Identification and Kinetics of Isoindenes. Nuclear Magnetic Resonance, Trapping, and Flash Photolysis Studies[1]

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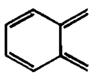
Abstract: Transients absorbing in the 400-550-nm range have been observed in the flash photolysis of a series of 1,1-diarylindenes. These transients are assigned as isoindenes, and have been studied by ultraviolet spectroscopy, low-temperature NMR, chemical trapping, and flash photolysis techniques. Irradiation of 1,1,3-triphenylindene at 254 nm in cyclopentane at −70 °C gives an orange solution (λ_{max} 478 nm) which contains 1,2,3-triphenylisoindene. ^1H NMR (−70 °C) resonances at δ 4.45 and 6.80 are assigned to the methine and vinylic protons of 1,2,3-triphenylisoindene. Reaction with 4-phenyl-1,2,4-triazoline-3,5-dione at −70°C gave the Diels-Alder adduct of the azo compound and 1,2,3-triphenylisoindene. The structure of the adduct was assigned from mass and NMR (^1H and ^{13}C) spectra and elemental analysis. The isoindene formed 1,2,3-triphenylindene in quantitative yield on warming to room temperature. The kinetics of the 1,5 hydrogen shift by which a series of isoindenes rearrange to stable indenes were studied by flash photolysis. The transient decay was first order, and rate constants (deoxygenated hexane, 20 °C) follow: 1,1-diphenylindene, 36 s^{-1}; 1-*p*-cyanophenyl-1-phenylindene, 14 s^{-1}; 1-*p*-bromophenyl-1-phenylindene, 27 s^{-1}; 1-*p*-methoxyphenyl-1-phenylindene, 44 s^{-1}; 1,1,3-triphenylindene, 1.21 s^{-1}. Kinetic isotope effects of k_H/k_D = 3.7 and 6.5 for the decay of 1,2,3-triphenylisoindene and 1,2-diphenylisoindene (2-H and 2-D), respectively, show that the hydrogen shift is rate determining. The 1,5 hydrogen shift in 1,2-diphenylisoindene has E_a = 13.1 kcal/mol and $\Delta S^{\ddagger} = -8.9$ eu, and in 1,2,3-triphenylisoindene has E_a = 14.4 kcal/mol and $\Delta S^{\ddagger} = -19.7$ eu. The ground-state energy of isoindene relative to indene is estimated to be 20 kcal/mol, which is compared with theoretically calculated values.

The *o*-xylene system **1** and the related isoindene **2** have been studied theoretically[2,3] and experimentally,[2,4-11] and have been detected by matrix isolation[2] and flash photolysis.[9,11]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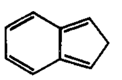
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These reactive species have been proposed as intermediates in a number of reactions,[4-17] and have been identified by trapping in Diels-Alder reactions.[7,11,13,15]

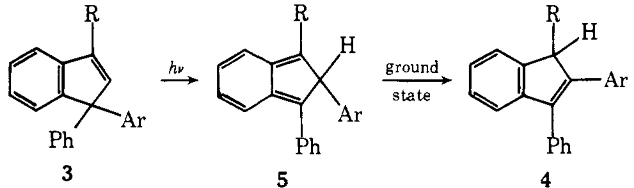
Isoindene derivatives have been invoked as intermediates in the photorearrangement of 1,1-diarylindenes.[12] Thus, the rearrangement of **3** to give **4** has been proposed to proceed via isoindene **5**. The latter was formed, according to this scheme, by an excited state phenyl shift, and reacted further to give stable product by a ground state hydrogen shift, as shown in Scheme I.

We have employed this photochemical reaction to study the excited state migration of aryl groups.[12c,d,18] For this work, it was important to obtain direct evidence of the intermediacy of **5**, and the present paper reports the results of these experiments. We used several different techniques to observe and characterize the isoindenes. Flash photolysis, low-temperature NMR spectroscopy, and a trapping experiment all gave independent evidence for the structure of the intermediate **5**. Flash photolysis was also used to study the decay kinetics of the transients. In the following Results section, the structural evidence for **5** is described first, and then the decay kinetics are discussed.

Results

Structural Evidence. A. Electronic Spectra. Flash photolysis of hexane solutions of the 1,1-diarylindenes **3a–e** (2×10^{-4} M) showed the presence of transients with lifetimes of 20–70 ms. The absorption spectra are consistent with isoindene structures for the transients. Significantly, the absorption is at longer wavelength (400-500 nm) than that of the parent *o*-xylylene, which absorbs at 313-417 nm,[2] and the red shift is consistent with conjugation of the phenyl group in **5**. The absorptions of **3a,c,d, e** are similar, and this is also consistent with with the isoindene structure, since in the photomigration which produces **5**, the substituted phenyl group is predominantly at carbon 2.[18] Finally, the transient from 1,1,3-triphenylindene (**3b**), which has two phenyl groups conjugated with the isoindene system, absorbs at still longer wavelength (400-550 nm) than the monophenyl derivatives. The latter compares favorably with the spectra of α,ω-diphenyl-*o*-xylylenes, described by Quinkert and co-workers.[11]

