

Photoreactions of Photochromic 1-(2,5-Dimethyl-3-furyl)-1-fluoren-9-ylideneethane and Related Compounds

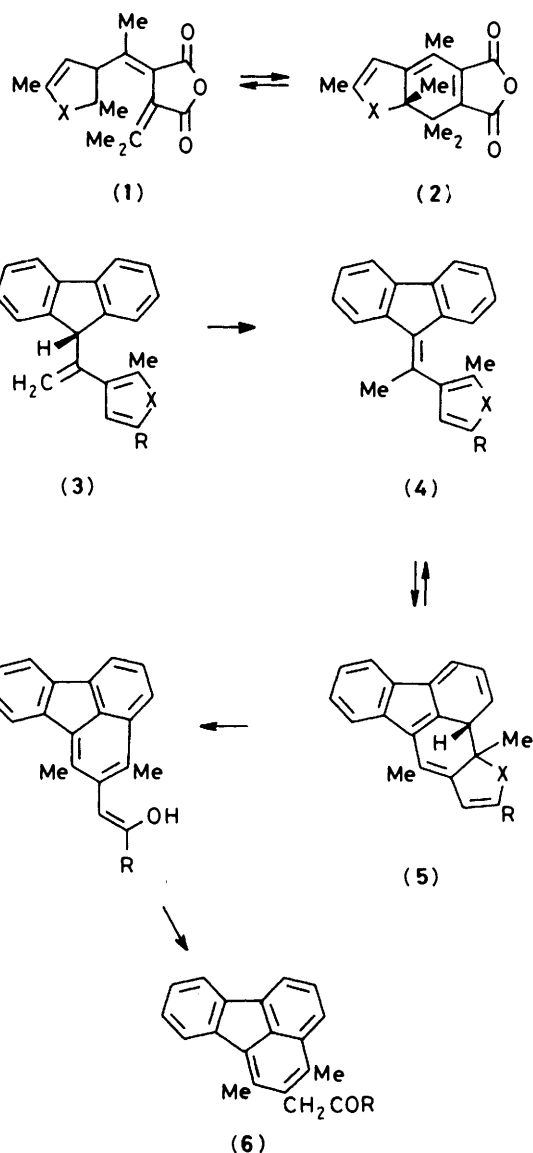
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1-(2,5-Dimethyl-3-furyl)-1-fluoren-9-ylideneethane and its 3-thienyl analogue, in the crystalline state and in poly(propylene isophthalate) glass, changed from pale yellow to deep blue on irradiation at 366 nm; this change is reversed on exposure to white light. In solution, the title compound was photorearranged quantitatively into 1,3-dimethylfluoranthen-2-ylpropan-2-one on exposure to u.v. light. The photochromism and photoreactions of related compounds are described.

