

Photochemical Reactions of Aromatic Compounds. Part XX.¹ Photocycloaddition of 9-Cyanoanthracene to Furan and Mono- and Dimethylfurans²

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Photoreaction of 9-cyanoanthracene (1) with furan (2a), and with 2-methyl- (2b), 3-methyl- (2c), and 2,5-dimethyl-furan (2d) affords the (4 + 4) cycloadducts, 9-cyano-9,10,11,13-tetrahydro-9,10[2',5']-furananthracene (5a) and its methyl substituted derivatives (5b—d), respectively, in good yields. Irradiation of (1) in the presence of thiophen (3) or 1-methylpyrrole (4) gives no cycloadduct. An exciplex mechanism is suggested for these reactions on the basis of fluorescence measurements and kinetics.

PHOTOCYCLOADDITIONS of unsaturated compounds to aromatic rings have been investigated as synthetic routes for novel cyclic compounds¹⁻⁷ and have been discussed in relation to exciplexes.^{1-3,5} Recent papers have described several new examples of photocycloaddition to anthracene, *viz.* (4 + 2n) photocycloaddition of conjugated dienes⁶ and cycloheptatriene⁷ to anthracene, intramolecular photocycloaddition of 1-(9-anthryl)-3-(1-naphthyl)propane,⁸ and photochemical cross-dimerisations between two different anthracenes⁹ and between anthracenes and tetracene.¹⁰ It has been suggested that these photoreactions involve exciplexes, but evidence is lacking.

However, photocycloaddition of heteroaromatic compounds to anthracene have not been reported. In previous papers,^{3a,c} we have reported photocycloaddition of furan to cyanonaphthalenes, giving novel heterocyclic compounds. We now describe the photoreactions of 9-cyanoanthracene (1) with furan (2a), the methylated furans (2b—d), thiophen (3), and 1-methylpyrrole (4) and provide evidence for the formation of exciplexes

† The n.m.r. spectrum of 2,5-dihydrofuran ring in (5a) is similar to that of the cycloadduct of 1-cyanonaphthalene with furan; see ref. 3a.

¹ Part XIX, K. Mizuno, C. Pac, and H. Sakurai, *J. Amer. Chem. Soc.*, 1974, **96**, 2993.

² Preliminary communication, K. Mizuno, C. Pac, and H. Sakurai, *Chem. Letters*, 1973, 309.

³ (a) C. Pack, T. Sugioka, and H. Sakurai, *Chem. Letters*, 1972, 39, 667; (b) C. Pac, T. Sugioka, K. Mizuno, and H. Sakurai, *Bull. Chem. Soc. Japan*, 1973, **46**, 238; (c) T. Sugioka, C. Pac, and H. Sakurai, *Chem. Letters*, 1972, 791; (d) C. Pac, K. Mizuno, T. Sugioka, and H. Sakurai, *ibid.*, 1973, 187; (e) K. Mizuno, C. Pac, and H. Sakurai, *J.C.S. Chem. Comm.*, 1973, 219.

⁴ (a) D. Bryce-Smith, *Pure Appl. Chem.*, 1973, **34**, 193; (b) T. Teitei, D. Welles, and W. H. F. Sasse, *Austral. J. Chem.*, 1973, **26**, 2129; (c) T. R. Chamberlain and J. J. McCullough, *Canad. J. Chem.*, 1973, **51**, 2578; (d) N. C. Yang and J. Libman, *J. Amer. Chem. Soc.*, 1972, **94**, 9228; (e) T. Miyamoto, T. Mori, and Y. Odaira, *Chem. Comm.*, 1970, 1598; (f) S. Farid, J. C. Doty, and J. L. R. Williams, *J.C.S. Chem. Comm.*, 1972, 711.

between the excited singlet (1) and the heterocyclic compounds.

