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Photochemistry of *o*-Vinylbenzaldehyde: Formation of a Ketene Methide Intermediate and Its Trapping with Secondary Amines

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Abstract: Irradiation of *o*-vinylbenzaldehyde (**1**) in the presence of primary and secondary amines results in N−H addition across the two chromophores of **1**, to give *o*-ethylbenzamides **6**. Photoreaction of deuterium-labeled aldehyde **15** with piperidine gave an amide (**17**) carrying a deuterium at the β-carbon of the ethyl side chain whereas use of *N*-deuteriopiperidine led to deuterium incorporation at the α-carbon (**14**). These results are explained on the basis of a 1,5 hydrogen shift in the excited state of **1** to give a ketene methide intermediate (**7**) which becomes trapped with amines. Upon 308 nm laser excitation of **1** in acetonitrile or benzene solution, a weak transient absorption having $\lambda_{\max}$ at 380 nm was observed. Irradiation of **1** isolated in an argon matrix with 313 nm light also revealed formation of an intermediate with a UV absorption maximum around 380 nm. Its IR spectrum displayed characteristic ketene stretching vibrations at 2086 and 2098 cm^{-1}, providing definitive support for the ketene methide structure **7**.

Introduction

In the context of the interest in novel transformations of bichromophoric molecules, we have reported preliminary results on the photochemistry of *o*-vinylbenzaldehyde (**1**).[1−3] This substrate combines features of two very extensively studied chromophores, i.e., benzaldehyde (**2**) and styrene (**3**).[4] Its photoreactions with amines are of particular interest since on irradiation in the presence of amines, both arylcarbonyl and arylalkenyl compounds are known to form adducts, albeit of different types. In the case of benzaldehydes, α-C−H adducts (**2** → **4**) are obtained, whereas with styrenes, linkage through the nitrogen atom is the predominant reaction course (**3** → **5**) (see Scheme 1).[5] The mechanism proposed in both cases involve electron transfer quenching of the substrate excited state by ground state amine to form an exciplex which undergoes proton transfer to yield a radical pair which, in turn, can combine, disproportionate, or diffuse apart.[5] However, in carbonyl compounds the photoreaction occurs largely from the triplet manifold, whereas a singlet reaction has been proposed for styrenes.[5]

As reported earlier,[1,2] irradiation of **1** in the presence of secondary amines did not afford products characteristic of benzaldehyde or styrene. Instead, an amidic adduct entailing N−H addition across the two chromophores of **1** was obtained in good yield (**6**; 80−86%). It was suggested that, on excitation of **1**, a 1,5 hydrogen shift occurs to give a ketene methide intermediate which becomes trapped by the amine (**1** → **7** → **6**). This proposal was supported by deuterium-labeling experiments.[1,2] Although ketene methide intermediacy is well established for some elimination and ring-opening reactions,[6−8] formation of **7** from **1** involves an unprecedented migration of an acyl hydrogen to a vinyl terminus. Therefore, additional spectroscopic evidence on this point was sought. Meanwhile, Wilson and co-workers reported that low-intensity irradiation of *o*-(diphenylvinyl)benzaldehyde (**8**) does not afford products, such as **10**, expected from a ketene methide intermediate (**9**).[9] Transient spectroscopic studies also indicated that no strongly absorbing transients were produced on such irradiation of **8**. However, under high-intensity argon laser-jet irradiation, **10** was obtained in 12−16% yield. It was argued that, in the lowest excited state of **8**, a [1,5$_s$] sigmatropic shift of hydrogen, to give **9**, is symmetry disallowed.[10] On the other hand, some of the higher excited states of **8** have a symmetry suitable for an

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(2) Kessar, S. V.; Mankotia, A. K. S. *J. Chem. Soc., Chem. Commun.* **1993**, 1828.

(3) In bichromophoric molecules novel photoreactions not manifest in individual chromophores can arise due to mutual interaction: Morrison, H. *Acc. Chem. Res.* **1979**, *12*, 383.

(4) Gilbert, A.; Baggot, J. *Essentials of Molecular Photochemistry*, 1st ed.; Blackwell Scientific Publications: Oxford, 1991; Chapters 6 and 7.

