Synthesis of Phenanthro[9,10-*b*]furans by the Photolysis of Dihydro-furobenzodioxins [1]

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The synthesis of some phenanthro[9,10-*b*]furans by the photolysis of 3a,9a-dihydrofuro[2,3-*b*][1,4]benzodioxins in alcoholic solution is described. This method can be used to overcome factors which prevent photocyclisation in the parent furans.

Two main approaches previously have been adopted for the synthesis of phenanthro[9,10-b]furans (1). The first involves the use of a preformed phenanthrene unit to which the furan ring is added at the 9,10-position, and was used by Japp and Klingemann [2] to synthesise 2-methylphenanthro[9,10-b]furan (1b) from 9,10-phenanthroquinone and acetone. Much more recently this quinone has been treated [3,4] with benzylidenetriphenylphosphorane to give 2,3-dihydro-2,3-diphenylphenanthro[9,10-b]furan, which can be oxidised [3] with N-bromosuccinimide to the furan (1f). The utilisation of a photochemical route, an oxidative dehydrocyclisation of 2,3-diphenylfuran, to synthesise phenanthro-[9,10-b]furan (1a) has been exploited.[5] This approach to the synthesis of phenanthrene rings has obvious attractions but current theory [6] has pointed out that while the parent compound (1a) can be produced by this route the method fails when applied to some aryl-substituted 2,3-diphenylfurans. Previously we have demonstrated [7] that there are ways of circumventing such problems; in particular while the direct photolysis of tetracyclone did not afford the phenanthrocyclopentenone (2), the photolysis of the adduct (3) gave an excellent yield of the phenanthrene. The success of this approach prompted an extension to the synthesis of phenanthro[9,10-b]furans.

The synthesis of the adducts (4) for the study is described in the preceding paper.[8] All the adducts exhibited either a strong absorption in the u.v. at 290 nm or else showed a long tail into that region and so Pyrex-filtered light was utilised for the irradiation of the alcoholic suspensions of the sparingly soluble adducts. Irradiation of adduct (4a) could be followed either by its slow dissolution or (more profitably) by t.l.c., which

[1] Preliminary communication, D. T. Anderson and W. M. Horspool, *Chem. Comm.*, 1971, 615.

[2] F. R. Japp and F. Klingemann, *Ber.*, 1888, **21**, 2932.

[3] W. W. Sullivan, D. Ullman, and H. Shechter, *Tetrahedron Letters*, 1969, 457.

[4] H. J. Bestmann and H. J. Lang, *Tetrahedron Letters*, 1969, 2101.

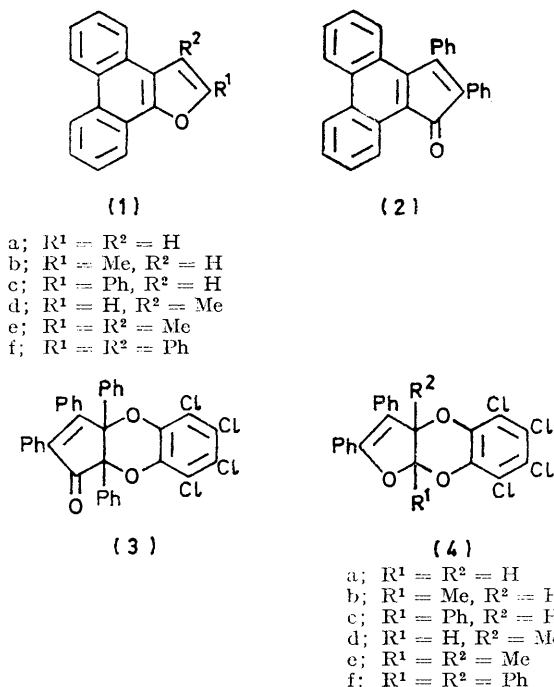[5] A. Padwa and R. Hartman, *J. Amer. Chem. Soc.*, 1966, **88**, 3759.

[6] W. H. Laarhoven, T. J. M. M. Cuppen, and R. J. F. Nivard, *Rec. Trav. chim.*, 1968, **87**, 687.

[7] W. M. Horspool, *J. Chem. Soc.* (C), 1971, 400; *Chem. Comm.*, 1969, 467.