RESULTS

Irradiation of a benzene solution of (1) containing a large excess of (2a) gave a 1 : 1-cycloadduct (5a) in 50% isolated yield, accompanied by 20% of 9-cyanoanthracene photodimer (7). The product (5a) was isolated by chromatography on silica gel and characterised by spectroscopic methods. The mass spectrum of (5a) showed no molecular ion but intense fragment peaks at *m/e* 203 and 68, while the dihydro-isomer (6a) exhibited a molecular ion at *m/e* 273. The u.v. spectrum of (5a) showed similar absorption maxima to that of 9,10-dimethyl-9,10-dihydroanthracene,¹¹ indicating the presence of the 9,10-dihydroanthracene chromophore. The i.r. spectrum showed absorptions at 2240 (C≡N), 1628 (C=C), and 1052 cm⁻¹ (C—O—C).

N.m.r. spectra † were recorded at 60 and 100 MHz. In the 60 MHz spectra the signals of H-14 and -15 appeared as a broad singlet (δ 5.92) at a similar chemical shift to the olefinic protons of 2,5-dihydrofuran [δ 5.78br (s)],¹² indicating the nearly symmetrical nature of the double bond.

⁵ (a) J. Cornelisse, V. Y. Merritt, and R. Srinivasan, *J. Amer. Chem. Soc.*, 1973, **95**, 6197; (b) K. E. Wilzbach and L. Kaplan, *ibid.*, 1971, **93**, 2073; (c) R. M. Bowman, T. R. Chamberlain, C. W. Huang, and J. J. McCullough, *ibid.*, 1974, **96**, 692; (d) R. A. Caldwell and L. Smith, *ibid.*, 1974, **96**, 2994.

⁶ (a) N. C. Yang and J. Libman, *J. Amer. Chem. Soc.*, 1972, **94**, 1405; (b) N. C. Yang, J. Libman, L. Barret, jun., M. H. Hui, and R. L. Loesch, *ibid.*, p. 1406; (c) G. Kaupp, *Angew. Chem.*, 1972, **84**, 718.

⁷ T. Sasaki, K. Kanematsu, and H. Hayakawa, *J. Amer. Chem. Soc.*, 1973, **95**, 5632.

⁸ E. A. Chandross and A. H. Schiebel, *J. Amer. Chem. Soc.*, 1973, **95**, 611.

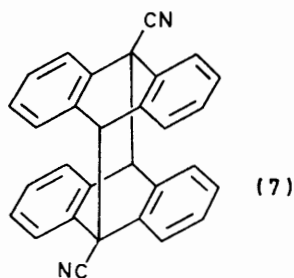
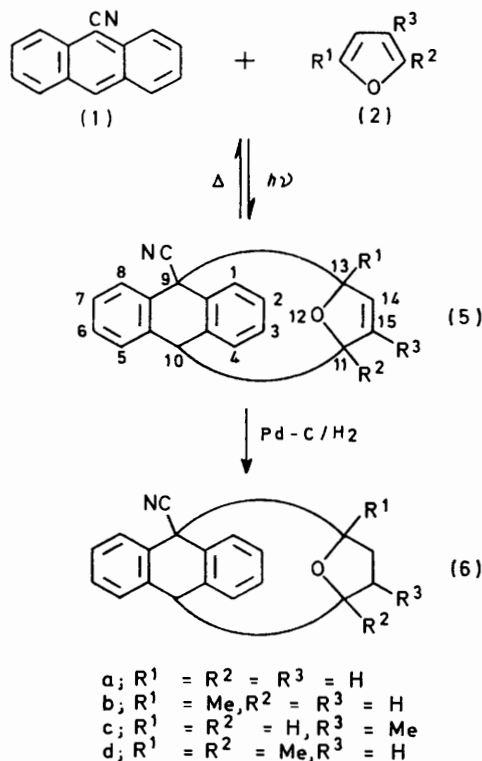
⁹ H. Bouas-Laurent and R. Lapouyade, *Chem. Comm.*, 1969, 817.

¹⁰ H. Bouas-Laurent and A. Castellan, *Chem. Comm.*, 1970, 1648.

¹¹ D. D. Phillips and J. Gason, *J. Amer. Chem. Soc.*, 1952, **74**, 2934.

¹² P. K. Korver, P. J. Van Der Haak, N. Steinberg, and T. J. De Boer, *Rec. Trav. chim.*, 1965, **84**, 129.