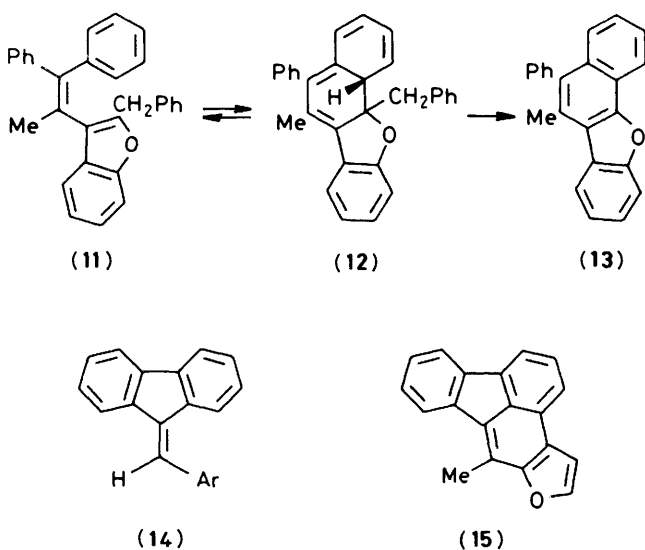
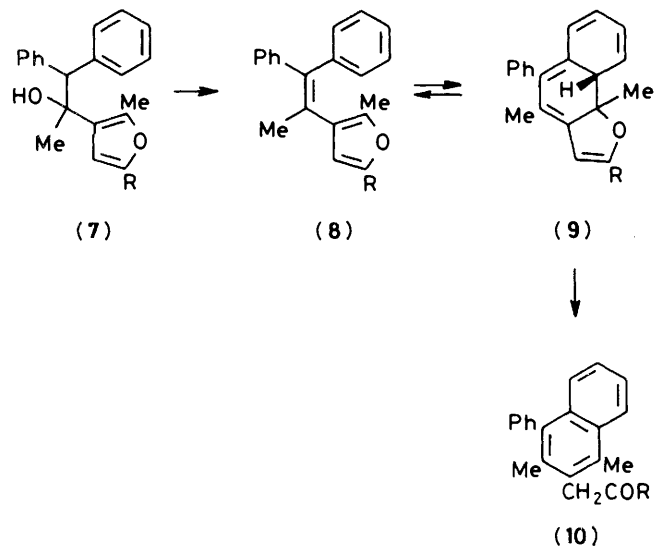
In the preceding paper,¹ we showed that the photochromic hydrocarbon, 2-fluoren-9-ylidene-4-methylpent-3-ene photocyclises to give a red intermediate which undergoes 1,7- and 1,9-hydrogen shifts. While the fatigue-resistant photochromic 2-[1-(2,5-dimethyl-3-furyl)- and -(3-thienyl)ethylidene]-3-isopropylidenesuccinic anhydrides (1; X = O or S) undergo ring-closure on irradiation (366 nm) to give the thermally stable red 7,7a-dihydrobenzo-furan and -thiophene derivatives (2; X = O or S) respectively,^{2,3} they are not suitable for some applications because of their susceptibility to hydrolysis. It was of interest to establish whether the fluorenylidene derivatives (4; X = O, R = H or Me) and (4; X = S, R = Me), and the diphenylmethylene compounds (8; R = H or Me), without a functional group, would be photochromic, and to investigate their photochemical stability. It was considered that the coloured forms of these compounds might not undergo hydrogen shift reactions because of the distortions caused by the annelated five-membered heterocyclic rings. These derivatives were photochromic and did not undergo thermal or photochemical hydrogen shifts; however, they underwent a facile photocleavage of the heterocyclic rings, providing a method of preparing aryl substituted propan-2-ones, which are difficult to synthesise by alternative procedures.

Fluoren-9-ylmagnesium bromide¹ reacted with 3-acetyl-2,5-dimethylfuran, 3-acetyl-2-methylfuran, and 3-acetyl-2,5-dimethylthiophene to give the alkenes (3; X = O, R = Me) (3; X = O, R = H), and (3; X = S, R = Me), respectively, which were then isomerised to the 3-furyl- and 3-thienyl-ethylidene derivatives of fluorene (4; X = O, R = Me), (4; X = O, R = H), and (4; X = S, R = Me) by treatment with ethanolic potassium hydroxide. The three fluorene derivatives, (4; X = O, R = H), (4; X = O, R = Me), and (4; X = S, R = Me), as crystals or dissolved in poly(propylene isophthalate) glass, changed from pale yellow to deep blue on irradiation at 366 nm. The colour change was reversed with white light and the blue colour faded when the crystals or glass were kept in the dark at ambient temperature. The colour changes could be carried out repeatedly on filter papers impregnated with the photochromic compounds, without apparent degradation or loss of sensitivity. The photochromic properties are lost when the crystals are moistened with or dissolved in common organic solvents, e.g. toluene, diethyl ether. We believe that the blue colour is due to the intermediates (5; X = O, R = H), (5; X = O, R = Me), and (5; X = S, R = Me). The quantitative photorearrangement of compound (4; X = O, R = Me) in ethanol into the ketone (6; R = Me) is indicative of the intermediacy of the coloured compound (5; X = O, R = Me). Ethanol facilitates the cleavage of the C-O bond in compound (5; X = O, R = Me).