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(8) For a general discussion of the reactivity of ketene methide intermediates see: (a) Kessar, S. V. *Pure Appl. Chem.* **1987**, *59*, 381. (b) Kessar, S. V.; Singh, P.; Vohra, R.; Kaur, N. P.; Venugopal, D. *J. Org. Chem.* **1992**, *57*, 6716. (c) Kuzuya, M.; Miyake, F.; Okuda, T. *Tetrahedron Lett.* **1980**, *21*, 2185.

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(10) It was pointed out by Wilson and co-workers that while intramolecular hydrogen abstraction by vinylic carbon is known, it is rarely observed with olefins that are not conjugated to heteroatoms or constrained in small rings:[9] (a) Mawhorter, L. G.; Carlson, S. E.; Bedont, R. A. *J. Org. Chem.* **1979**, *44*, 3698. (b) McCullough, J. J. *Acc. Chem. Res.* **1980**, *13*, 270. (c) Hornback, J. M.; Barrows, R. D. *J. Org. Chem.* **1982**, *47*, 4285.

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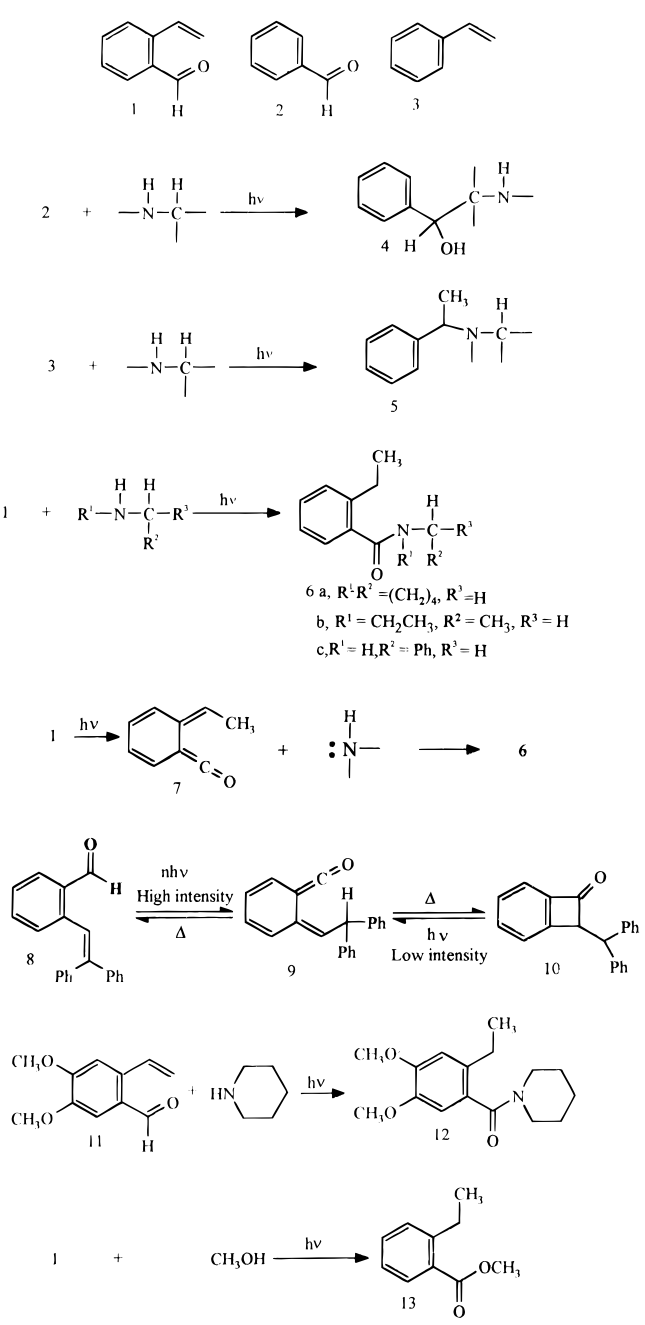
Scheme 1



allowed [$1,5_s$] sigmatropic shift, and this course is probably followed under high-intensity irradiation conditions.[9] In this context, our results on the photochemistry of **1** are even more interesting, and are now discussed in detail along with additional flash photolysis and matrix isolation evidence.