Photochemical (4 + 4) addition of the methyl-substituted furans (2b—d) to (1) to give the adducts (5b—d) occurred similarly. 3-Methylfuran (2c) gave a quantitative



yield of the adduct (5c). The location of the methyl group in (5c) at C-15 was assigned from the n.m.r. data; the signal of H-13 is broadened by a small coupling (*J*

1.0 Hz) with H-14 whereas the signal of H-11 appears as a sharp doublet.

2-Methylfuran (2b) and 2,5-dimethylfuran (2d) at 0–5° gave the (4 + 4) cycloadducts (5b) and (5d) in quantitative yields, respectively. The adducts (5b) and especially (5d) were thermally unstable and rapidly decomposed into (1) at room temperature, so that they could not be isolated in pure form. Irradiation at ambient temperature did not lead to accumulation of the adducts, but only resulted in the gradual formation of (7), so procedures involving these adducts were carried out at <0°. For example, after irradiation of (1) and (2b) at 0–5°, evaporation of volatile materials below 0° under high vacuum left solid (5b) exclusively, whose structure was determined from the n.m.r. spectrum of a mixture containing a small amount of (1) (Table I). Since (5d) immediately decomposed at >5°, the n.m.r. spectrum was not recorded.

After irradiation at 0–5°, however, hydrogenation of the solutions over palladium-charcoal gave the dihydro-compounds (6b) and (6d) in quantitative yields. The spectral properties of (6b) and (6d) (Table I) were in accord with the structures assigned.

In contrast to the photoreactions with furan, irradiation of (1) with thiophen (3) or 1-methylpyrrole (4) gave no crossadduct and resulted in quantitative formation of the dimer (7).

DISCUSSION

A singlet mechanism for the photocycloaddition with (2a) was established by quantum yield measurements and fluorescence quenching studies. The quantum yield measurements are shown in Figure 1. From the slope (44 mol dm⁻³) and the intercept (5.0), the *k_qτ* value was calculated as 0.11 dm³ mol⁻¹, which was in excellent agreement with the value (0.1 ± 0.03 dm³ mol⁻¹) obtained from fluorescence quenching studies. In the case of (2b—d), quantum yield measurements were not carried out, because of difficulties owing to rapid decomposition of the adducts (5b) and (5d). However, it is reasonable to propose a common singlet mechanism for the photocycloaddition with (2a—d), since fluorescence quenching was more efficient with (2b) and (2d) than with (2a). Since the photocycloaddition of 1-naphtho-nitrile with furan occurs from a singlet exciplex,^{3a} an exciplex mechanism can also be expected to operate in the photocycloaddition of (1) with (2a—d).

TABLE I

Spectral data of products

Product	N.m.r. ^a [δ (CDCl ₃) (<i>J</i> in Hz)]	ν_{\max} (KBr)/cm ⁻¹	<i>m/e</i>
(5a) ^b	4.07 (1H, d, <i>J</i> _{10,11} 6.5), 4.71 (1H, dd, <i>J</i> _{11,15} 1), 4.86 (1H, d, <i>J</i> _{13,14} 1), 5.88 (1H, dd, <i>J</i> _{14,15} 6), 5.96 (1H, dd), 7.35 (8H, m)	2240, 1628, 1052, 1039	203, 68
(5b) ^d	1.64 (3H, s), 4.03 (1H, d, <i>J</i> _{10,11} 7), 4.68 (1H, dd, <i>J</i> _{11,15} 1.6), 5.62 (1H, d, <i>J</i> _{14,15} 5.8), 5.77 (1H, dd), 7.3 (8H, m)		203, 82
(5c)	1.56 (3H, s), 4.06 (1H, d, <i>J</i> _{10,11} 6.5), 4.40 (1H, d), 4.80 (1H, s), 5.42br (1H, s), 7.35 (8H, m)	2245, 1640, 1042	203, 82
(6a) ^c	1.60 (2H, m), 1.90 (2H, m), 4.09 (1H, d, <i>J</i> _{10,11} 7), 4.42 (1H, t, <i>J</i> _{11,15} 7), 4.57 (1H, d, <i>J</i> _{13,14} 7), 7.35 (8H, m)	2240, 1055	273 (<i>M</i> ⁺), 203, 70
(6b)	1.59 (3H, s), 1.60 (4H, m), 4.07 (1H, d, <i>J</i> _{10,11} 7), 4.40 (1H, t, <i>J</i> _{11,15} 7), 7.35 (8H, m)	2237, 1045	287 (<i>M</i> ⁺), 203, 84
(6d)	1.40 (3H, s), 1.60 (3H, s), 1.70br (4H, s), 3.84 (1H, s), 7.35 (8H, m)	2250, 1070	301 (<i>M</i> ⁺), 203, 98

