Transients in the Flash Photolysis of Indan-2-ones. Absorption Spectra and Decay Kinetics of *o*-Xylylenes

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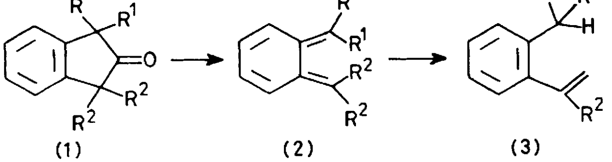
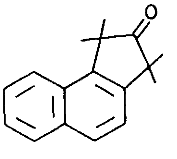
Summary Transients assigned as *o*-xylylenes have been observed in the flash photolysis of methylated indan-2-ones; the transient decay kinetics to give styrenes (*via* the 1,5-hydrogen shift) have been studied.

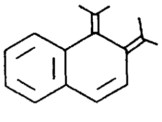
Formation of *o*-xylylenes was demonstrated in the irradiation of aryl-substituted indan-2-ones.[1] An *o*-xylylene-type intermediate was also proposed in the formation of the styrene (**3b**) from 1,1,3,3-tetramethylindan-2-one (**1b**).[2]



(1) (2) (3)



(4)



(5)

a; R¹ = H, R² = Me
b; R¹ = R² = Me
c; R¹ = R² = CD₃

In spite of considerable current interest in *o*-xylylene species,[3] their direct observation in the above reaction has apparently not been reported. We now report the observation and decay kinetics of transients, assigned as *o*-xylylenes, in flash photolysis of a series of methylated indan-2-ones.

Irradiation† of the indan-2-ones (**1a**—**c**) and (**4**) gave the corresponding isopropenyl-2-alkylbenzene derivatives (Table),‡ which were expected on the basis of the work by Starr and Eastman[2] on (**1b**). Flash photolysis§ of these indanones showed the presence of transients absorbing in the range 300—400 nm. The absorption maxima for (**2a**) and (**2b**), which are at shorter wavelengths than that for the parent *o*-xylylene[3a] (λ_{max} 375 nm) in spite of the alkyl substitution, strongly suggests that their structures are non-planar, and are twisted about the 'essential' single bonds[4] of the non-aromatic ring; inspection of models confirms this conclusion.

Table. Products and transients in the photolysis of indan-2-ones.

Indanone	Products isolated	Transient Compound	λ_{max}/nm	Decay rate constant[a]/s^{-1}
(**1a**)	1-Isopropenyl-2-methylbenzene	(**2a**)	360	$7{\cdot}5 \times 10^{-2}$
(**1b**)	1-Isopropenyl-2-isopropylbenzene	(**2b**)	350	$3{\cdot}9 \times 10^{-3}$
(**4**)	1-Isopropenyl-2-isopropylnaphthalene	(**5**)	b	Long lived[c]

[a] At 26 °C. [b] Maximum obscured by ketone absorption. [c] Survives indefinitely in the dark.

The first-order rate constants for decay of the transients, as determined by kinetic spectrophotometry, are also given in the Table. The rates of decay of the transients are dependent on the intensity of the light in the monitoring beam, *i.e.*, the transients are susceptible to secondary photolysis. The data refer to limiting values at low intensities of the monitoring beam. The decay rates did not change on the addition of acid or base.

To characterize the decay process for these transients, the hydrogen kinetic isotope effect and activation parameters were measured. Thus, the transients from (**1b**) and (**1c**) showed a kinetic isotope effect (k_H/k_D) of 5·4 (38·5 °C). Activation parameters were: (**1a**), $E_a = 15{\cdot}7$ kcal mol^{-1}, $\Delta S^\ddagger = -12{\cdot}9$ cal mol^{-1} K^{-1}; (**1b**), $E_a = 19{\cdot}0$ kcal mol^{-1}, $\Delta S^\ddagger = -7{\cdot}5$ cal mol^{-1} K^{-1} (temperature range 20—50 °C).

The isotope effect and the negative entropies of activation are consistent with a concerted 1,5-hydrogen shift as the decay process.[5] For example, thermal tautomerization of penta-1,3-diene[6] has $\Delta S^\ddagger = -7{\cdot}1$ cal mol^{-1} K^{-1}, and the rearrangement shows a large isotope effect, which is expected for a symmetrical transition state. The activation energies are also reasonable, since the 1,5-shift in penta-1,3-diene is 35·4 kcal mol^{-1}.[6]

In the proposed structures for the transients, particularly (**2b**) and (**5**), the molecule cannot adopt the planar geometry necessary for the allowed suprafacial 1,5-hydrogen shift. This suggests that the thermal decay may involve the previously unknown antarafacial 1,5-hydrogen shift.[7] This process is photochemically allowed, and would explain the secondary photolysis of the transients.

† The indanone (10^{-1}—10^{-2} M) in purified hexane, in a quartz or Pyrex tube, was deaerated and irradiated in a Rayonet photoreactor with 'RPR 3000 A' lamps. These give light in the 280—340 nm range.

‡ Progress of the reaction was followed by g.l.c. (5′ × ⅛″ tube containing 10% Carbowax 20M on 60—80 mesh Chromosorb W, or 5′ × ⅛″ tube containing 7% QF-1 on Chromosorb W). With (**1a**) and (**1b**), the styrenes were the only significant products; with (**4**), secondary products appeared after 60% reaction.

§ Flash photolysis was carried out as described in ref. 5.

The relative thermal stability of (**5**) is consistent with thermochemical calculations.[8] Thus, the calculated enthalpy changes for conversion of (**2a**), (**2b**), and (**5**) into their respective products are $-30{\cdot}4$, $-28{\cdot}4$, and $+3{\cdot}2$ kcal mol^{-1}, respectively.

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