

Addition of Furans to Electron-rich Olefins through Photo-induced Electron-transfer in the Presence of Electron Acceptors

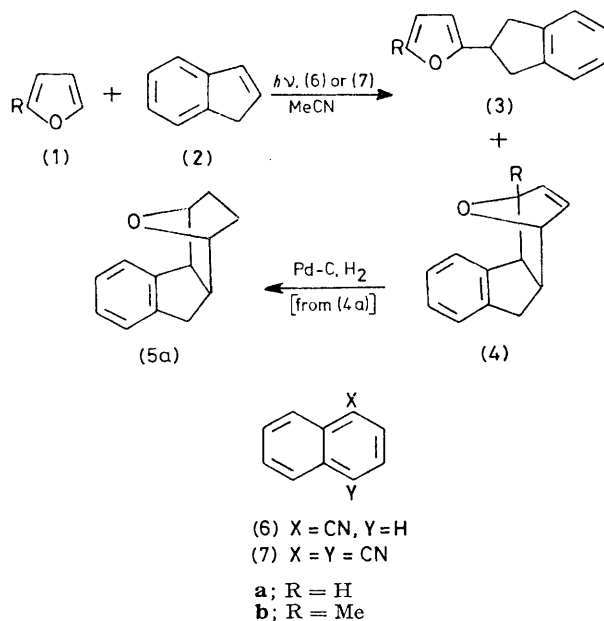
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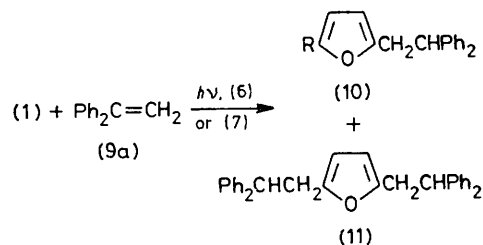
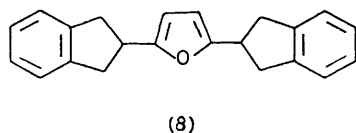
Summary Photoaddition of furan and 2-methylfuran to aromatic olefins such as indene and 1,1-diphenylethylene in the presence of 1-cyanonaphthalene or 1,4-dicyanonaphthalene gives (4 + 2) cycloadducts and/or alkyl-substituted furan derivatives.

The photocycloaddition of furan (**1a**) to aromatic rings,^{1a} ketones,^{1b} and electron-deficient olefins^{1c} has been widely investigated. However, the photoaddition of (**1a**) to electron-rich olefins is not well known.² Recently, Farid and his co-workers³ and we⁴ independently reported the photocycloaddition between two different electron-rich olefins in the presence of an electron acceptor. We now report the photoaddition of (**1a**) and (**1b**) to electron-rich aromatic olefins such as (**2**), (**9a**), and (**9b**) in the presence of the cyanonaphthalenes (**6**) or (**7**).

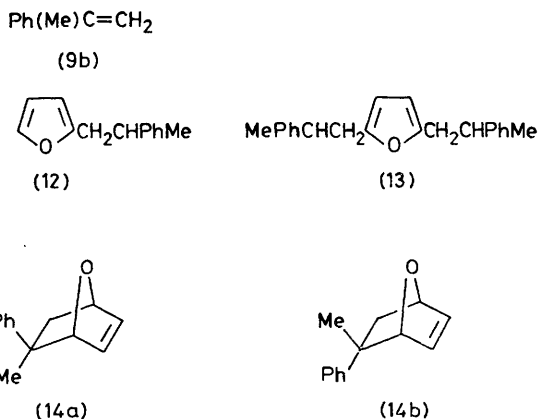
(m.p. 95.5–97 °C; 10%) with *ca.* 60% recovery of (**6**).† These products were isolated by column chromatography on silica gel, and their structures were assigned from their analytical and spectral properties, especially their 100 MHz ¹H n.m.r. spectra. Also, hydrogenation of (**4a**) on 5% Pd-charcoal afforded (**5a**) (m.p. 45–47 °C), and (**4a**) was confirmed to be a (4 + 2) cycloadduct since it was not hydrolysed in acidic ethanol. Similarly, irradiation of (**1b**) and (**2**) in the presence of (**6**) gave (**4b**) (10%) and (**3b**) (75%). However, no photoaddition took place upon irradiation of solutions of 2,5-dimethylfuran or thiophen and (**2**) in the presence of (**6**) under the same conditions.



Irradiation of an acetonitrile solution containing (**1a**) (100 mmol), (**2**) (10 mmol), and (**6**) (1 mmol) through Pyrex with a 300 W high-pressure mercury arc for 25 h gave (**4a**) (m.p. 48–49 °C; 35%), (**3a**) (20%), and (**8**)



The reactivity of other aromatic olefins was also examined. Irradiation of a solution of (**1a**) or (**1b**) and (**9a**) in the presence of (**7**) gave (**10a**) (49%) and (**11**) (m.p. 61–63 °C; 19%) or (**10b**) (50%) respectively with 70–80% recovery of (**7**).‡ Similarly, irradiation of (**1a**) and (**9b**) in the presence of (**7**) gave the photoproducts (**12**), (**13**), (**14a**), and (**14b**) although in low yields. In these reactions, 1,2-, 1,3-, and 1,4-dicyanobenzene could be used as electron acceptor in place of (**6**) and (**7**).