Results and Discussion

Preparative Experiments. Irradiation of an equimolar solution of aldehyde **1** and piperidine (0.0034 M) in acetonitrile with Pyrex-filtered UV light from a medium-pressure mercury lamp gave the amide **6a** in 85% isolated yield. Similarly, amides **6b** (86%) and **6c** (85%) were obtained from reaction of **1** with diethylamine and benzylamine, respectively. Photolysis of dimethoxy aldehyde **11** in the presence of piperidine produced the amide **12** (80%). Irradiation of an equimolar solution of **1** and methanol in acetonitrile did not afford the corresponding methanol adduct **13**. However, when methanol was used in 10 M excess or as a solvent, the ester **13** was obtained in low yield (30%). Efforts to trap the proposed intermediate **7** with added dienophiles were unsuccessful. Thus, from photolysis of a solution of **1** in acetonitrile containing excess (~10 M) cyclohexene, methyl acrylate, acrylonitrile, dimethyl fumarate, or maleic anhydride, no adducts could be isolated.[11]

Quantum Yields. The efficiency of the reaction of **1** with amines was investigated by measuring quantum yields for disappearance of **1**. The quantum yield for disappearance of **1** in the presence of an equimolar concentration (0.0034 M) of piperidine in acetonitrile was found to be ~0.06. According to the proposed reaction path, this quantum yield should be dependent on the formation of **7** as well as on its trapping with the added amine. The quantum yield did, in fact, increase with increasing amine concentration ($\phi \approx 0.17$ at 0.1 M piperidine) but not in a linear manner. The standard double reciprocal plot of quantum yield vs amine concentration showed a downward curvature which was irregular and not easily amenable to kinetic analysis.[12] A similar dependence on amine concentration was observed in decay of the transient **7** generated by laser flash photolysis (vide infra).

Photoaddition of amines to **1** was not appreciably sensitive to solvent polarity, and disappearance quantum yields in benzene were similar to those obtained in acetonitrile. Addition of triplet quenchers (0.0034 M) such as *trans*-piperylene or cyclohexa-1,3-diene did not depress the quantum yield. Similarly, when prior nitrogen purging of the photolysate was omitted, the oxygen, dissolved in the solvent under air-saturated conditions, had no adverse effect on the reaction efficiency. These experiments suggest involvement of a singlet or a very short lived triplet excited state.

Deuterium-Labeling Studies. Irradiation of an equimolar mixture of **1** and *N*-deuteriopiperidine afforded an amide, the ^{1}H NMR spectrum of which revealed deuterium incorporation at the α-carbon of the side chain (**14**). On the other hand, photoreaction of deuterium-labeled aldehyde **15** with piperidine gave an amide (**17**) carrying a β-deuterium atom in the side chain. These results are in conformity with ketene methide intermediacy as shown in Scheme 2. Evidence for an isotopic effect in the hydrogen transfer step, leading to the intermediate **7**, could be obtained from photolysis of partially deuterated *o*-vinylbenzaldehyde. Thus, irradiation of a mixture of **15** (78%) and **1** (22%) in the presence of an equimolar quantity of piperidine revealed, by ^{1}H NMR spectral analysis,[13] acyl deuterium enrichment in the recovered *o*-vinylbenzaldehyde (84% **15** after 20 min and 96% **15** after 65 min). It is clear that, under these conditions, **15** is consumed at a slower rate than **1** ($k_5 > k_6$). Interestingly, irradiation of partially deuterated aldehyde in the absence of amine led to depletion of the acyl deuterium. Thus, when a mixture of **15** (78%) and **1** (22%) was irradiated for 75 min, the ^{1}H NMR spectrum of the recovered aldehyde showed the presence of 46% deuterium and 54% protium at the acyl position. The deuterium lost from the acyl carbon was incorporated into the side chain by formation of **18** (~16%) + **19** (~14%). These results can be understood in terms of reversion of **16** to **15** or, after rotation about the C−C single bond, to **18** and **19**. The latter process results in replacement of the acyl deuterium of **15** with protium from the β-carbon of the side chain. It seems that in the presence of added piperidine this reversion is suppressed to a large extent (k_4[amine] $\gg k_{1-3}$).