When the photoreaction is carried out in toluene, some photodegradation occurs. On prolonged irradiation (366 nm) of compound (4; X = O, R = H) in ethanol or toluene, the aldehyde (6; R = H) is formed; when the thiophene (4; X = S, R = Me) in ethanol or toluene is irradiated at 366 nm, only black intractable oils are obtained.

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The photochromism and photoreactions of the related compounds 2-(2-methyl-3-furyl)-1,1-diphenylprop-1-ene (**8**; R = H), its 5-methyl derivative (**8**; R = Me), and 2-(2-benzyl-3-benzo[*b*]furyl)-1,1-diphenylprop-1-ene (**11**) were investigated. The three alkenes were photochromic in the crystal and in poly(propylene isophthalate) glass, but not in common organic solvents, changing reversibly from colourless to orange-red. While irradiation (366 nm) of compound (**8**; R = H) in ethanol or toluene gave a complex mixture of products in which the aldehyde (**10**; R = H) could not be detected, a similar photoreaction of the methyl derivative (**8**; R = Me) gave the ketone (**10**; R = Me) in quantitative yield.

These results indicate that the 5-methyl-3-furyl derivatives (**4**; X = O) and (**8**; R = Me) can be used to synthesise conveniently and quantitatively the methyl ketones (**6**; R = Me) and (**10**; R = Me). The photorearrangement of 2-(2-benzyl-3-benzo[*b*]furyl)-1,1-diphenylprop-1-ene (**11**) follows a different course; on irradiation (366 nm), it cyclises and eliminates toluene to give 6-methyl-5-phenylbenzo[*b*]naphtho[2,1-*d*]furan (**13**).

The thermochromic arylidene fluorenes (**14**) are not photochromic and do not undergo photocyclisation.⁴ In this study, it

Table. N.m.r. data for fluorenyl, fluorenylidene, diphenylmethyl, and diphenylmethylene compounds^a

Compound	δ /p.p.m.				
	2-Me	5-R	4-H	9-H	=CH ₂
(3; X = O, R = H)	2.27	6.80d	5.28d	4.70	5.17d 5.42d
(3; X = O, R = Me)	1.98	2.20	4.98	4.60	5.05d 5.24d
(3; X = S, R = Me)	2.20	2.28	5.92	4.72	5.00d 5.27d
	2-Me	5-R	4-H	=CMe	
(4; X = O, R = H)	2.08	7.01	6.38d	2.63	
(4; X = O, R = Me)	2.03	2.34	5.97	2.62	
(4; X = S, R = Me)	2.15	2.48	6.54	2.63	
(8; R = H)	1.99	7.21d	6.30d	1.72	
(8; R = Me)	2.00	2.23	5.92	1.70	
	2-Me	5-R	4-H	MeCOH	1'-H ^b
(7; R = H)	1.97	6.48d	6.04d	1.43	4.04
(7; R = Me)	1.91	2.12	5.63	1.40	4.00

^a d = Doublet (*J* 2 Hz).

has been shown that 9-[1-(2-furyl)ethylidene]fluorene (**15**) is not photochromic and is photodegraded on prolonged irradiation with u.v. light.

Experimental

U.v. spectra were measured in hexane or in poly(propylene isophthalate) glass (unless stated otherwise) on a Unicam SP1700B spectrometer; n.m.r. spectra were obtained with a Perkin-Elmer R32 (90 MHz) spectrometer (tetramethylsilane as internal standard and deuteriochloroform as solvent). Photo-reactions were carried out with 50–100 mg of reactant in solution (*ca.* 3 cm³) in a quartz cuvette (10-cm pathlength), and exposed to irradiation (366 nm) from a 250 W mercury-discharge lamp (type ME/D Thorn Lighting) with a filter (type OX1, Chance, Pilkington) focussed on to the solution, which was stirred by a magnetic Teflon-coated bar. Chromatography was carried out on Spence Type H alumina with petroleum (light petroleum, fraction of b.p. 60–80 °C) as eluant. Solutions were dried over anhydrous MgSO₄. Reagents and solvents were purified before use. Ether refers to diethyl ether. N.m.r. results for compounds (**3**), (**4**), (**7**), and (**8**) are given in the Table.

