

Photochemical Cyclisation of 2-Iodostilbenes

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Evidence for the non-regiospecific nature of the photocyclisation of certain 2-iodostilbenes to phenanthrenes is presented.

THE non-oxidative photocyclisation of 2-halogenostilbene derivatives, first used by Kupchan¹ in the synthesis of aristolochic acid, has also been employed to prepare didydroaporphines^{2,3} and benz[*a*]anthracenes,⁴ with only one product being reported from each photolysis. In the case of the 2-iodostilbenes a radical intermediate has been suggested,¹ but in the case of 2-chlorostilbenes, a dihydrophenanthrene intermediate appears more likely² (see Scheme 1). The usefulness of the iodo-group in directing the cyclisation to, presumably, the iodine-bearing carbon atom, has been adequately demonstrated¹ in cases (*e.g.* nitrostilbenes) where cyclisation of the non-iodo-substituted stilbene does not take place.

We have carried out an oxidative photocyclisation of 3'-acetoxy-3,5-dimethoxystilbene in the presence of a catalytic quantity of iodine, and obtained equal amounts

of 5- and 7-acetoxy-2,4-dimethoxyphenanthrene, the products being separable by p.l.c.⁵ The accepted⁶ mechanism for this reaction appears to involve an electrocyclic reaction, giving initially the *trans*-4a,5a-dihydrophenanthrenes, followed by dehydrogenation with iodine or oxygen as oxidant.

In an endeavour to evaluate the regiospecificity of the non-oxidative photocyclisation of 2-iodostilbenes, in cases where cyclisation of the radical (formed at the site of carbon-iodine cleavage) could compete with an electrocyclic cyclisation, we irradiated 3-acetoxy-2-iodo-3',5'-dimethoxystilbene in the absence of free iodine, and obtained both the 7- (I) (80%) and the 5-acetoxyphenanthrene (II) (20%) (Scheme 2; R = OMe). If this reaction involves initial homolytic cleavage followed by cyclisation at the radical site only (as previously

¹ S. M. Kupchan and H. C. Wormser, *Tetrahedron Letters*, 1965, 359; *J. Org. Chem.*, 1965, 3792.

² M. P. Cava, S. C. Havlicek, A. Lindert, and R. J. Spangler, *J. Org. Chem.*, 1970, 175.

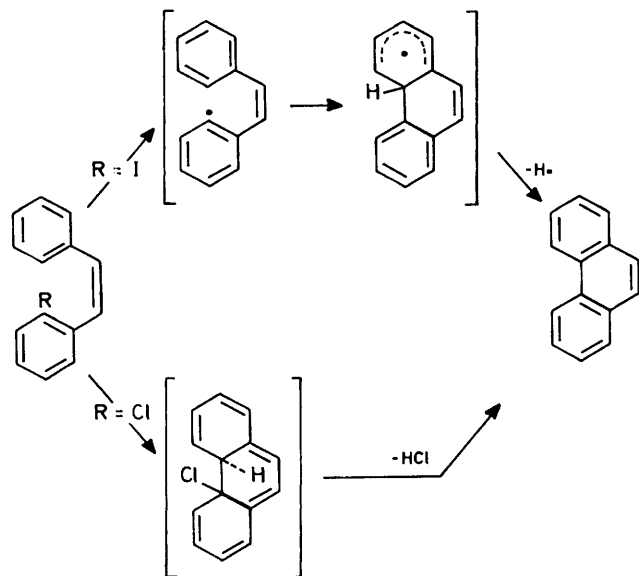
³ M. P. Cava, P. Stern, and K. Wakisaka, *Tetrahedron*, 1973, 2245.

⁴ J. Blum, F. Grauer, and E. D. Bergmann, *Tetrahedron*, 1969, 25, 3501.

⁵ R. M. Letcher and L. R. M. Nhamo, *J.C.S. Perkin I*, 1973, 1263.