[8] D. T. Anderson and W. M. Horspool, preceding paper.

showed, after a few hours, the presence of a u.v.-fluorescent spot moving faster than the starting material. This material was isolated by chromatography over alumina and had m.p. and i.r. data consistent with phenanthro-[9,10-*b*]furan.[5] The fact that a phenanthrene ring had

(1)

a; $R^1 = R^2 = H$
b; $R^1 = Me$, $R^2 = H$
c; $R^1 = Ph$, $R^2 = H$
d; $R^1 = H$, $R^2 = Me$
e; $R^1 = R^2 = Me$
f; $R^1 = R^2 = Ph$

(2)

(3)

(4)

a; $R^1 = R^2 = H$
b; $R^1 = Me$, $R^2 = H$
c; $R^1 = Ph$, $R^2 = H$
d; $R^1 = H$, $R^2 = Me$
e; $R^1 = R^2 = Me$
f; $R^1 = R^2 = Ph$

been formed by the photolysis was confirmed by the n.m.r. spectrum, which exhibited a multiplet (2H) at τ 1·25—1·45. Such low-field absorptions are typical of the 4- and 5-protons of a phenanthrene (phenanthrene itself[9] shows τ 1·35). Little information could be obtained from the spectrum of this furan (1a) in deuteriochloroform but in [²H₆]acetone a more readily interpretable spectrum was obtained (Table). It has been assumed in the assignments that, in common with spectra of other furans,[10] the α ring hydrogen atom resonates at lower field than the β hydrogen atom. This assumption has some experimental backing from the observations that the β hydrogen atom of 2-methyl-phenanthro[9,10-*b*]furan (1b), obtained from the photolysis of adduct (4b), resonates at τ 3·22 while the α hydrogen atom of the 3-methylfuran (1d), from the photolysis of adduct (4d), gives a signal under the envelope of the phenanthrene hydrogen atoms. The details of these spectra along with those of 2,3-dimethylphenanthro-[9,10-*b*]furan (1e), from adduct (4e), are recorded in the Table.

The mechanism for the formation of these compounds is thought to parallel the route to the phenanthrocyclopentenones reported previously.[7] The outline is given in the Scheme and involves photochemical cyclisation of the *cis*-stilbene portion, yielding a dihydro-

phenanthrene. In more conventional cyclisations of *cis*-stilbene derivatives an oxidant (O_2, I_2, *etc.*) is usually necessary to effect the removal of hydrogen[11] but in the present example, where oxidants are excluded, either a second photochemical step, or a thermal reaction

TABLE

N.m.r. spectra of phenanthro[9,10-*b*]furans (1) (τ; $CDCl_3$)

Phenanthrofuran	Phenanthrene ring protons	Furan ring protons	Substituents
(1a)	1·25—1·45 (m,2H) 1·55—2·00 (m,2H) 2·20—2·50 (m,5H) 2·75 (m,1H)	Under $CHCl_3$ and phenanthrene signals	
(1a) in $(CD_3)_2CO$	1·0—1·25 (m,2H) 1·55—1·75 (m,2H) 2·15—2·40 (m,4H)	1·94 (d,1H, J 2 Hz, α-H) 2·46 (d,1H, J 2 Hz, β-H)	
(1b)	1·26—1·49 (m,2H) 1·65—2·08 (m,4H) 2·24—2·58 (m,4H)	3·22 (s,1H, β-H)	7·48 (s,3H)
(1c)	1·21—1·49 (m,2H) 1·49—2·20 (m,4H) 2·25—2·65 (m,8H)		
(1d)	1·14—1·40 (m,2H) 1·50—1·75 (m,2H) 2·24—2·50 (m,5H)	α-H under highest field phenanthrene resonance	7·40 (s,3H)
(1e)	1·15—1·55 (m,2H) 1·55—1·78 (m,2H) 2·25—2·50 (m,4H)		7·50br (s,6H)
(1f)	1·25—1·65 (m,3H) 2·25—2·83 (m,15H) Aryl singlet at 2·46		

brings about elimination of tetrachlorocatechol as indicated. Apart from our examples the utilisation of a leaving group in the aromatisation step is not well exemplified, although recently Rio and Hardy[12] have reported loss of an acetoxy-group in a manner similar to the above.