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(11) On irradiation of **1** in acetonitrile, without any additives, slow dimerization of **1** was observed (refs 1 and 2).

(12) For a similar observation in photoreactions of carbonyl compounds with amines see: Parola, A. H.; Rose, A. W.; Cohen, S. G. *J. Am. Chem. Soc.* **1975**, *97*, 6202.

(13) In experiments with deuterated substrate **15**, the extent of acyl deuterium incorporation was estimated from the ratio of the acyl hydrogen signal at δ 10.28 to an aryl proton signal at δ 7.85 in the ^{1}H NMR spectrum recorded on a 300 MHz Bruker instrument.

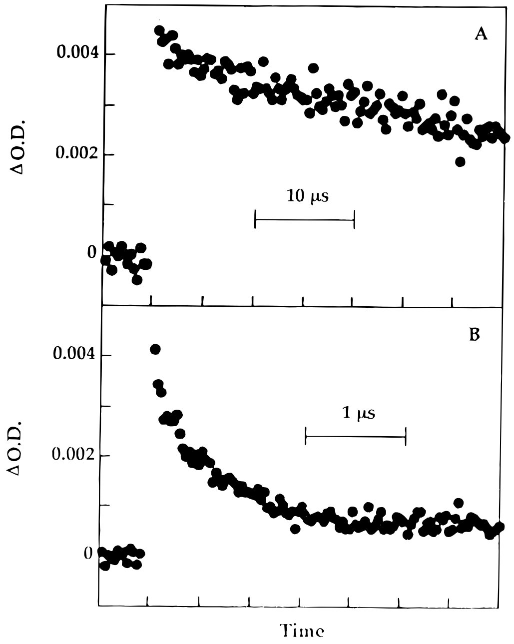
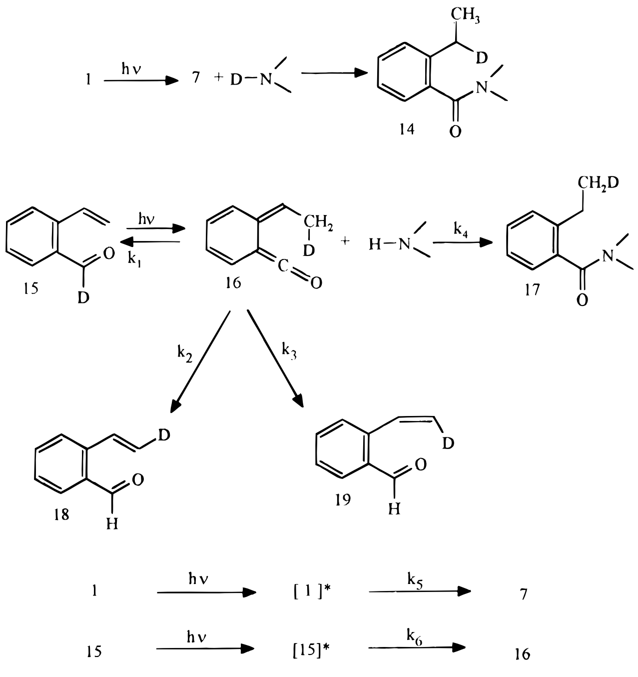


Figure 1. Transient decay traces (monitored at 380 nm) recorded upon 308 nm laser excitation of *o*-vinylbenzaldehyde in acetonitrile solution in the absence (A) and in the presence (B) of piperidine (0.1 M).

Scheme 2



Laser Flash Photolysis and Matrix Isolation. Upon 308 nm laser excitation of **1** in acetonitrile or benzene solution, a weak transient absorption (τ > 100 μs) having λ_{max} at 380 nm was observed (Figures 1 and 2). Neither the decay nor the yield of this transient was affected by oxygen. This absorption was tentatively assigned to ketene methide **7**. The electronic spectrum generated for this intermediate through MOPAC/ZINDO calculations showed a single absorption band, in the range 300−700 nm, with a maximum at 390 (Figure 2, inset), in good agreement with experimental observation.