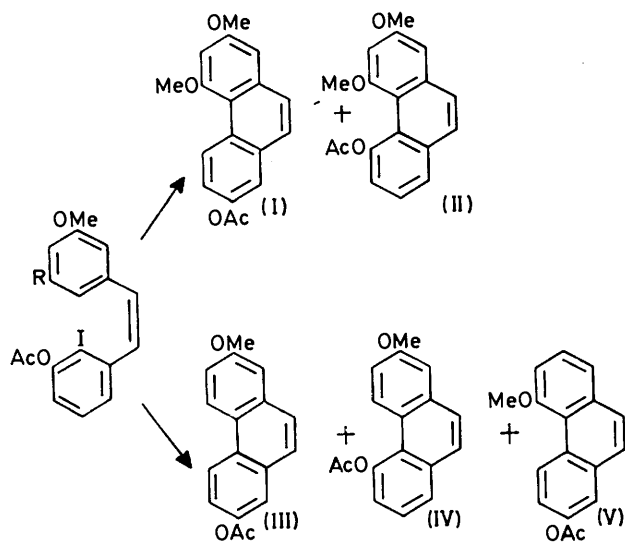
⁶ J. H. M. Cuppen and W. H. Laarhoven, *J. Amer. Chem. Soc.*, 1972, 94, 5914.

reported^{1,4}), we would expect the 5-acetoxy-derivative (II) to be the sole product. Similarly, we obtained a mixed product when 3-acetoxy-2-iodo-3'-methoxystilbene



SCHEME 1

was irradiated under non-oxidative conditions; three different products (Scheme 2; R = H) were obtained in



SCHEME 2

the ratios 1 : 3 : 1. The ¹H n.m.r. spectrum of the major product exhibited two low field proton signals (H-4 and -5), both doublets with *ortho*-coupling, showing the substance to be 2-methoxy-7-phenanthryl acetate (III). The two minor products each exhibited one low field proton signal (doublet showing *ortho*-coupling), which in one of the compounds showed a considerable change in chemical shift on conversion into the corresponding phenol, suggesting that it was 2-methoxy-5-phenanthryl acetate (IV) and the other 4-methoxy-7-phenanthryl

acetate (V). In these examples the 2-iodo-group does not promote cyclisation at the iodine-bearing carbon atom, but actually appears to inhibit this cyclisation. We observed during these photolyses of the iodo-compounds, that shortly after beginning the irradiation the colourless solution became purple-brown, no doubt due to the presence of iodine from the carbon-iodine cleavage; presumably the liberated iodine could then be employed in an oxidative photocyclisation to give the observed major products.

Conclusions from these results rely on the purity of the iodo-stilbenes and the correctness of placing the iodo-substituent in the stilbenes (or the precursor benzaldehydes). The 3-hydroxy-2-iodobenzaldehyde⁷ did indeed appear to be homogeneous and was different from the alternative 3-hydroxy-6-iodobenzaldehyde, which if it were present could give rise to the major products by coupling at the radical site. We prepared 3-hydroxy-6-iodobenzaldehyde⁸ and found it to exhibit an n.m.r. spectrum consistent only with a 1,2,4-trisubstitution pattern, confirming that the structures of the iodo-stilbenes are correct.

The foregoing results show that the iodo-group cannot be usefully employed to direct cyclisation selectively to the iodine-bearing carbon atom, unless the non-iodo-substituted stilbene itself does not undergo cyclisation; it also seems that the less hindered electrocyclic cyclisation to the 4a,5a-dihydrophenanthrene takes place in preference to the cyclisation involving the proposed^{1,4} radical. We have also observed that the reactions gave products in the same ratio in both ethanol and cyclohexane (reaction slightly faster), and that when carried out in deoxygenated ethanol or cyclohexane (refluxed and then cooled, all in a stream of oxygen-free nitrogen) the reactions took much longer, but gave the products in the same ratio, implying that all products are formed *via* a similar oxidative step.