Poly(propylene isophthalate) glass was prepared by Martin T. Goosey, Plessey Research (Caswell) Ltd. by heating dimethyl isophthalate (15.5 g) with propane-1,2-diol (14.4 g), calcium acetate (25 mg), and antimony trioxide (6 mg) at 210 °C for 10 h, and then at 270 °C under vacuum for 13 h. The photochromic compound (10% w/w) was dissolved in the molten glass (m.p. 80–87 °C) which was sandwiched between glass microscope slides and allowed to cool. The absorption spectra of the coloured forms of compounds (**4**; X = O, R = Me), (**8**; R = H), (**8**; R = Me), and (**11**), measured for thin films in poly(propylene isophthalate) (10% w/w) after irradiation (366 nm), showed maxima at 574, 455, 460, and 458 nm and minima at 506, 392, 406, and 415 nm, respectively.

1-(2,5-Dimethyl-3-furyl)-1-fluorene-9-ylideneethane (**4**; X = O, R = Me).—3-Acetyl-2,5-dimethylfuran² (17.25 g, 0.125 mol) in xylene (50 cm³) was added to fluorene-9-ylmagnesium bromide [prepared from fluorene (20.75 g, 0.125 mol and *ca.* 2.5-fold excess of ethylmagnesium bromide) in xylene (150 cm³). The reaction mixture was heated for 2 h at 125 °C and poured onto ice and dilute hydrochloric acid. The organic layer was washed

with water, dried, filtered, and the solvent was removed. The residual oil (29 g) was 1-(2,5-dimethyl-3-furyl)-1-fluoren-9-yl-ethene (**3**; X = O, R = Me) containing a small amount of unchanged ketone and fluorene. The ethene (**3**; X = O, R = Me) (**8** g) was boiled (0.5 h) with 10% ethanolic KOH (100 cm³). The solution was acidified with hydrochloric acid, ethanol was removed, and the mixture extracted with ether. The organic layer was dried, the ether evaporated, and the residue was chromatographed. 1-(2,5-Dimethyl-3-furyl)-1-fluoren-9-ylidene-ethane (**4**; X = O, R = Me) (2.26 g) was obtained as pale yellow prisms from ethanol, m.p. 248 °C (Found: C, 87.7; H, 6.2. C₂₁H₁₈O requires C, 88.1; H, 6.3%); λ_{\max} . 234, 250, 259, 280, and 331 nm (log ϵ 4.66, 4.54, 4.48, 4.13, and 4.04).

1,3-Dimethylfluoranthene-2-ylpropan-2-one (**6**; R = Me).—Irradiation of the alkene (**4**; X = O, R = Me) in ethanol gave the ketone (**6**; R = Me) in quantitative yield, as yellow needles from ethanol, m.p. 148 °C (Found: C, 88.1; H, 6.3%); ν_{\max} . 1725s cm⁻¹(C=O); λ_{\max} . 221, 247, 268, 283, 294, 332, 350, and 368 nm (log ϵ 4.50, 4.17, 4.61, 4.24, 4.44, 3.87, 3.92, and 3.89); δ 2.19 (3 H, s, CH₃CO), 2.63 and 2.72 (6 H, both 1- and 3-Me), 4.01 (2 H, s, CH₂CO), and 7.20—8.05 (7 H, m, arom.).

1-Fluoren-9-ylidene-1-(2-methyl-3-furyl)ethane (**4**; X = O, R = H).—3-Acetyl-2-methylfuran (12.4 g, 0.1 mol) and fluoren-9-ylmagnesium bromide (0.1 mol) in xylene, gave 1-fluoren-9-yl-1-(2-methyl-3-furyl)ethene (**3**; X = O, R = H) which underwent a base-catalysed isomerisation to 1-fluoren-9-ylidene-1-(2-methyl-3-furyl)ethane (**4**; X = O, R = H), as pale yellow needles from ethanol, m.p. 102—104 °C (Found: C, 88.0; H, 5.8. C₂₀H₁₆O requires C, 88.2; H, 5.9%); λ_{\max} . 234, 259, and 320 nm (log ϵ 4.58, 4.44, and 4.04). Irradiation of the alkene (**4**; X = O, R = H) in ethanol or toluene gave 1,3-dimethylfluoranthene-2-yl-ethanal (**6**; R = H); δ 2.65 and 2.75 (6 H, both s, 2- and 4-Me), 4.08 (2 H, d, *J* 2 Hz, CH₂), 7.95—8.10 (7 H, m, arom.), and 9.78 (1 H, t, *J* 2 Hz, CH=O).