^a 100 MHz. ^b λ_{\max} (CH₃CN) 262 (ϵ 720), 269 (1130), and 277 nm (1640). ^c λ_{\max} (CH₃CN) 267 (ϵ 487), 271 (403), and 275 nm (768).

^d Contaminated with a small amount of (1).

In this regard, it is interesting that the $k_q\tau$ values obtained from fluorescence quenching increase as the

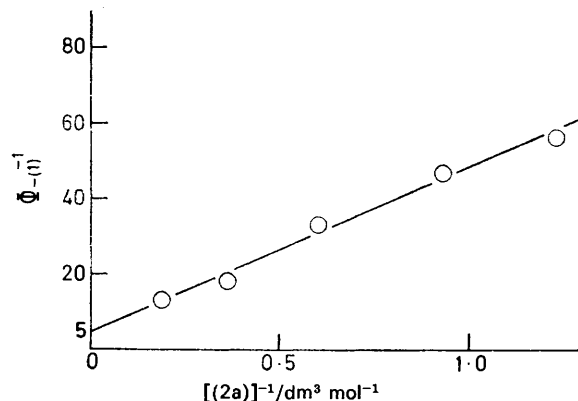


FIGURE 1 Plots of Φ_{-1}^{-1} vs. $[(2a)]^{-1}$ for degassed cyclohexane solutions, where $[(1)] = 1.3 \times 10^{-4} \text{ mol dm}^{-3}$

ionisation potentials of the quenchers decrease, indicating the charge-transfer nature of the fluorescence

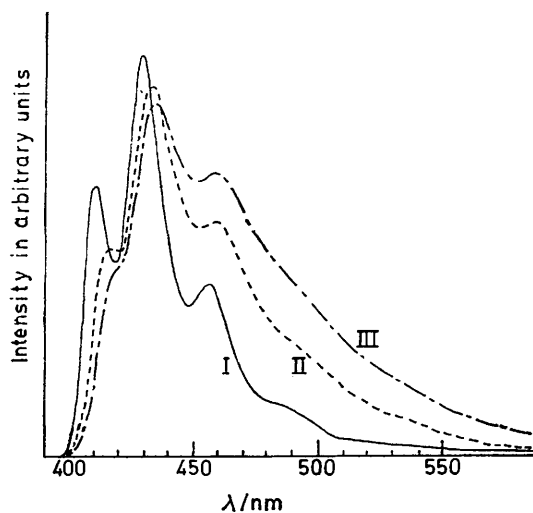


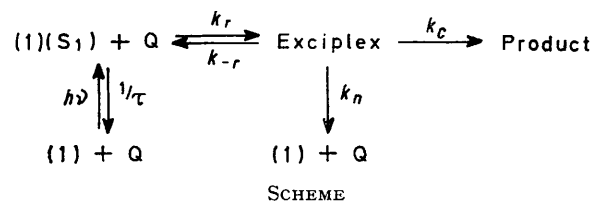
FIGURE 2 Fluorescence spectra of (1) solutions $\{[(1)] = 5 \times 10^{-4} \text{ mol dm}^{-3}\}$: I, in cyclohexane in the absence of quencher; II, in cyclohexane in the presence of 1.0 mol dm^{-3} (2d); and III, in cyclohexane in the presence of 1.0 mol dm^{-3} (4)

quenching. Moreover, fluorescence quenching by (2d) and (4) was accompanied by enhancement of the longer wavelength emission, resulting in the appearance of new weak emission at longer wavelength (Figure 2). This observation cannot be ascribed to a solvent effect of the added quenchers on the fluorescence of (1), since the fluorescence spectrum of a tetrahydrofuran solution of (1) exhibited a simple bathochromic shift accompanied by some broadening but no new emission. Appearance of a new emission provides direct evidence for the formation of exciplexes.* Thus, these observations appear to support an exciplex mechanism for both the fluorescence quenching and the photocycloaddition.