EXPERIMENTAL

I.r. spectra were recorded for KBr discs, u.v. spectra for solutions in 95% ethanol, and n.m.r. spectra for solutions in deuteriochloroform with Me₄Si as internal standard, unless otherwise stated. P.l.c. refers to chromatography on preparative layer (1 mm thick) plates coated with Merck silica gel GF₂₅₄ developed in chloroform. Unless otherwise stated, irradiations were carried out with a 125 W high-pressure lamp 15 cm above the solution.

Photolysis of 3'-Acetoxy-3,5-dimethoxystilbenes.—A Wittig reaction of 3,5-dimethoxybenzyltriphenylphosphonium chloride and 3-acetoxybenzaldehyde with *n*-butyl-lithium gave a 1 : 1 mixture of *cis*- and *trans*-3'-acetoxy-3,5-dimethoxystilbene (55% yield) as an oil which could not be induced to crystallise even under the influence of light from a tungsten lamp filtered through Pyrex glass. Irradiation of the stilbene (1.1 g) in cyclohexane (800 cm³) (containing 0.005% iodine) was continued for 6 h, after which the phenanthrene absorption (λ 260 nm) had reached its maximum intensity. The solution was evaporated to a gum, δ 9.46 (0.5 H, d, *J* 10 Hz), 7.6—6.5 (6.5 H, m), 4.0

⁷ T. A. Henry and T. M. Sharp, *J. Chem. Soc.*, 1924, 1049.

⁸ H. H. Hodgson and E. W. Smith, *J. Chem. Soc.*, 1937, 76.

(1.5 H, s), 3.88 (3 H, s), 3.8 (1.5 H, s), 2.31 (1.5 H, s), and 2.3 (1.5 H, s) which on p.l.c. separated into two distinct bands (R_F 0.9 and 0.7), the upper of which was found to contain 2,4-dimethoxy-7-phenanthryl acetate (I) (0.38 g), m.p. 124–126°, and the lower 2,4-dimethoxy-5-phenanthryl acetate (II), obtained as a gum (0.40 g); both were identical (i.r. and n.m.r. spectra) with authentic samples.⁵

Photolysis of 3-Acetoxy-3-iodo-3',5'-dimethoxystilbene.—3-Hydroxy-2-iodobenzaldehyde, m.p. 160–162° (lit.,⁹ 159–160°), δ [(CD₃)₂CO] 10.12 (1 H, s), 9.5br (1 H, s), and 7.4–7.15 (3 H, m), on treatment overnight with acetic anhydride–pyridine gave 3-acetoxy-2-iodobenzaldehyde as an oil, δ 2.36 (3 H, s), 7.1–7.9 (3 H, m), and 10.10 (1 H, s). A Wittig reaction of the iodo-acetate and 3,5-dimethoxybenzyltriphenylphosphonium chloride gave a mixture of the *cis*- and *trans*-stilbenes as an oil (68% yield) which, after irradiation of a solution in n-hexane in a Pyrex flask with a tungsten lamp, afforded prisms of *trans*-3-acetoxy-2-iodo-3',5'-dimethoxystilbene, m.p. 130–132°, ν_{\max} 1760 and 1575 cm⁻¹, λ_{\max} 302 nm (log ϵ 4.534), δ 2.35 (3 H, s), 3.80 (6 H, s), and 6.4–7.4 (6 H, m), *m/e* 424 (M^+), 381 (base peak), 297, 255, 240, and 223 (Found: C, 50.75; H, 4.0; I, 29.8. C₁₈H₁₇IO₄ requires C, 50.95; H, 4.05; I, 30.0%). Irradiation of the *trans*-stilbene (250 mg) or a mixture of the *cis*- and *trans*-stilbenes in cyclohexane (500 cm³) for 1 h gave, after p.l.c., 2,4-dimethoxy-7-phenanthryl acetate (I) (100 mg) and 2,4-dimethoxy-5-phenanthryl acetate (II) (25 mg), both identical (i.r. and n.m.r. spectra) with authentic samples.⁵ When the irradiation was carried out in deoxygenated cyclohexane the same products were obtained and in the same proportions, but the reaction required 7 h for completion.

