# Photoreactivity of Conjugated Bichromophoric Molecules; an Unusual Dimerization of *o*-Vinylbenzaldehyde

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Irradiation of *o*-vinylbenzaldehyde **1a** affords the oxygen-bridged dimer **7a**, presumably, through an initial $[\pi^2{}_a + \pi^4{}_s]$ rearrangement; intermediacy of spiro triene **6** is supported by deuterium labelling experiments which also reveal the reversible nature of the concurrently occurring 1,5-hydrogen shift (**1** $\rightleftarrows$ **2**).

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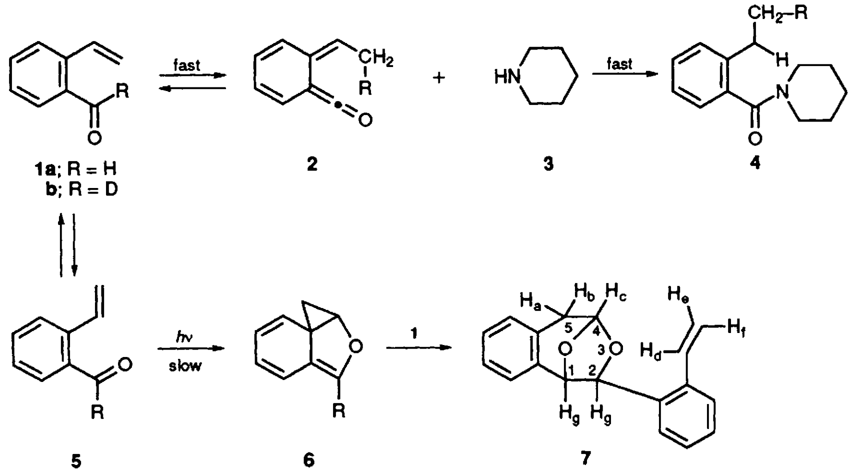
In the context of extensive investigations in the photochemistry of carbonyl compounds and styrenes,[1] it is of interest to see if some novel phototransformations ensue when these two chromophores are present in conjugation.[2] We now report that efficient conversion of *o*-vinylbenzaldehyde **1** to the oxygen-bridged compound **7** occurs on irradiation in



Scheme 1

benzene solution.†‡ This novel dimerization is rationalized in terms of an initial $[\pi^2{}_a + \pi^4{}_s]$ rearrangement[3] to the spiro compound **6** which then adds across the carbonyl group of a second molecule of **1** (Scheme 1). Further, deuterium labelling evidence§ is presented to support the intermediacy of **6** and to show that under these conditions the earlier proposed 1,5-hydrogen shift[4] also occurs but is largely reversible ($\mathbf{1} \rightleftarrows \mathbf{2}$).

Preparative photoreaction of deuteriated aldehyde **1b**¶ (R = D) with piperidine **3** afforded the amide **4b**[4] (70%) with the incorporation of one deuterium atom in the methyl group (R = D), in accord with the pathway **1** → **2** → **4**.[7] Incomplete irradiation|| of an equimolar mixture of partially deuteriated **1b** (R = D, 78%) and **3** showed acyl deuterium enrichment[4] (R = D, 84% after 20 min; 96% after 65 min) in the unreacted aldehyde, indicating an appreciable isotopic effect for the step **1** → **2**. Interestingly, similar irradiation of **1b** (R = D, 78%) alone led to depletion of acyl deuterium in the unreacted aldehyde (R = D, 46% after 75 min), with corresponding deuterium incorporation at the β-vinylic position (16% D at the *E* position and 14% D at the *Z* position). Further, formation of **7** was negligible up to this stage and $^1$H NMR spectroscopic signals corresponding to it became appreciable only after 3.45 h irradiation. These results can be readily understood in terms of the relatively fast formation of **2**, from the excited state of **1**, and its efficient capture by **3**. In the absence of **3**, almost complete reversion of **2** to **1** takes place. The lifetime of **2**, however, is sufficient to allow rotation of the methyl group which leads to the incorporation of deuterium at the β-vinylic position. Taking advantage of this fact, it is possible to distinguish between β and α (no deuterium incorporation) vinylic carbons in the finally formed dimer **7**. Preparative irradiation of 78% deuteriated **1b** gave the dimer **7b** with the following deuterium incorporation values: $H_g$ 57, 50; $H_a$ 18, $H_b$ 10, $H_e$ 21, $H_f$ 16% ($H_c$ and $H_d$ nil).** Deuterium enrichment in $H_a$ and $H_b$ but not for $H_c$, shows that the β-vinylic carbon of the starting aldehyde **1** ends up as C-5 in the product **7** in accord with the pathway shown in Scheme 1.††

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## References

1 P. J. Wagner, *Rearrangements in Ground and Excited States*, ed. P. de Mayo, Academic Press, New York, 1980, vol. 3; P. J. Wagner and B. S. Park, in *Organic Photochemistry*, ed. A. Padwa, Dekker, New York, 1991, vol. 11, p. 227; F. D. Lewis, *Adv. Photochem.*, 1986, **13**, 165; *Photoinduced Electron Transfer*, Part C, ed. M. A. Fox and M. Chanon, Elsevier, Amsterdam, 1988; F. D. Lewis, G. D. Reddy, S. Schneider and M. Gahr, *J. Am. Chem. Soc.*, 1991, **113**, 3498.