Amines were found to effectively quench the 380 nm transient (Figure 1). Quenching rate constants for piperidine showed a non-first-order dependence on amine concentration (Figure 3) in agreement with the quantum yield studies (vide supra).

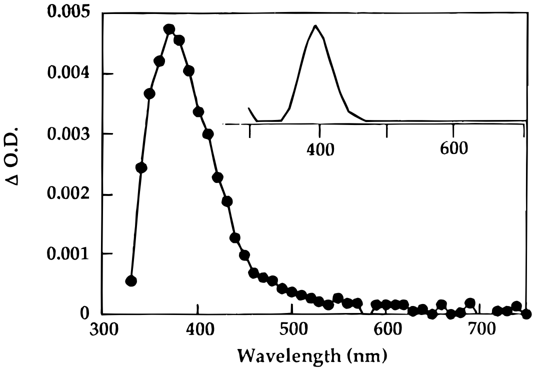


Figure 2. Transient absorption spectrum recorded immediately after 308 nm laser excitation of *o*-vinylbenzaldehyde in acetonitrile solution. Inset: calculated electronic spectrum for an intermediate ketene.

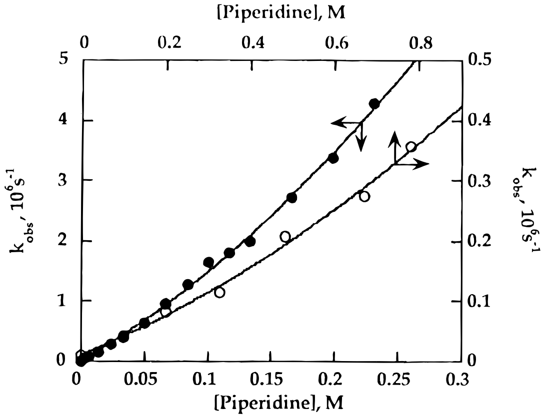


Figure 3. Observed transient decay constant monitored at 380 nm in acetonitrile (●) and methanol (○) solutions as a function of piperidine concentration.

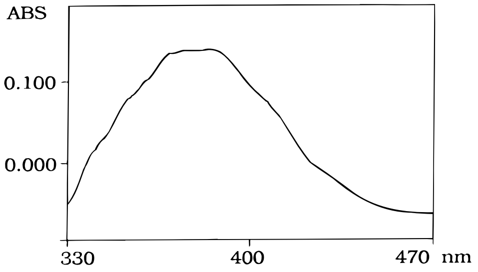


Figure 4. Difference electronic absorption spectrum of *o*-vinylbenzaldehyde isolated in an argon matrix, obtained by subtraction of the spectrum recorded before irradiation from the spectrum recorded after irradiation for 180 min through a 313 nm interference filter.

Irradiation of **1** isolated in an argon matrix (10 K) with 313 nm light revealed the formation of an intermediate with a UV absorption maximum around 380 nm (Figure 4). Its IR spectrum displayed characteristic ketene stretching vibrations at 2086 and 2098 cm^{-1}, providing definitive support for the proposed intermediate **7** (Figure 5). The UV and IR data obtained in the present work are similar to those reported for ketene methide intermediate **21** (λ_{max} = 390 nm, $\nu_{C=C=O}$ = 2075−2115 cm^{-1}) formed on matrix isolation or flash photolysis of benzocyclobutenone (**20**).[6,7] Generated in an argon matrix, **7** undergoes secondary photochemical reaction with 365 nm light to form 2-methylbenzocyclobutenone (**22**) ($\nu_{C=O}$ = 1776 and 1811 cm^{-1}) (Scheme 3).