SCHEME

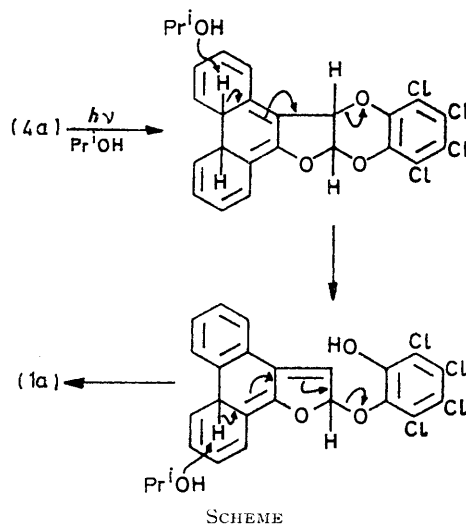We have also studied the reactions of the adducts of 2,3,5-triphenyl- and tetraphenyl-furan. This was

[9] R. C. Fahey and G. C. Graham, *J. Phys. Chem.*, 1965, **69**, 4417; T. J. Batterham, L. Tsai, and H. Ziffer, *Austral. J. Chem.*, 1964, **7**, 163; P. M. G. Barin, K. D. Bartle, and J. A. S. Smith, *Tetrahedron*, 1965, **21**, 1087.

[10] R. F. M. White in 'Physical Methods in Heterocyclic Chemistry,' ed. A. R. Katritzky, Academic Press, New York, vol. II, 1967.

[11] F. Sternitz, *Org. Photochem.*, 1967, **1**, 247.

[12] G. Rio and J.-C. Hardy, *Bull. Soc. chim. France*, 1970, 3578.

particularly important in the light of experiments [6] with 2,3,5-triphenyl- and tetraphenyl-furan [6] which demonstrated that although photodecomposition took place, no phenanthrenes could be isolated. These experiments reinforced the theoretical treatment of the photoreaction of tetraphenylfuran which predicted [6] the failure of the photocyclisation on the grounds that $\Sigma Fr^* < 1$. (The criterion for an allowed photochemical cyclisation is $\Sigma Fr^* > 1$, e.g. $\Sigma Fr^* = 1.016$ for 2,3-diphenylfuran which does photocyclise.[5,6]) Obviously the formation of a tetrachloro-1,2-benzoquinone–furan adduct greatly modifies the orbitals capable of photoexcitation. Thus, in addition to the tetrachlorocatechyl group, only an isolated electron rich cis-stilbene portion is left which might be expected to undergo photocyclisation. An analogy for such a cyclisation in a simple stilbene has not, to our knowledge, been reported, although several αα-disubstituted stilbenes have been shown to photocyclise. Nevertheless the disruption of the furan chromophore by adduct formation obviously overcomes the electronic factors which inhibit cyclisation in the parent furan, and photolysis of adducts (4c) and (4f), under the conditions described above, gave good yield of 2-phenyl- and 2,3-diphenylphenanthro[9,10-b]furans (1c) and (1f), respectively. The identity of this latter furan was proven by comparison with an authentic sample.[3] While there is no doubt that a phenanthrofuran has been synthesised both in the photochemical route and the thermal route [3] there are major discrepancies in the physical characteristics of the compound recorded by us, compared with those of the earlier study.[3] In particular there is no mention of the low-field resonances in the n.m.r. which are characteristic of 9,10-disubstituted phenanthrenes,[9] and there is a large discrepancy in the double doublet resonances (τ 4·26 and 5·08 in our study compared with 4·19 and 4·33 in the other [3]) for 2,3-dihydro-2,3-diphenylphenanthro[9,10-b]furan. The reason for this difference is not known.

There is interest in the correlation between stilbene analogues which do photocyclise and their mass spectral fragmentation pattern.[13] Rules have been suggested [13] for successful photocyclisation which modify the approach of Laarhoven et al.,[6] and propose that if photocyclisation is to occur then electron impact must give a cyclised ion of $>5\%$ abundance.