2 Such substrates do not seem to have been investigated inspite of the attention commanded by photochemistry of bifunctional molecules in general; H. Morrison, *Acc. Chem. Res.*, 1979, **12**, 383.

3 To our knowledge such a rearrangement is unprecedented with aromatic carbonyl compounds. In fact, it was discounted for *o*-phthalaldehyde in view of the involved sacrifice of aromatic resonance energy (J. C. Scaiano, M. V. Encinas and M. V. George, *J. Chem. Soc., Perkin Trans. 2,* 1980, 724). Thus, the present findings may have implications for the long raging controversy about the mechanism of the photoreactions of this substrate also; see J. Gebicki, S. Kuberski and R. Kaminski, *J. Chem. Soc., Perkin Trans. 2*, 1990, 765 and the references cited therein.

4 S. V. Kessar, A. K. S. Mankotia and G. Gujral, *J. Chem. Soc., Chem. Commun.*, 1992, 840.

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† Preparative photoreactions were carried out with a 450 W medium-pressure mercury lamp in a Pyrex immersion well using $5.0 \times 10^{-3}$–$3.0 \times 10^{-2}$ mol dm$^{-3}$ solutions in benzene. Use of acetonitrile or chloroform as solvent gave similar results. The pure dimer **7a** (m.p. 125–126 °C) was isolated in 60% yield by chromatography over silica gel. A small quantity of 3-(*o*-vinyl phenyl)isocoumarin was found in one chromatographic fraction but no other pure materials could be isolated. No reaction of **1** was observed in the absence of irradiation.

‡ Satisfactory spectral data and elemental analyses by high resolution mass spectrometry were obtained for **1b**, **4b** and **7a**. **1b**, $^1$H NMR (300 MHz, $CDCl_3$), δ −5.51 (dd, 1H, $-CH{=}C\mathit{H}_2$), 5.70 (dd, 1H, $-CH{=}C\mathit{H}_2$), 7.40–7.48 (m, 1H, ArCH), 7.50–7.61 (m, 3H, ArH) and 7.85 (dd, 1H, ArH), no signal corresponding to acyl hydrogen (observed at δ 10.28 in **1a**). **7a**, $^1$H NMR (300 MHz, $CDCl_3$), δ −2.96 (d, *J* 17.08 Hz, 1H, $H_a$) 3.24 (dd, *J* 17.12, 2.78 Hz, 1H, $H_b$), 4.94 (s, 1H, $H_g$), 5.42–5.45 (a singlet superimposed on one of the doublet of a double doublet, *J* 11.02, 1.36 Hz, 2H, $H_g$ and $H_e$), 5.70 (dd, *J* 17.23, 1.22 Hz, 1H, $H_f$), 6.20 (d, *J* 2.67 Hz, 1H, $H_c$), 6.85–6.97 (m, 1H, $H_d$), 7.15–7.40 (m, 6H, ArH) and 7.47–7.56 (m, 2H, ArH); $^{13}$C NMR spectrum off-resonance decoupled (300 MHz, $CDCl_3$), δ −35.88 (t, 5-C), 80.36, 83.38 (doublets, 1-C, 2-C), 102.45 (d, 4-C), 117.25 (t, $ArCH{=}\mathit{C}H_2$) and 134.08 (d, $Ar\mathit{C}H{=}CH_2$), the peaks at 131.05, 135.00, 137.58 and 138.35 corresponding to four quaternary carbons in the aromatic rings appeared as singlets while other aromatic carbons appeared as doublets. Negative peaks at δ 35.88 and 117.25, corresponding to out-of-phase $CH_2$ groups, were observed in the INEPT (insensitive nuclei enhanced by polarization transfer) spectrum of **7a**; its 2D-homonuclear shift correlated with the $^1$H NMR spectrum showed the coupled proton pairs as: $H_a$–$H_b$, $H_c$–$H_b$; $H_e$–$H_f$, $H_d$–$H_e$ and $H_d$–$H_f$. Appropriate $^1$H–$^{13}$C couplings were shown in a 2D $^1$H–$^{13}$C-connectivities experiment.

§ The extent of deuterium incorporation was estimated by comparing the integral value of the relevant signal to that of a clear reference signal from the same molecule (a one proton double doublet at δ 7.85 for **1**, and a two proton multiplet at δ 7.47–7.56 for **7**).

¶ For deuterium exchange of the acyl hydrogen of **1a**, it was converted into an α-siloxynitrile, b.p. 105–108 °C/4–5 mmHg, which was exposed to lithiumtetramethylpiperidide at −78 °C in tetrahydrofuran for 1 h and the reaction mixture quenched with $D_2O$.

|| Incomplete irradiations were carried out using $3.5 \times 10^{-1}$ to $4.5 \times 10^{-1}$ mol dm$^{-3}$ solutions in $CDCl_3$ in a NMR tube placed parallel to the preparative irradiation immersion well, at a distance of 1 cm.

** Slight over-all deuterium enrichment in **7b** could be a consequence of some side reaction emanating from **2**, *e.g.* its trapping with **1a**, see footnote †.

†† Formation of **7** was not quenched with oxygen dissolved in the solvent or with addition of *trans*-piperylene ($3.1 \times 10^{-3}$–$3.3 \times 10^{-1}$ mol dm$^{-3}$) suggesting involvement of a singlet or a very short-lived triplet excited state.