected in our earlier studies.



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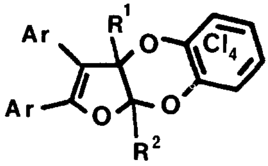

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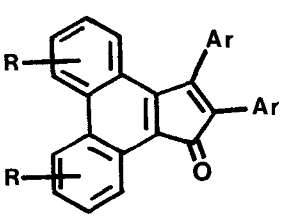

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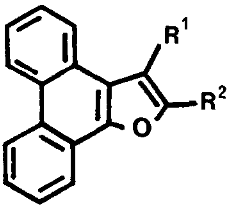

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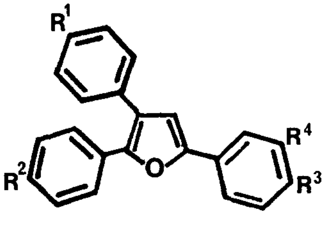
The phenylated furans (5) required for the study were readily synthesised from the appropriate 1,2,4-triarylbuten-1,4-dione by refluxing with concentrated hydroiodic acid[7]. The dihydrobenzodioxins were then prepared by refluxing each of the furans (5) with tetrachloro-1,2-benzoquinone in benzene. The adducts (6) were precipitated by the addition of light petroleum to the benzene solution and recrystallised to afford cream coloured crystals of the desired product.[7] N.m.r. spectroscopy readily demonstrated, by the upfield shift of the single furan hydrogen, that the cycloaddition had taken place on the singly-substituted double bond of the furan. This had previously been recorded for the parent adduct (6a).[4]



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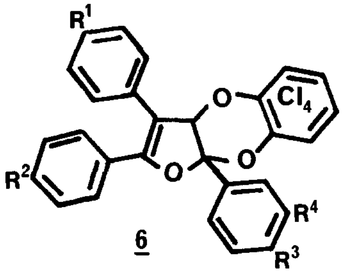

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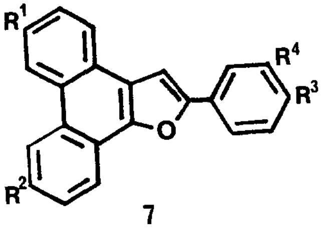

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(a)	$R^1=R^2=R^3=R^4=H$	(a)	55%, m.p. 163-164°
(b)	$R^1=R^2=Me$, $R^3=R^4=H$	(b)	45%, m.p. 160-162°
(c)	$R^1=R^2=R^4=H$, $R^3=Me$	(c)	56%, m.p. 150-152°
(d)	$R^1=R^2=R^4=H$, $R^3=MeO$	(d)	58%, m.p. 146-148°
(e)	$R^1=R^2=R^3=H$, $R^4=MeO$	(e)	57%, m.p. 155-157°
(f)	$R^1=R^2=R^4=H$, $R^3=Br$	(f)	49%, m.p. 173-175°
(g)	$R^1=R^2=Me$, $R^4=H$, $R^3=Br$	(g)	62%, m.p. 161-162°
(h)	$R^1=R^2=R^4=H$, $R^3=CN$	(h)	67%, m.p. 169-171°

All the adducts (6) showed the same characteristics which had been recorded for the parent adduct (6a) and had an absorption envelope stretching from 240 nm to 340 nm. The irradiations were therefore carried out under conditions similar to our previous study.[5] Thus irradiation of the parent (6a) and of adducts (6b) and (6c) gave only the corresponding phenanthrofuran derivatives (7a, 44%), (7b, 71%), and (7c, 73%) respectively. However, when a bromo-substituent was introduced into the 4-position of the 9a-aryl group, adduct (6f), irradiation under the same conditions as the above gave both the phenanthrofuran (7f, 44%) and the parent furan (5f, 47%). Irradiation of adduct (6g) followed the same pattern and gave (7g, 43%), and (5g, 43%). A more pronounced effect was observed with a cyano-substituent, adduct (6h), when the phenanthrofuran product (7h, 7%), much the minor product, and the furan (5h, 66%) were isolated. It is thus clear that the inclusion of an electron withdrawing group (either inductive or conjugative) at the para-position of the 9a-aryl group changes the reaction path from one where the cis-stilbene cyclisation-elimination process is operative to a situation where this is in competition with a retro-Diels-Alder reaction.[8] Interestingly similar behaviour was encountered on irradiation of the adduct (6e) which yielded the phenanthrofuran (7e, 33%) and the furan (5e, 38%).

The adducts (6) can be considered as trichromophoric systems with a cis-stilbene, an isolated aryl group, and a tetrachlorocatechyl moiety. When the 9a-aryl group is unsubstituted or has a methyl group (6a-c) only the cis-stilbene system has an absorption above 290 nm, the cut-off point for the Pyrex filter. However, substitution in the aryl group (6d-h) moves the aryl absorption to a longer wavelength and thus this group, or a charge transfer between the aryl group and the tetrachlorocatechyl moiety, becomes accessible to excitation through Pyrex. It is this latter absorption which leads to the retro-Diels-Alder process. The above rationalisation has some support from irradiations of the adducts (6a, c-e, g) using a low pressure mercury lamp and a quartz filter. Under these conditions all of the adducts used yield both the products of cis-stilbene cyclisation and of retro-Diels-Alder activity.

Table Product (%) from irradiation of adducts (6) at 254 nm.

Adduct	Products (%)	
6a	5a(43)	7a(35)
6c	5c(32)	7c(28)
6d	5d(44)	7d(24)
6e	5e(31)	7e(23)
6g	5g(44)	7g(8)

Current work in hand is designed to identify the processes responsible for the observed reactions in particular attention is being paid to the possibility of charge-transfer involvement.

References

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2. D.T. Anderson and W.M. Horspool, J. Chem. Soc. Perkin Trans. 1, 532 (1972).
3. (a) W.M. Horspool, J. Chem. Soc. (C), 400 (1971); (b) W.M. Horspool, J. Chem. Soc. Chem. Commun., 467 (1969).
4. D.T. Anderson and W.M. Horspool, J. Chem. Soc. Perkin Trans. 1, 536 (1972); D.T. Anderson and W.M. Horspool, J. Chem. Soc. Chem. Commun., 615 (1971).
5. The reactions were carried out under nitrogen in propan-2-ol with a medium pressure mercury arc lamp and a Pyrex filter.
6. For reviews see: F.R. Stermitz, Org. Photochem., ed. O.L. Chapman, 1, 247 (1967) and E.V. Blackburn and C.J. Timmons, Quart. Rev., 23, 482 (1969).
7. Satisfactory spectroscopic and microanalytical data were obtained for all new compounds.
8. Previously we have observed a Retro-Diels Alder only when the cis-stilbene cyclisation could not take place i.e. with the adduct formed from 2,3-diphenyl-indenone and tetrachloro-1,2-benzoquinone - see ref. 3(a).

(Received in UK 13 June 1983)