† Yields of crossadducts are based on consumed aromatic olefins. U.v. measurements showed no indication of the formation of charge-transfer complexes between (**1a**) (**2**), and (**6**), in the ground state.

‡ Reaction of triplet (**2**) with (**1a**) gave indene dimer as the main product accompanied by a small amount of (**3a**) and (**4a**). However, the reaction of triplet (**9a**) with (**1a**) gave no isolable products, although Cantrell reported that the addition of triplet (**9a**) to (**1a**) gives 55% of a 1:1 adduct, m.p. 83–84 °C (see ref. 2).

TABLE. Rate constants for fluorescence quenching of (6) and calculated ΔG values^a

Compd.	$E_{1/2ox}^b$ /V	$k_q^d \times 10^{-9}$ /s ⁻¹ dm ³ mol ⁻¹	$\Delta G^{e,f}$ /kJ mol ⁻¹
(1a)	1.46	1.27	-20.29
(1b)	1.18	7.37	-47.30
2,5-Dimethylfuran	0.95	14.12	-69.49
Thiophen	1.56	0.36	-10.64
1-Methylpyrrole	0.74	17.71	-89.75
(2)	1.23	10.74	-42.48
(9a)	1.40	15.97	-26.08
(9b)	1.45	21.01	-21.25
(6)	(-2.25) ^e		

^a Oxidation and reduction potentials were obtained by cyclic voltammetry: Pt electrode, tetraethylammonium perchlorate (0.1 mol dm⁻³) in acetonitrile solution, vs. Ag/0.01 mol dm⁻³ AgClO₄. ^b The oxidative process was not reversible and the half-wave potentials were estimated from cyclic voltammograms obtained at a 100 mV s⁻¹ sweep rate. ^c Reduction potential. ^d For air-saturated acetonitrile solutions; [6] = 2.7 × 10⁻⁴ mol dm⁻³. These values were calculated by using a lifetime of 8.9 ns for (6) (D. R. Arnold and A. J. Maroulis, *J. Amer. Chem. Soc.*, 1976, **98**, 5931). ^e Calculated values in acetonitrile, using equation (1). Coulombic term estimated to be 5.44 kJ mol⁻¹. ^f These values were calculated by using an excited singlet energy of (6) of 372.79 kJ mol⁻¹ (S. L. Murov, in 'Handbook of Photochemistry,' Marcel Dekker, New York, 1970).

In acetonitrile, the fluorescence of (6) and (7) was efficiently quenched by (1a), (1b), (2), (9a), (9b), 1-methylpyrrole, and 2,5-dimethylfuran, and Weller's equation (1) gave a negative ΔG value for the electron transfer from these quenchers to photo-excited (6) and (7) (Table).⁵

¹ (a) J. C. Berridge, D. Bryce-Smith, A. Gilbert, and T. S. Cantrell, *J.C.S. Chem. Comm.*, 1975, 611; C. Pac, T. Sugioka, and H. Sakurai, *Chem. Letters*, 1972, 39 and 667; K. Mizuno, C. Pac, and H. Sakurai, *J.C.S. Perkin I*, 1974, 2360; (b) D. R. Arnold, *Adv. Photochem.*, 1968, **6**, 301; (c) A. Schönberg, in 'Preparative Organic Photochemistry,' Springer-Verlag, Berlin, 1968.

² T. S. Cantrell, *Chem. Comm.*, 1970, 1633.

³ S. Farid, S. E. Hartman, and T. R. Evans, in 'The Exciplex,' eds. M. Gordon and W. R. Ware, Academic Press, New York, 1975, p. 327.

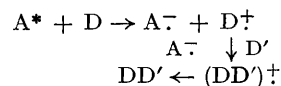
⁴ K. Mizuno, R. Kaji, and Y. Otsuji, *Chem. Letters*, 1977, 1027.

⁵ D. Rehm and A. Weller, *Israel J. Chem.*, 1970, **8**, 259.

⁶ R. A. Neunteufel and D. R. Arnold, *J. Amer. Chem. Soc.*, 1973, **95**, 4080; C. Pac, A. Nakasone, and H. Sakurai, *ibid.*, 1977, **99**, 5806; S. Farid and S. E. Schealer, *J.C.S. Chem. Comm.*, 1973, 677.

$$\Delta G/\text{kJ mol}^{-1} = 96.48[E(D/D^+)_{\nu} - E(A^-/A)_{\nu}] - \frac{e^2/\epsilon_a}{e^2/\epsilon_a - E_{0,0}} \quad (1)$$

These results suggest the electron-transfer mechanism in the Scheme for the photoadditions. Electron-transfer from



A* = excited singlet of (6) or (7);

D = aromatic olefin; D' = (1a) or (1b)

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(2) and (9a) to the excited singlet of (6) or (7) preferably occurs to give cation radicals (D⁺) of (2) and (9a) and anion radicals (A⁻) of (6) or (7).^{4,6} Nucleophilic attack of (1a) or (1b) (D') on D⁺ results in the formation of the heterodimer cation radicals (DD'⁺), which give the corresponding crossadducts.

Evidence for the intermediacy of cation radicals was provided by the following observations. (i) The formation of crossadducts such as (3a or b) and (4a or b) was completely quenched in the absence of (6) or (7), or in non-polar solvents such as benzene or cyclohexane. (ii) Addition of 2,5-dimethylfuran or 1-methylpyrrole, which have much lower oxidation potentials than those of (2) and (9a), quenches the formation of (3a or b) and (4a or b).

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