A simplified exciplex mechanism is shown in the Scheme from which rate equations (i) and (ii) are

* A charge-transfer complex is not formed in the ground state, since the u.v. spectrum of (1) in the presence of (2a-d) or (4) is identical with that in the absence of quencher.

derived. The decay pathways of $(1)(S_1)$ and exciplex involve all the unimolecular processes except the product forming path. The reversible dissociation of exciplex should be taken into account, since exciplex formation of 1-naphthonitrile-furan is known to be reversible.^{3a}



$$F_0/F = 1 + k_q\tau[Q] \quad (i)$$

$$1/\Phi_{-1} = (1 + 1/k_q\tau[Q])(1 + k_n/k_c) \quad (ii)$$

$$k_q = k_r(k_n + k_c)/(k_{-r} + k_n + k_c)$$

The value of k_q with each quencher can be calculated by estimating the life-time of excited singlet (1) as 3–4 ns, from the oxygen quenching method.¹³ On the basis of the assumption proposed by Hammond *et al.*,¹⁴ a linear relationship between ionisation potentials and logarithmic k_q values is obtained (Table 2 and Figure 3),

TABLE 2

Values of $k_q\tau$ from fluorescence quenching

Quencher	Ionisation potential (eV)	$k_q\tau/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ a}$	$10^{-9}k_q/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ b}$
(2a)	9.04 ^c	0.1 ± 0.03	0.03
(2b)	8.31 ^e	2.7 ± 0.03	0.9
(2d)	8.01 ^{c,d}	22.0	7.3
(4)	7.95 ^e	30.6	10.2

^a Air-saturated cyclohexane solution; $[(1)] = 5 \times 10^{-4} \text{ mol dm}^{-3}$. ^b The value of k_q is calculated by estimating the life-time of the excited singlet (1) as 3 ns; see ref. 13. ^c D. W. Turner, *Adv. Phys. Org. Chem.*, 1966, 4, 31. ^d Estimated value from the ionisation potential of 2,3-dimethylfuran. ^e A. D. Baker, D. Betteridge, N. R. Kemp, and R. E. Kirby, *Analyt. Chem.*, 1970, 42, 1064.

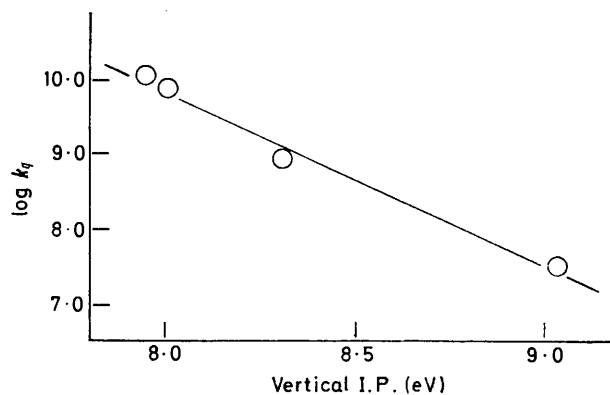


FIGURE 3 Correlation of quenching rate constants (k_q) for (1) with the vertical ionisation potentials of the quencher

again probably supporting the exciplex mechanism. A relatively high value of the limited quantum yield for

¹³ I. B. Berlman, 'Handbook of Fluorescence Spectra of Aromatic Molecules,' Academic Press, New York and London, 1965, p. 36.

¹⁴ D. A. Labianca, G. N. Taylor, and G. S. Hammond, *J. Amer. Chem. Soc.*, 1972, 94, 3679.

disappearance of (1) [$\Phi_{(1)} = 0.2$] would eliminate a triplet mechanism, since the fluorescence efficiency of (1) is reported to be higher than 0.8.¹⁵

The stereochemistry of this photocycloaddition can be discussed in terms of the intermediates. Only (4 + 4) addition took place, unlike the photoaddition of (1) with acyclic 1,3-dienes^{6b} and of anthracene with cyclopentadiene^{6c} and cycloheptatriene,⁷ which were interpreted by the sequence exciplex \rightarrow biradical \rightarrow cycloadduct.* Moreover, the photocycloadditions with (2b) and (2c) were regiospecific. Although it is uncertain whether the photoaddition of (1) with (2a—d) is

Irradiation in preparative experiments was carried out with an Eikosha PIH 300 W high-pressure mercury arc for benzene solutions (30 ml) containing (1) (0.3 g) and (2a—d) (5 ml) in a test-tube. Column chromatography was carried out on silica gel (Merck kieselgel 60). Elemental analyses and spectral data are listed in Tables 1 and 3.