However all the adducts (4) examined by us merely fragmented by a retro-Diels–Alder process to afford the parent furan and tetrachloro-1,2-benzoquinone with no evidence for cyclodehydrogenation being a major contributing path. Such behaviour does not cast doubt on the previous work [13] but merely points to the difficulties of correlating mass spectral fragmentation with photoprocesses, particularly when there is an alternative straightforward route for molecular disruption.

[13] E. V. Blackburn, C. E. Loader, and C. J. Timmons, *J. Chem. Soc. (C)*, 1970, 163.

EXPERIMENTAL

All irradiations were carried out with alcoholic suspensions and under a positive pressure of nitrogen in a Hanovia annular apparatus with a Pyrex immersion well and a 450 W medium pressure mercury arc lamp. U.v. spectra were recorded on a Unicam SP 800, n.m.r. spectra on a Perkin-Elmer R10 60 MHz instrument, and i.r. spectra on a Perkin-Elmer 137 spectrometer. Chromatography was carried out with Spence grade H alumina; light petroleum refers to the fraction of b.p. 40—60°.

Irradiation of the Dihydrofurobenzodioxin (4a).—The benzodioxin (4a) (0·7 g) was suspended in propan-2-ol (500 ml) and irradiated for 6 h under a flow of nitrogen, used, in addition to a magnetic stirrer, to stir the suspension. At the end of the irradiation all the material had dissolved. The solvent was removed under reduced pressure and the dark crystalline material obtained was chromatographed on alumina. Benzene eluted a pale yellow solid (0·24 g, 73%) which was identified as phenanthro[9,10-b]furan (1a), m.p. 117—118° (after crystallisation from light petroleum and sublimation) (lit.,[5] m.p. 118·5—119°).

Irradiation of the Dihydrofurobenzodioxin (4b).—The adduct (4b) (0·5 g) was suspended in propan-2-ol (500 ml) and irradiated for 6·5 h. The solvent was removed and the residue was chromatographed on alumina; benzene eluted a crystalline solid. Recrystallisation from cyclohexane gave 2-methylphenanthro[9,10-b]furan (1b) (0·21 g, 88%), m.p. 127·5—128° (lit.,[2] m.p. 123—124°), $\nu_{max.}$ (Nujol) 1590, 1360, 1170, 1110, 1040, 950, 810, 760, and 730 cm^{-1}, $\lambda_{max.}$ (MeOH) 358 (ε 1560), 341 (1380), 324 (980), 308 (13,300), 295 (11,700), 280 (15,900), 269sh, 257 (68,400), 250 (50,700), and 240 nm (37,800) (Found: C, 88·2; H, 5·2. Calc. for $C_{17}H_{12}O$: C, 87·9; H, 5·2%).

Irradiation of the Dihydrofurobenzodioxin (4d).—(a) The adduct (4d) (0·5 g) was irradiated and the product worked-up as above. Benzene eluted a pale yellow oil which slowly crystallised. Recrystallisation from cyclohexane followed by vacuum sublimation gave 3-*methylphenanthro*[9,10-b]*furan* (1d) (0·19 g, 78%), m.p. 125·5—126°, $\nu_{max.}$ (Nujol) 1605, 1350, 1150, 1120, 1110, 1060, 1000, 760, and 720 cm^{-1}, $\lambda_{max.}$ (MeOH) 354 (ε 667), 338 (637), 321 (514), 305 (6970), 293 (6290), 281 (8750), 257 (29,800), 251 (26,000), 244sh, and 224 nm (17,000) (Found: C, 87·6; H, 5·1. $C_{17}H_{20}O$ requires C, 87·9; H, 5·2%)

(b) The adduct (4d) (0·5 g) was irradiated in methanol (500 ml) as described above. The same product was isolated but in 68% yield.

Irradiation of the Dihydrofurobenzodioxin (4e).—The adduct (4e) (0·44 g) was irradiated in propan-2-ol for 6·25 h. Work-up and chromatography (benzene) gave the desired product (crude yield 0·18 g, 84%). Recrystallisation from cyclohexane gave the pale yellow 2,3-*dimethylphenanthro*[9,10-b]*furan* (1e) (0·15 g, 69%), m.p. 161·5—162°, $\nu_{max.}$ (Nujol) 1620, 1590, 1360, 1190, 1120, 1080, 760, and 730 cm^{-1}, $\lambda_{max.}$ (MeOH) 362 (ε 1630), 344 (1530), 311 (12,700), 300 (11,200), 282 (15,500), 259 (54,900), and 252 nm (46,400) (Found: C, 87·7; H, 5·6. $C_{18}H_{14}O$ requires C, 87·8; H, 5·7%).