Formation and Reactivity of Ketene Methide Intermediate 7. Formation of **7** from **1** involves a novel transfer of an acyl hydrogen to a vinylic carbon. In fact, in view of the ubiquity

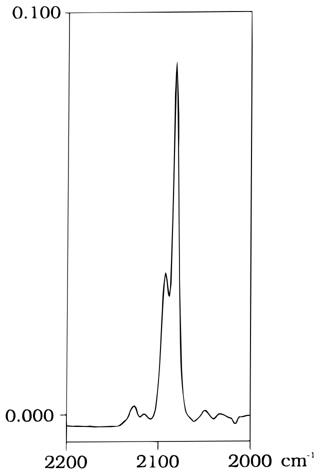
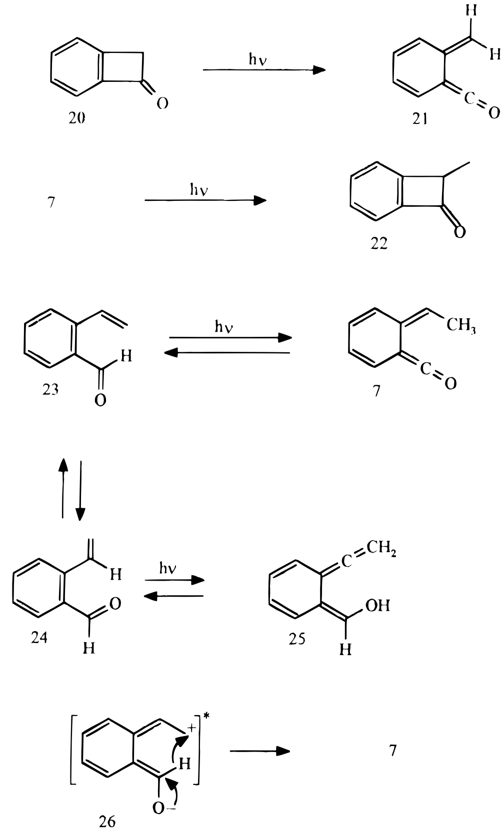


Figure 5. Expanded ketene stretching region of the IR spectrum of *o*-vinylbenzaldehyde isolated in an argon matrix after irradiation for 150 min through a 313 nm interference filter.

Scheme 3



of the light-induced hydrogen abstraction by the carbonyl group, hydrogen transfer in the other direction (**24** → **25**) could have been envisaged.[14] We have found no chemical or spectroscopic evidence for the latter reaction course. This could be a consequence of an unfavorable conformational equilibrium in the ground state of *o*-vinylbenzaldehyde, i.e., a low population of **24** which is the conformer suitable for hydrogen transfer leading to **25**.[15a] However, AM1 calculations (MOPAC version 6.0) do not show any appreciable difference in stability of minimum energy conformations approximating **23** and **24** (**24** was calculated to be less stable than **23** only by 0.3 kcal). Moreover, carbonyl and vinyl stretching vibrations of matrix-isolated aldehyde **1** point toward a mixture of rotamers trapped from the gas phase. As an alternate explanation, some charge transfer character in the excited state of **1** favoring hydrogen (hydride) movement in the observed direction may be considered, e.g., **26** → **7**. However, lack of sensitivity of the photoreaction to solvent polarity does not support this contention. It seems that the observed hydrogen shift can be best rationalized in terms of the large difference in the strength of acyl (~87 kcal/mol) and vinyl (~107 kcal/mol) carbon−hydrogen bonds;[15b] i.e., the reaction is driven by the thermodynamic factors. The observation of Wilson et al.[9] that low-intensity irradiation of **8** does not lead to a ketene methide intermediate is perhaps a consequence of insufficient energy or a steric constraint to a [1,5$_a$] sigmatropic shift in the lowest excited state of this highly conjugated molecule.[16]

Finally, the low reactivity of **7** in comparison to that reported for the ketene methide **21** merits comment.[8] The latter intermediate, when generated by photolysis of **20**, can be readily trapped with dienophiles or methanol.[7b] In contrast, we failed to obtain $\pi^4 + \pi^2$ adducts from **7** (vide supra), and its reaction with methanol was slow. This could be a consequence of rapid retro hydrogen transfer (**7** → **23**) of the type shown by deuterium-labeling experiments (vide supra). A similar pathway is not available to **21** as it is devoid of the necessary allylic hydrogen. The situation is somewhat reminiscent of enols formed on photolysis of aromatic carbonyl compounds carrying an *o*-alkyl substituent. The (*Z*)-enols rapidly revert back and cannot be trapped with dienophiles[17] nor exchange hydroxylic hydrogen,[18] unlike the (*E*)-enols. However, electronic or steric factors may also be responsible for the low reactivity of **1** compared to **21**.[19]