Materials.—9-Cyanoanthracene (1) was prepared from anthracene-9-carbaldehyde according to the reported method and was recrystallised three times from glacial acetic acid (80% yield, m.p. 179°)¹⁶ and (2c) was prepared according to the method described in the literature.¹⁷ Commercial (2a), (2b), (2d), (3), and (4) (Tokyo Kasei) were refluxed and distilled over calcium chloride under a

TABLE 3
Elemental analyses of products
Found (%)

Product	M.p. (°C)	Found (%)			Formula	Required (%)		
		C	H	N		C	H	N
(5a)	144.5 ^{a,b}	84.1	4.85	5.15	C ₁₉ H ₁₃ NO	83.9	4.55	5.0
(5c)	165—165.5 ^{a,b}	84.2	5.3	4.9	C ₂₀ H ₁₅ NO	84.25	5.05	4.7
(6a)	175.0—175.5 ^a	83.5	5.55	5.15	C ₁₉ H ₁₅ NO	83.3	5.3	4.9
(6b)	164.5—165.5 ^a	83.6	5.95	4.9	C ₂₀ H ₁₇ NO	83.45	5.75	4.7
(6d)	160.5—161.5 ^c	83.7	6.35	4.65	C ₂₁ H ₁₉ NO	83.5	6.15	4.45

^a From methanol. ^b Decomp. ^c From methanol-benzene.

stepwise or concerted, these observations would appear to suggest a different mechanism from the biradical mechanism and to imply important effects of the exciplex-configuration on both the addition mode and orientation, such that the exciplexes of (1)—(2a—d) possess a finite sandwich type of configuration favourable to (4 + 4) addition. Such a hypothesis was previously suggested by us^{3d} and by other authors.^{5,6b}

Finally, it should be noted that (4) quenched fluorescence of (1) in a near diffusion-controlled rate *via* exciplex formation but gave no adduct. Since the pyrrole ring is well known to be more aromatic than furan, cycloaddition to pyrrole would require a higher activation energy, and this would disfavour this reaction. Thus, ionisation potentials of quenchers are important in exciplex formation, but the exciplex \rightarrow product pathway appears to depend on the chemical nature of quenchers.

EXPERIMENTAL

General.—U.v. spectra were measured with a Hitachi 124 and i.r. spectra with a Hitachi EPI-S2 spectrophotometer. N.m.r. spectra were obtained with a Hitachi-Perkin-Elmer R-24 spectrophotometer (60 MHz) and a JEOL JNM JS-100 instrument (100 MHz) for solutions in deuteriochloroform containing tetramethylsilane as internal standard. Mass spectra were recorded with a Hitachi RMU-6E instrument. Fluorescence spectra were recorded with a Hitachi MPF-2A spectrofluorometer. Analytical g.l.c. was carried out with a Shimadzu GC-2C machine equipped with a flame-ionisation detector using a column of SE-30 (5% on Shimalite W, 0.75 m) at 200°. M.p.s were measured for samples in capillaries.

* The (4 + 4) photoaddition of anthracene with acyclic dienes was suggested to be concerted.^{6a}

¹⁵ E. J. Bowen and J. Sahu, *J. Phys. Chem.*, 1959, **63**, 4; W. H. Melhuish, *ibid.*, 1961, **65**, 229.

¹⁶ L. F. Fieser and J. L. Hartwell, *J. Amer. Chem. Soc.*, 1938, **60**, 2555.

nitrogen stream prior to use. Benzene was purified as described previously¹⁸ and spectrograde cyclohexane (Nakarai Chemicals) was used without further purification.

