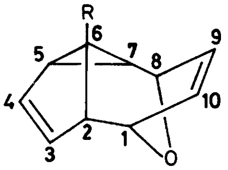
Stereo- and Regio-specific Photochemical Cycloaddition of Furan to Benzonitrile and Phenylacetylene

Andrew Gilbert* and Paul Rodwell

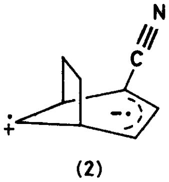
Chemistry Department, University of Reading, Whiteknights, P.O. Box 224, Reading, Berkshire RG6 2AD, U.K.

Benzonitrile and phenylacetylene undergo exclusive regio- and stereo-specific 2,6-, 2′,5′-photocycloaddition of furan: excited state interaction between the substituent and furan is considered to orient the addends and direct the reaction of this specific mode of attack.

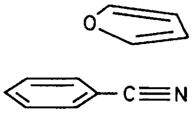
The photoreaction of benzene and methylbenzenes with furan displays poor selectivity yielding products which reflect 1,4-, 2′,5′-; 1,3-, 2′,5′-; 1,3-, 2′,3′-; and 1,2-, 2′,3′-cycloaddition and thus has limited synthetic interest.[1,2] We now report that the mode and stereo- and regio-selectivities of the reaction of such addends can be controlled by a conjugative substituent on the benzene ring. Thus in marked contrast to the previous reports, 254 nm irradiation of benzonitrile and furan gave a single product which was freed from residual starting arene following vacuum distillation by flash chromatography to yield crystals (m.p. 63.5—64.5 °C) to which structure (**1**) was assigned on the basis of the following data: ^{1}H n.m.r. spectrum ($CDCl_3$), δ values: 6.60 (d of 4 lines, H-9, $J_{9,10}$ 6.0, $J_{8,9}$ 1.55, $J_{1,9}$ 0.6 Hz), 6.30 (d of d, H-10, $J_{10,1}$ 1.8 Hz), 5.96 (d of d, H-4, $J_{4,5}$ 2.6, $J_{4,3}$ 5.6 Hz), 5.46 (d of 4 lines, H-3, $J_{3,7}$ 1.4, $J_{3,2}$ 2.2 Hz), 5.08 (t, H-8, $J_{8,7}$ 1.8 Hz), 4.50 (t, H-1, $J_{1,2}$ 2.4 Hz), 3.26 (t, H-2), 2.91 (d of d, H-5, $J_{5,7}$ 7.7 Hz), and 1.50 (d of t, H-7); $\nu_{max.}$ 2215 cm^{-1}; M^+, 171.0681, pure by t.l.c. and g.l.c. analysis, calc. 171.0682. Unlike photocycloadditions of ethenes to benzenoid compounds,[3] the present addition is greatly favoured by high concentrations of benzonitrile: the proportions of the addends best suited for preparative purposes are 9:1 (by volume) of benzonitrile and furan respectively when gram quantities of (**1**) can be obtained from 100 ml in 48 h using a 30 W low pressure mercury arc lamp.



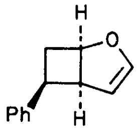
(**1**) R = C≡N
(**4**) R = C≡CH
(**5**) R = CH=CH$_2$



(**2**)



(**3**)



(**6**)

meta Photocycloaddition of ethenes to benzonitrile occurs exclusively or highly selectively at the 2,4-positions of the arene and this is interpreted in terms of nitrile group stabilisation of the intermediate (**2**) formed on collapse of the exciplex.[4] For the present system such stabilisation factors are apparently of little importance and the reaction specificity in forming (**1**) is rationalised by interaction between the cyano group and the furan which directs the addends into the orientation (**3**), probably in an intermediate exciplex, which then gives the *exo* 2,6-, 2′,5′-cycloaddition. Furan quenches benzonitrile fluorescence in iso-octane solution with $k_q \simeq 1.1 \times 10^{10}$ l mol^{-1} s^{-1} but emission attributable to an exciplex was not observed and no evidence for a ground state complex between the addends was obtained. On the other hand benzonitrile and 2,5-dimethylfuran do form an emissive exciplex ($\lambda_{max.}$ 362 nm) but in this system specificity of the photoreaction is lost and a multicomponent mixture is formed. Methyl substitution in the benzonitrile, however, has no observable effect on the reaction specificity and *o*-, *m*-, and *p*-toluonitriles and furan yield 1 : 1 adducts which are derived exclusively from the 2,6-, 2′,5′-*exo* reaction.

On the argument that reaction selectivity reflects substituent controlled preferential alignment of the addends as in (**3**), then phenylacetylene should behave analogously to benzonitrile and indeed irradiation of its 10% (v/v) solution in furan gave (**4**)[†] as the sole adduct (m.p. 64—65 °C)[‡] along with minor amounts of 1-phenylazulene and 1-phenylnaphthalene.[5] It would appear that the vinyl group also has some directing influence since styrene and furan, despite their expected non-ideal alignment for addition to the benzene ring still yield the 2,6-, 2′,5′-*exo* product (**5**)[‡] but in a 1:2 respective ratio with the [2π + 2π] adduct (**6**): α-methylstyrene, however, only gave the latter type of product which may indicate that the orientation of the addends is subject to steric perturbation.

The specific formation of (**1**), (**4**), and (**5**) in gram quantities illustrates the potential of employing substituent orienting factors in arene photocycloadditions to improve reaction selectivity to the point of synthetic usefulness.

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[†] Higher concentrations of phenylacetylene produced the dimers described in ref. 5 as the major products.

[‡] All new compounds exhibited spectra consistent with the assigned structures and gave satisfactory analytical data. ^{1}H N.m.r. spectra ($CDCl_3$) (**4**): δ 6.55 (d of 4 lines, H-9, $J_{9,10}$ 5.8, $J_{8,9}$ 1.56, $J_{1,9}$ 0.6 Hz), 6.21 (d of d, H-10, $J_{10,1}$ 1.8 Hz), 5.97 (d of d, H-4, $J_{4,5}$ 2.6, $J_{4,3}$ 5.6 Hz), 5.40 (d of 4 lines, H-3, $J_{3,7}$ 1.4, $J_{3,2}$ 2.2 Hz), 5.01 (t, H-8, $J_{8,7}$ 1.8 Hz), 4.46 (t, H-1, $J_{1,2}$ 2.35 Hz), 3.09 (t, H-2), 2.48 (d of d, H-5, $J_{5,7}$ 7.6 Hz), 2.00 (s, –C≡C–H), 1.23 (d of t, H-7); (**5**): δ 6.39 (d of 4 lines, H-9, $J_{9,10}$ 6.0, $J_{8,9}$ 1.52, $J_{1,9}$ 0.6 Hz), 6.03 (d of d, H-10, $J_{10,1}$ 1.75 Hz), 5.97 (d of d, H-4, $J_{4,3}$ 5.4, $J_{4,5}$ 2.56 Hz), 5.48 (d of d, vinyl, J_{trans} 17.0, J_{cis} 10.7 Hz), 5.41 (d of 4 lines, H-3, $J_{3,7}$ 1.4, $J_{3,2}$ 2.2 Hz), 5.02 (br.t, H-8, $J_{8,7}$ 1.8 Hz), 4.86 (d of d, vinyl), 4.78 (d of d, vinyl, $J_{gem.}$ 1.12 Hz), 4.51 (br.t, H-1, $J_{1,2}$ 2.4 Hz), 3.15 (t, H-2), 2.93 (d of d, $J_{5,7}$ 7.4 Hz), 1.03 (d of t, H-7).

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