Conclusions

We have shown that on UV irradiation of *o*-vinylbenzaldehyde (**1**) an unprecedented monophotonic shift of the acyl hydrogen to the β-vinyl carbon occurs. The formed ketene methide intermediate **7** reverts to **1** by back hydrogen transfer but can be trapped effectively with secondary amines to afford *o*-ethylbenzamides. Failure to observe any transients or an adverse effect of triplet quenchers indicates involvement of a rapid, possibly concerted singlet pathway for the formation of **7** from **1**. As such, a [1,5$_a$] sigmatropic shift in the first excited state of **1** may be involved in this transformation.

Experimental Section

Materials. *o*-Vinylbenzaldehyde was prepared from 3,4-dihydroisoquinoline[20] (bp 60−65 °C, 1 Hgmm), as reported by Dale et al.,[21] and purified by distillation (bp 113−115 °C, 18 Hgmm) and column chromatography over silica gel (Acme synthetic chemicals, 100−200

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[14] Transfer of the side chain alkyl hydrogen in styrenes has been reported only occasionally (see ref 10). The shift of the acyl hydrogen to the carbonyl oxygen in phthalaldehyde is well documented: (a) Scaiano, J. C.; Encinas, M. V.; George, M. V. *J. Chem. Soc., Perkin Trans. 2* **1980**, 724. (b) Gebicki, J.; Kuberski, S. *J. Chem. Soc., Perkin Trans. 2* **1990**, 765.

[15] (a) Wagner, P. J. In *Handbook of Organic Photochemistry and Photobiology*; Horspool, W. M., Song, Pill-Soon, Eds.; CRC Press: Boca Raton, FL, 1995; p 449. (b) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 2nd ed.; Harper and Row: New York, 1981; p 147.

[16] In a footnote Wilson et al. refer to our unpublished flash photolysis results with **1** and also mention these possibilities (ref 9b).

[17] (a) Porter, G.; Tchir, M. F. *J. Chem. Soc. A* **1971**, 3772. (b) Wagner, P. J.; Chem, C. P. *J. Am. Chem. Soc.* **1976**, *98*, 239. (c) Scaiano, J. C. *Acc. Chem. Res.* **1982**, *15*, 252. (d) Scaiano, J. C.; Netto-Ferreira, J. C. *J. Am. Chem. Soc.* **1991**, *113*, 5800.

[18] (a) Gebicki, J.; Reimschussel, W.; Zurawinska, B. *J. Phys. Org. Chem.* **1990**, *3*, 38. (b) Michalak, J.; Wolszczak, M.; Gebicki, J. *J. Phys. Org. Chem.* **1993**, *6*, 465.

[19] It may be noted that **9** is also sluggish in its reaction with methanol (ref 9). Further, methyl substitution in the ortho position of **21** drastically depresses its reactivity toward methanol (ref 7).

[20] Pelletier, J. C.; Cava, M. D. *J. Org. Chem.* **1987**, *52*, 616.

[21] Dale, W. J.; Starr, L.; Strobel, C. W. *J. Org. Chem.* **1961**, *26*, 2225.

mesh). Compound **8** was secured from 6,7-dimthoxy-3,4-dihydroisoquinoline[22] (bp 155−160 °C, 1 Hgmm) in a similar way. *N*-Deuteriopiperidine was obtained by repeated shaking of piperidine with D_2O, drying over CaH_2, and distillation. For deuterium exchange of the acyl hydrogen of **l**, it was converted into an α-siloxynitrile, bp 105−108 °C, 4−5 Hgmm, which was exposed to LTMP (2 equiv) at −78 °C in THF for 1 h and the reaction mixture quenched with D_2O.