Quantum Yields.—Cyclohexane was used as solvent and the concentration of (1) was 1.28×10^{-4} mol dm⁻³. Monochromatic light at 365 nm was isolated from a high-pressure mercury arc (450 W) by using a combined glass filter of Toshiba UV-35 and UV-D1B and the light intensity (I_0) was determined with a potassium ferrioxalate actinometer to be 3.014×10^{-7} einstein cm⁻² min⁻¹. Samples placed in an optical cell (10 × 10 × 45 mm) were thoroughly degassed by four freeze-thaw cycles under a high vacuum (<10⁻³ mmHg) and then irradiated by 365 nm light. Decrease of the absorbance at 362 nm (ϵ_{cd}) during the irradiation was monitored at appropriate time intervals (t /min). Plots of natural logarithms of ($e^{\epsilon_{cd}} - 1$) *vs.* t were linear. Quantum yields [$\Phi_{(1)}$] for the disappearance of (1) were obtained from the slopes of the lines by applying the equation $\ln(e^{\epsilon_{cd}} - 1) = -1000\epsilon_{(1)}I_0t + A$, where ϵ is the molar absorption coefficient of (1) at 362 nm (6.73×10^4 dm² mol⁻¹) and A is a constant.

Photoreaction with Furan.—After irradiation for 60 h at ambient temperature, a precipitate was filtered off to yield the photodimer (7) (10 mg, 3.3%). Column chromatography with benzene-hexane (3:1) as eluant gave (1) (70 mg, 23.3% recovered) and then 9-cyano-9,10,11,13-tetrahydro-9,10[2',5']-furananthracene (5a) (195 mg, 50%) which was recrystallised from methanol, m.p. 144.5° (decomp.). Further elution with benzene gave the dimer (7) (50 mg, 16.7%). Hydrogenation of a methanolic solution of (5a) (50 mg) over Pd-charcoal gave 9-cyano-9,10,11,13,14,15-hexahydro-9,10[2',5']-furananthracene (6a), in quantitative yield.

Photoreaction with 2-Methylfuran.—Irradiation for 40 h at 0—5° resulted in complete disappearance of the yellow colour of (1), and t.l.c. of the solution on silica gel showed the formation of a product. Removal of solvent and (2b)

¹⁷ D. M. Burness, *Org. Synth.*, Coll. Vol. IV, 1967, pp. 628 and 649.

¹⁸ C. Pac, K. Mizuno, T. Tosa, and H. Sakurai, *J.C.S. Perkin I*, 1974, 561.

in vacuo at 0° left a white solid, which contained exclusively (5b) (t.l.c. and n.m.r.). The solid gradually turned yellow, owing to formation of (1). Pd-Charcoal (ca. 10 mg) was added to the irradiated solution and then the solution was stirred under hydrogen at 0—5° for 24 h. Filtration of the catalyst and evaporation of the solvent and (2b) left a solid which was recrystallised from methanol to yield pure 9-cyano-9,10,11,13,14,15-hexahydro-13-methyl-9,10-[2',5']-furanoanthracene (6b).

Photoreaction with 3-Methylfuran.—After irradiation at ambient temperature (37 h), removal of solvent and unchanged (2c) *in vacuo* left a solid, which was fairly pure (5c) (n.m.r.). The solid was recrystallised from methanol to yield pure 9-cyano-9,10,11,13-tetrahydro-15-methyl-9,10-[2',5']-furanoanthracene (5c) (390 mg, 93%).

Photoreaction with 2,5-Dimethylfuran.—After irradiation for 20 h at 0—5°, the irradiated solution was hydrogenated over Pd-charcoal (10 mg) at 0—5° for 24 h. Filtration of Pd-charcoal and evaporation of solvent and (2d) left a white solid which was recrystallised from methanol-benzene to yield pure 9-cyano-9,10,11,13,14,15-hexahydro-11,13-dimethyl-9,10[2',5']-furanoanthracene (6d).

Photoreaction with Thiophen and 1-Methylpyrrole.—Irradiation of a benzene solution containing (1) and (3) gave the dimer (7) (280 mg, 93%). Similarly, photoreaction with (4) afforded (7) (270 mg, 90%). In both cases, t.l.c. analyses of the irradiated solutions showed only starting materials and (7) and no crossadducts.

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