Sigmatropic Rearrangements of 1,1-Diarylindenes.[1] Direct Observation and Lifetimes of Isoindenes by Flash Photolysis

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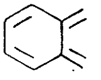
Summary Transients absorbing in the 400—550 nm range and assigned as arylisoindenes have been observed by flash photolysis of 1,1-diphenylindene, 1-*p*-cyanophenyl-1-phenylindene, and 1,1,3-triphenylindene; the first-order decay rates of these three transients were measured.

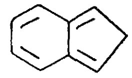
There has been considerable recent interest in the structures and properties of *o*-xylylene (**1**)[2] and the related isoindene (**2**). These reactive species have been studied both theoretically,[3] and experimentally,[2,4—11] particularly by means of trapping experiments.[5,7,8] *o*-Xylylene and its derivatives have also been detected by matrix isolation,[2,11] and flash photolysis techniques,[9,11b] while some isoindenes have been isolated at ambient temperatures.[5]

Isoindene derivatives were proposed as intermediates in the photo-rearrangement of 1,1-diarylindenes.[1,12] Thus, the rearrangement of (**3**) to give (**4**) was proposed to proceed *via* the isoindene (**5**).

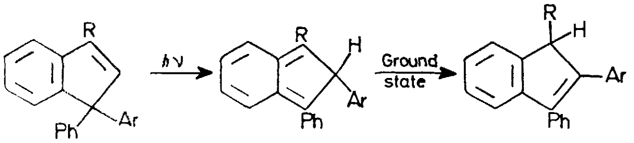
We now report the direct observation, by flash photolysis, of transients, assigned as isoindenes, in the photolysis of three 1,1-diarylindenes. The first-order rate constants for the disappearance of these three transients were also measured, thus giving information about substituent effects on the fast, 1,5-hydrogen shift.



(1)



(2)



(3) (5) (4)

a; R = H, Ar = Ph
b; R = Ar = Ph
c; R = H, Ar = p-CNC_6H_4

A solution of the diarylindene (**3a**—**c**),† 2×10^{-4}M in hexane,‡ was contained in a cylindrical cell 50 cm long, 2·6 cm diameter, which had a Vycor jacket and quartz ends. The cell and contents were exposed to a photolysis flash§ from the side, and after a predetermined delay, to spectroscopic flash from one end. The latter was essentially a continuum of white light, and the absorption of the solution was observed by recording the transmitted light photographically in a spectrograph.

The region of absorption of these transients (400—550 nm) is as expected for the arylisoindenes (**5**) based on the published spectrum of *o*-xylylene[2] and certain aryl derivatives.[11]¶ Also, the similarity in the absorption (400—500 nm) of the transients from (**3a**) and (**3c**) and the red-shifted absorption (425—550 nm) of that from (**3b**)¶ are consistent with the proposed isoindene intermediates. The appearance of product could also be seen in the photographs (absorption 300—350 nm).

Table

Results of kinetic spectrophotometry

Run[a]	Reactant	Wavelength monitored /nm	Transient lifetime /ms	Decay rate constant /s^{-1}
1	(3a)	450	28	36
2[b]		450	22	46
3[c]		340	25	40
4	(**2b**)	475	850	1·2
5	(3c)	450	72	14

[a] All measurements were at 20 °C. All solutions were *ca.* 2×10^{-4}M, in deaerated hexane, except run 2. [b] Saturated with oxygen, *ca.* 10^{-2}M, ref. 9b. [c] Appearance of product (**4a**) was monitored.

Lifetimes of the three transients were measured by kinetic spectroscopy in which the transmittance of the solution in the region of transient absorption was monitored as a function of time, after the photolysis flash. From photographs of oscillosope traces of plots of transmitted intensity *vs.* time, the variation of transient concentration with time was measured. The transients disappeared with first-order kinetics, and the lifetimes and rate constants are given in the Table.

It was also found that the rate of appearance of product (monitored at 340 nm) was equal to the decay rate of transient, in the case of 1,1-diphenylindene. This further supports the above mechanism for rearrangement of (**3a**) to give (**4a**). The lifetime of this transient was only slightly affected by saturation with oxygen.

The rates of aromatization of the transients from (**3a**) and (**3c**) are approximately one order of magnitude lower than the analogous species from *o*-alkyl-benzophenones,[9] which also formally undergo the 1,5-hydrogen shift Notably, the transient from (**3b**) rearranges more slowly

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† These were prepared by literature methods (refs. 1, 10, 13).

‡ Analytical grade hexane was further purified by treatment with fuming H_2SO_4.

§ The photolysis flash had 750 J energy, the spectroscopic flash had 180 J. The usual delay between the photolysis and spectroscopic flashes was 30 μs.

¶ The long-wavelength bands of these transients are red-shifted relative to that of *o*-xylylene, the latter being in the range 313—417 nm (ref. 2). Notably, the αω-diphenyl-*o*-xylylenes studied by Quinkert and his co-workers (ref. 11), absorb in the visible region. Photolysis of (**3b**) at low temperature gave a product having absorption bands at 276 and 485 nm, which was assigned as (**5b**) (ref. 11a).

which presumably indicates a lower ground-state energy for the αω-diarylisoindene. All these isoindenes rearrange much faster than cyclopentadienes[14] or indenes[14] which is consistent with thermochemical considerations.

The slower rearrangement of the transient from 1-*p*-cyanophenyl-1-phenylindene (**3c**) relative to that from 1,1-diphenylindene (**3a**) is interesting in that it shows that the transition state for the 1,5-hydrogen shift is electron deficient at C-2 of the five-membered ring (the migration start). This is consistent with the effect of a methyl group on the rate of thermal 1,5-hydrogen migrations.[10]

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