Scheme I



3a, R = H; Ar = Ph
b, R = Ar = Ph
c, R = H; Ar = Ph(*p*-CN)
d, R = H; Ar = Ph(*p*-Br)
e, R = H; Ar = Ph(*p*-OCH$_3$)

An electronic absorption spectrum of the transient from 1,1,3-triphenylindene (**3b**) was also obtained at −70 °C. Irradiation of **3b** with 254-nm light in pentane at −70 °C gave an orange solution with λ_{max} 478 nm, which was attributed to the transient 1,2,3-triphenylisoindene **5b**. The orange color faded to yellow (λ_{max} 440 nm) on warming to room temperature and the yellow color bleached completely in 1-2 h. The identity of the species responsible for the long-lived yellow color is unknown at present. However, it had vinylic proton resonances in the NMR (see Figure 1), and its presence was noted in the flash photolysis of 1,1,3-triphenylindene (see kinetics section).

For spectral comparison with **5b**, a sample of 2,2-dimethyl-1,3-diphenylisoindene (**6**) was prepared.[5]

The NMR spectrum of the sample of **6** (see Experimental Section) showed more than one methyl resonance, and this was attributed to contamination by **7**, formed by methyl migration.[13,19b] However, the ultraviolet spectrum of **6** had λ_{max} 444 nm, shifted 34 nm to the blue relative to **5b**. Apparently,

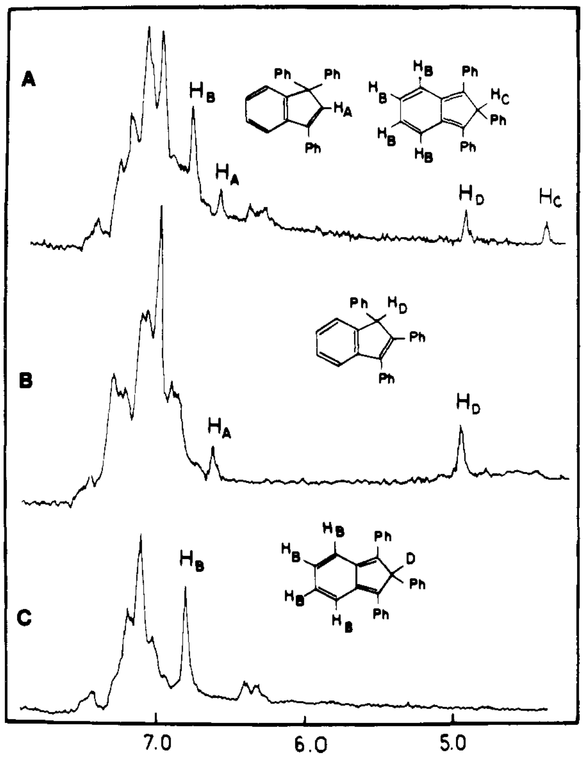
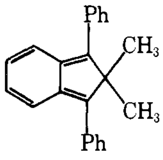


Figure 1. 100-MHz NMR spectra of **3b** irradiated in cyclopentane at −70 °C showing (A) reaction mixture immediately after irradiation; (B) the same mixture after warming to room temperature and recooling to −70 °C; and (C) reaction mixture immediately following a similar low-temperature irradiation of 1,1,3-triphenylindene-*2-d*.



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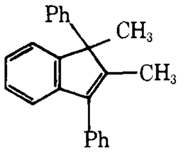

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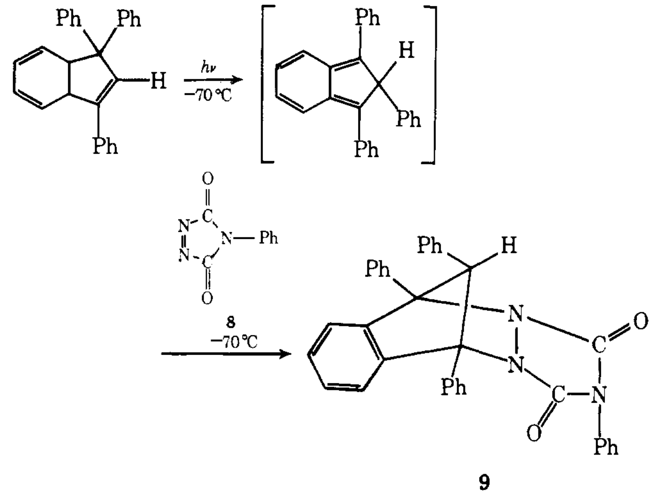
"spiroconjugation"[19-21] of the phenyl group at C-2 in **5b** is responsible for this difference in absorption. The fluorescence spectra of **5a** and **5b** were also recorded (λ_{max} 522 and 572 nm, respectively).