Representative Procedure for Preparative Scale Reaction of 1 with Amines. A solution of *o*-vinylbenzaldehyde (**1**) (135 mg, 1.02 mmol) and piperidine (100 mg, 1.15 mmol) in 300 mL of acetonitrile was irradiated under N_2 with Pyrex-filtered light from a 450 W medium-pressure Hanovia lamp, for 5 h. Concentration of the photolysate gave a residual oil which was dissolved in solvent ether (30 mL). The ethereal solution was washed successively with 10% hydrochloric acid (2 × 10 mL) and saturated aqueous sodium bicarbonate (2 × 10 mL). After drying over anhydrous sodium sulfate, the solvent was evaporated in vacuo to obtain an oil (206 mg) which was subjected to silica gel column chromatography (petroleum ether (60−80 °C)−ethyl acetate, 4:1), yielding 191 mg (86%) of amide **6a** as an oil: ^{1}H NMR (90 MHz, CCl_4) δ −1.18 (t, 3H, CH_3), 1.60 (br s, 6H, $3CH_2$), 2.60 (q, 2H, CH_2), 2.86−3.33 (m, 2H, NCH_2), 3.70 (br s, 2H, NCH_2), 6.96−7.40 (m, 4H, ArH); LRMS *m*/*e* 217, 216, 133, 132; HRMS for $C_{14}H_{19}NO$, *m*/*e* calcd 217. 1467, found 217. 1461. The spectral data of **6a** completely matched those of an authentic sample prepared by reaction of 2-ethylbenzoyl chloride with piperidine.

Quantum Yield Measurements. All quantum yield measurements were carried out in matched quartz tubes in a merry-go-round apparatus using 313 nm light from a medium-pressure mercury lamp, filtered through a 2.0×10^{-3} M solution of potassium chromate in 5% aqueous potassium carbonate.[23] A concentration of 3.4×10^{-3} M **1** was used, and its disappearance, up to 15% conversion, was monitored by its UV absorption at 308 nm. A benzophenone−benzhydrol actinometer was used for light intensity measurement.[24] ϕ values are based on an average of at least three runs (ϕ, ±10%).

Laser Flash Photolysis Studies. Laser experiments were carried out using the pulses from a Lumonics EX-510 excimer laser (Xe/HCl, 308 nm, ∼ 6 ns, ≤40 mJ/pulse). A flow sample cell (constructed of 7 × 7 mm^2 Suprasil tubing) was employed in order to ensure that fresh solution was irradiated by each laser pulse. Solutions were deaerated by bubbling with oxygen-free nitrogen through a container attached to the photolysis flow cell with Teflon lines. The temperature of the photolysis samples was 20−22 °C. The system is similar to that discussed in earlier publications.[25]

Calculations. Molecular modeling calculations were performed on a Tektronix CAChe workstation (software version 3.5) using the AM1 semiempirical method, as part of the MOPAC program version 6.1. Electronic spectra were calculated using the ZINDO program.

Matrix Isolation Studies. Since the sample pressure was insufficient to prepare a gaseous mixture, argon was passed over a solid substrate placed in the thermostated tube connected to the deposition line behind the needle valve. The tube was kept at −8 °C during deposition. Argon was deposited with a flow rate of 30 μmol min^{-1}, and the total amount deposited varied from 0.9 to 1.8 mmol. The sample vapor dilued by the argon carrier stream was condensed onto a cesium iodide window mounted on the expander stage of a Displex DE-202 (APD Cryogenics) cryostat. During deposition the window support was kept at 20 K. The matrix ratio was estimated to be 600−700.

Photochemical reactions were carried out with a high-pressure mercury lamp, HBO-200 (Narva). Interference filters FS 10−50 (Oriel) were used. IR spectra of matrix-isolated species were obtained wth an MB 100 (Bomen) FT-IR spectrometer equipped with a wide-band DTGS detector working at a resolution of 1 cm^{-1}. UV−vis absorption spectra were measured with a PU 8710 (Philips) spectrophotometer. The irradiation and measurements were performed at 10 K.

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[22] Popp, F. D.; Mcewen, E. W. *J. Am. Chem. Soc.* **1957**, *79*, 3773.

[23] Wagner, P. J.; Ersfeld, D. A. *J. Am. Chem. Soc.* **1976**, *98*, 4515.

[24] Moore, W. M.; Hammond, G. S.; Foss, R. P. *J. Am. Chem. Soc.* **1961**, *83*, 2789.

[25] (a) Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7747. (b) Scaiano, J. C.; Tanner, M.; Weir, D. *J. Am. Chem. Soc.* **1985**, *107*, 4396.