Photolysis of 3-Acetoxy-2-iodo-3'-methoxystilbene.—A Wittig reaction of 3-acetoxy-2-iodobenzaldehyde and 3-methoxybenzyltriphenylphosphonium chloride gave a mixture of *cis*- and *trans*-3-acetoxy-2-iodo-3'-methoxystilbene

as an oil (50%), ν_{\max} 1760, 1590, and 1570 cm⁻¹, λ_{\max} 299 nm (log ϵ 4.435), δ 2.30 (3 H, s), 3.75 (3 H, s), and 6.6–7.4 (9 H, m), *m/e* 394 (M^+), 352 (base peak), 277, 268, and 225 (Found: C, 51.85; H, 3.9; I, 32.2. C₁₇H₁₅IO₃ requires C, 51.8; H, 3.85; I, 32.2%), which could not be induced to crystallise even on irradiation with a tungsten lamp. Irradiation of the stilbene (0.5 g) in cyclohexane (800 cm³) for 6 h gave an oil whose n.m.r. spectrum showed it to consist of three phenanthrenes in the ratios 1 : 3 : 1. P.l.c. gave 4-methoxy-7-phenanthryl acetate (V) (R_F 0.9) as an oil (30 mg), λ_{\max} 250 (log ϵ 4.78) and 272 nm (4.25), δ 2.32 (3 H, s), 4.07 (3 H, s), 6.9–7.7 (7 H, m), and 9.65 (1 H, d, *J* 9.5 Hz, H-5), *m/e* 266 (M^+), 224 (base peak), and 209 [which on hydrolysis gave a phenol, δ 4.09 (3 H, s), 6.8–7.8 (7 H, m), 9.53 (1 H, d, *J* 10 Hz, H-5)]; 2-methoxy-7-phenanthryl acetate (III) (R_F 0.85) as needles (80 mg), m.p. 154–156° (methanol), λ_{\max} 253 (log ϵ 4.90), 276 (4.33), and 288.5 nm (4.26), δ 2.30 (3 H, s), 3.85 (3 H, s), 7.1–7.6 (6 H, m), 8.40 (1 H, d, *J* 10 Hz, H-4 or -5), and 8.45 (1 H, d, *J* 9.5 Hz, H-4 or -5), *m/e* 266 (M^+), 224 (base peak), 209, 195, and 181 (Found: C, 76.5; H, 5.3. C₁₇H₁₄O₃ requires C, 76.7; H, 5.3%); and 2-methoxy-5-phenanthryl acetate (IV) (R_F 0.8) as an oil (20 mg), λ_{\max} 254 (log ϵ 4.53) and 277 nm (4.07), δ 2.50 (3 H, s), 3.92 (3 H, s), 7.0–7.7 (7 H, m), and 8.96 (1 H, d, *J* 10 Hz, H-4), *m/e* 266 (M^+), 224 (base peak) [which on hydrolysis gave a phenol, δ 3.90 (3 H, s), 6.7–7.7 (7 H, m), and 9.52 (1 H, d, *J* 10 Hz, H-4)].

3-Hydroxy-6-iodobenzaldehyde.—Iodination⁸ of 3-hydroxybenzaldehyde gave needles, m.p. 129–130° (lit.,⁸ 130°), δ [(CD₃)₂CO] 3.0br (1 H, s, OH), 7.14 (1 H, dd, *J* 7 and 1.5 Hz, H-4), 7.37 (1 H, d, *J* 1.5 Hz, H-2), 7.95 (1 H, d, *J* 7 Hz, H-5), and 9.9 (1 H, s, CHO).

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⁹ G. Lock, *Monatsh.*, 1936, 325; T. A. Henry and T. M. Sharp, *J. Chem. Soc.*, 1922, 1059.