1-(2,5-Dimethyl-3-thienyl)-1-fluoren-9-ylideneethane (**4**; X = S, R = Me).—3-Acetyl-2,5-dimethylthiophene (3.85 g, 0.025 mol) and fluoren-9-ylmagnesium bromide (0.025 mol) in xylene gave 1-fluoren-9-yl-1-(2,5-dimethyl-3-thienyl)ethene (**3**; X = S, R = Me), which was converted by ethanolic KOH into 1-(2,5-dimethyl-3-thienyl)-1-fluoren-9-ylideneethane (**4**; X = S, R = Me) as described. After purification by chromatography and recrystallisation from ethanol, the product (**4**; X = S, R = Me) was obtained as pale yellow needles, m.p. 119—120 °C (Found: C, 83.0; H, 5.9. C₂₁H₁₈S requires C, 83.4; H, 6.0%); λ_{\max} . 234, 252, and 261 nm (log ϵ 4.67, 4.55, and 4.57). On irradiation, a solution of the alkene (**4**; X = S, R = Me) in toluene became dark and developed a deep blue fluorescence. Removal of the solvent under reduced pressure left a black solid which gave a very complex n.m.r. spectrum. No photoproducts could be identified.

1-Fluoren-9-ylidene-1-(2-furyl)ethane (**15**).—2-Acetylfuran (2.75 g, 0.025 mol) was treated with fluoren-9-ylmagnesium bromide [prepared from fluorene (4.25 g, 0.025 mol) and a 2.5-fold excess of ethylmagnesium bromide in xylene (30 cm³)]. The reaction mixture was heated for 2 h and poured onto ice-hydrochloric acid. The organic layer was separated, dried, the solvent removed, and the residue chromatographed, giving 1-fluoren-9-ylidene-1-(2-furyl)ethane (**15**) (0.71 g) as a light orange oil; δ 2.51 (3 H, d, *J* 1.5 Hz, Me), 6.50—6.45 (2 H, m, arom.), 6.70 (1 H, d, *J* 4 Hz, 4-H), 7.13 (1 H, q, *J* 4, 0.6 Hz, 5-H), 7.35 (1 H, m, *J* 1.5, 0.6 Hz, 3-H), and 7.45—7.52 (6 H, m, arom.). The orange oil in toluene was irradiated for 5 days. The n.m.r.

spectrum showed the presence of starting material, a multiplicity of minor peaks with a doublet (*J* 2 Hz) at δ 2.35. The photoproduct(s) were not identified.

2-(2-Methyl-3-furyl)-1,1-diphenylprop-1-ene (**8**; R = H).—3-Acetyl-2-methylfuran (2.48 g, 0.02 mol) was added to diphenylmethyl-lithium [prepared from diphenylmethane (3.36 g, 0.02 mol) and butyl-lithium (0.02 mol) in hexane]. The mixture was boiled for 5 h and poured onto crushed ice—dilute hydrochloric acid. The organic layer was separated, washed with water, dried, and the solvent removed. The n.m.r. spectrum of the residual oil (4.75 g) showed that it contained mainly 2-(2-methyl-3-furyl)-1,1-diphenylpropan-2-ol (**7**; R = H) with small amounts of 3-acetyl-2-methylfuran and diphenylmethane. The alcohol (**7**; R = H) was dehydrated by heating with toluene-*p*-sulphonic acid in toluene using a Dean and Stark apparatus to remove any water. The product was chromatographed. One fraction gave the propene (**8**; R = H) which was crystallised from methanol, giving colourless prisms, m.p. 83 °C (Found: C, 88.1; H, 6.6. C₂₀H₁₈O requires C, 87.6; H, 6.6%); λ_{\max} . 208 nm (log ϵ 4.58).