Irradiation of the Dihydrofurobenzodioxin (4c).—The adduct (4c) (0·5 g) was irradiated in propan-2-ol for 6·5 h. Work-up with benzene as solvent gave a crystalline solid. Recrystallisation from cyclohexane gave 2-*phenylphenanthro*[9,10-b]*furan* (1c) (0·25 g, 85%), m.p. 169·5—170°, $\nu_{max.}$ (Nujol) 1610, 1240, 1170, 1160, 1120, 1080, 1060, 1040, 960, 920, 820, 760, and 700 cm^{-1}, $\lambda_{max.}$ (MeOH) 361

(ε 6850), 336sh, 324 (30,000), 262 (43,800), and 227 nm (31,200) (Found: C, 89·3; H, 4·9. $C_{22}H_{14}O$ requires C, 89·8; H, 4·7%).

Irradiation of the Dihydrofurobenzodioxin (4f).—The adduct (4f) (0·5 g) was irradiated in propan-2-ol for 8 h. Work-up with benzene as solvent gave a solid (crude yield 0·24 g, 79%). Recrystallisation from benzene–light petroleum and three times from cyclohexane gave 2,3-diphenylphenanthro[9,10-*b*]furan (1f) (0·14 g, 48%), m.p. 202·5—203° (lit.,[3] m.p. 194°), $\nu_{max.}$ (Nujol) 1605, 1120, 1100, 1080, 1040, 960, 800, 770, and 710 cm^{-1}, $\lambda_{max.}$ (MeOH) 361 (ε 4990), 334sh, 325 (26,600), 263 (41,800), and 254 nm (40,800) (Found: C, 91·2; H, 4·7. Calc. for $C_{28}H_{18}O$: C, 90·8; H, 4·9%).

Attempted Photocyclisation of 2,3,5-Triphenylfuran.— The furan (1·48 g) was dissolved in cyclohexane (500 ml) containing iodine (0·064 g) and the solution was irradiated for 3·5 h, after which time the iodine colour had disappeared. T.l.c. showed the presence of two fluorescent spots, the first having the same R_F value as the starting material. Removal of the solvent under vacuum gave a brown oil whose n.m.r. spectrum did not exhibit the characteristic resonances of the phenanthrofurans. Chromatography of the oil on alumina with benzene gave only one product (0·14 g), which has yet to be identified.

Attempted Reduction of 2,3-Diphenylphenanthro[9,10-b] furan (1f).—The phenanthrofuran (0·22 g) in ethyl acetate (40 ml) containing 33% palladium–charcoal (0·04 g) was hydrogenated (1 atmos); uptake 13 ml in 0·5 h. Work-up gave a quantitative yield of unchanged starting material.

2,3-Dihydro-2,3-diphenylphenanthro[9,10-b]furan.— This compound, m.p. 145—147° (lit.,[4] m.p. 146—147°), was synthesised by the method of Sullivan *et al.*,[3] τ (CDCl$_3$) 1·25—1·75 (m, 3H), 2·25—2·55 (m, 3H), 2·60—2·85 (m, 12H), and 4·67 (dd, $\Delta\nu_{AB}$ 50 Hz, J 6 Hz, 2H).

Oxidation of 2,3-Dihydro-2,3-diphenylphenanthro[9,10-b]-furan (1f).—The dihydrofuran (0·5 g) was dissolved in carbon tetrachloride and *N*-bromosuccinimide (0·26 g) was added. The mixture was heated with a 150 W tungsten lamp for 2 h, filtered, and evaporated to dryness, and the residue was chromatographed on alumina. Benzene eluted 2,3-diphenylphenanthro[9,10-*b*]furan (0·4 g), m.p. 202·5—203° (lit.,[3] m.p. 194°) (from cyclohexane). A mixed m.p. determination with this material and that obtained from photochemical route showed no depression.