The alkene (**8**; R = H) in toluene was irradiated for 3 days. The solvent was removed and replaced by CDCl₃ (0.4 cm³). The n.m.r. spectrum showed only the starting compound. In a second experiment, the alkene (**8**; R = H) in ethanol was irradiated for 7 days. The ethanol was removed and the n.m.r. spectrum of the residual oil showed the presence of starting material and a multiplicity of minor peaks with no low absorption characteristic of the aldehyde (**10**; R = H).

2-(2,5-Dimethyl-3-furyl)-1,1-diphenylprop-1-ene (**8**; R = Me).—The reaction of diphenylmethyl-lithium [prepared from diphenylmethane (3.36 g, 0.02 mol) and butyl-lithium (0.02 mol) in hexane] and 3-acetyl-2,5-dimethylfuran gave 2-(2,5-dimethyl-3-furyl)-1,1-diphenylpropan-2-ol (**7**; R = Me) with small amounts of starting ketone and diphenylmethane. The impure alcohol (**7**; R = Me) was dehydrated by heating with toluene-*p*-sulphonic acid in toluene. Chromatography of the product gave the propene (**8**; R = Me) as pale yellow plates from ethanol, m.p. 124—125 °C (Found: C, 87.6; H, 7.0. C₂₁H₂₀O requires C, 87.5; H, 7.0%); λ_{\max} . 209 nm (log ϵ 4.51).

Irradiation of the prop-1-ene (**8**; R = Me) in toluene gave a quantitative yield of 1,3-dimethyl-4-phenyl-2-naphthylpropan-2-one (**10**; R = Me) as colourless needles from methanol, m.p. 95—96 °C (Found: C, 87.8; H, 7.0. C₂₁H₂₀O requires C, 87.5; H, 7.0%); ν_{\max} . 1730s cm⁻¹(C=O); λ_{\max} . 238 and 290 nm (log ϵ 4.72 and 3.85); δ 2.08 (6 H, s, 1- and 3-Me), 2.60 (3 H, s, CH₃CO), 3.94 (2 H, s, CH₂CO), and 7.10—7.50 and 7.9—8.1 (9 H, m, arom.).

2-(2-Benzyl-3-benzo[*b*]furyl)-1,1-diphenylprop-1-ene (**11**).—3-Acetyl-2-benzylbenzofuran (5 g, 0.02 mol) was treated with diphenylmethyl-lithium [prepared from diphenylmethane (3.36 g, 0.02 mol) and butyl-lithium (0.02 mol) hexane]. Work-up as before gave 2-(2-benzyl-3-benzo[*b*]furyl)-1,1-diphenylpropan-2-ol which was dehydrated using toluene-*p*-sulphonic acid in toluene to yield 2-(2-benzyl-3-benzo[*b*]furyl)-1,1-diphenylprop-1-ene (**11**). The latter was purified by chromatography and recrystallised from ethanol to give colourless prisms, m.p. 129—132 °C (Found: C, 89.9; H, 6.1. C₃₀H₂₄O required C, 89.8; H, 6.0%); λ_{\max} . 210 nm (log ϵ 4.65); δ 2.05 (3 H, s, Me), 3.58 (2 H, s, CH₂), and 6.90—7.60 (19 H, m, arom.).

6-Methyl-5-phenylbenzo[*b*]naphtho[2,1-*d*]furan (**13**).—Irradiation of the alkene (**11**) in toluene or ethanol gave 6-methyl-5-phenylbenzo[*b*]naphtho[2,1-*d*]furan (**13**) as colourless needles from ethanol m.p. 164—165 °C (Found: C, 89.1; H, 5.3. C₂₃H₁₆O requires C, 89.6; H, 5.2%); λ_{\max} . 256, 265, and 290 nm

(log ϵ 4.63, 4.79, and 4.25); δ 2.70 (3 H, s, Me) and 6.95—7.65 (13 H, m, arom.).

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