B. Nuclear Magnetic Resonance Spectrum. Irradiation of **3b** in cyclopentane at −70 °C (in a quartz NMR tube) gave the orange color described above. The ^1H NMR spectrum of this solution at −70 °C is shown in Figure 1A. In Figure 1B the spectrum of the same solution which had been warmed to 20 °C and recooled to −70 °C is shown. This contained reactant (**3b**) and product (**4b**) only; the absence of resonances H_B and H_C assigned to the transient isoindene will be noted. Figure 1C shows the spectrum of the transient solution from 2-deuterio-1,1,3-triphenylindene photolysis. While the methine resonances at higher field are absent, the singlet assigned to the four vinyl protons (H_B) at δ 6.80 in the transient is unchanged. These changes are consistent with the presence of **5b** in the low-temperature spectra. The NMR spectrum of the 2,2-dimethylisoindene **6** also showed a broad singlet at −70 °C at δ 6.90, attributed to the four vinylic protons. At room temperature, this resonance appeared as a complex multiplet, which simplified to a pattern similar to the vinylic proton resonance in 1,3-cyclohexadiene, on irradiation of the methylene protons in a decoupling experiment. Thus, these multiplets were assigned to the similar AA′BB′ systems in **6** and in cyclohexadiene.

Scheme II



C. Trapping of Isoindene 5b. Intermediate *o*-xylylenes and isoindenes have been trapped in several systems, by utilizing their reactivity in Diels–Alder reactions. However, in the photolysis of 1,1-diarylindenes, it was found that the better dienophiles, such as maleic anhydride, acrylonitrile, or acetylene dicarboxylic esters, acted as quenchers of the photochemical reaction, and attempts to trap the proposed isoindenes failed. The discovery that 1,2,3-triphenylisoindene was long lived at −70 °C suggested an alternative way of chemically trapping the intermediate. Thus, when a preirradiated solution of 1,1,3-triphenylindene (**3b**) in pentane was treated with the highly reactive dienophile 4-phenyl-1,2,4-triazoline-3,5-dione (**8**) at −70 °C, an adduct assigned the structure **9** was obtained, Scheme II.

The adduct **9** had mp 269 °C. It showed infrared bands at 1787 and 1731 cm^{-1} (cyclic imide) and peaks in the mass spectrum at *m/e* 519 (2) (parent ≡ $C_{35}H_{25}N_3O_2$), 344 (100), 343 (91), and 267 (29). The last three would result from retro-Diels–Alder fragmentation.

The ^1H NMR ($CDCl_3$) spectrum showed multiplets at δ 7.8–7.5 (7 H), 7.4–7.2 (10 H), and 7.1–6.8 (5 H). A doublet of doublets showed at δ 6.38 (2 H, J = 8.0 and 2.0 Hz). A singlet at δ 4.08 (1 H) is assigned to the methine hydrogen. The ^{13}C NMR spectrum ($CDCl_3$ or CD_2Cl_2) showed resonances at δ 157.5 (C=O groups), 127.9–123.3 (aromatic system), and 82.8 and 80.1, under conditions of proton decoupling. On removal of the decoupling field, the resonance at δ 82.8 remained a singlet while that at δ 80.1 became a doublet. The former is assigned to the two bridgehead carbons, while the latter is assigned to the single carbon bridge.

The above results provide ample evidence for the identity of the transient from photolysis of **3b**. Unfortunately, because of their shorter lifetimes, similar low-temperature experiments did not allow characterization of the transients from **3a** or **3c–e**. It is assumed in the following section on kinetic spectroscopy that the species whose absorption was monitored are the isoindenes analogous to **5b**.

Kinetic Studies. The lifetimes of the transients were determined by kinetic absorption spectroscopy (the transmittance of the solution in the region of the absorption by the transient was observed at times after the photolysis flash). All the transients in hexane solution disappeared by first-order kinetics (in the photolysis of **3b** an absorption due to an additional long-lived intermediate was present). The experimental conditions, lifetimes, and rate constants are shown in Table I. Usually the decay of the transient was monitored. However, the absorption of **4a** from the photolysis of **3a** could be distinguished easily from that of the transient and reactant. In this case it was found that the rate constant for the disappearance

Table I. Results of Kinetic Spectrophotometry

Expt[a]	Reactant	Wavelength monitored, nm	Transient lifetime, ms	Rate constant, s^{-1}
1	**3a**	450	28	36
2	**3a**	450	22	46
3[b]	**3a**	340	25	40
4	**3b**	475	850	1.21
5	**3c**	450	72	14
6	**3d**	450	37	27
7	**3e**	450	23	44

[a] All runs were in purified, deoxygenated hexane at 20 °C, except run 2 in which the solution was oxygen saturated. [b] Appearance of product was monitored.

of transient **5a** was within the experimental error of the rate constant for the appearance of the produce **4a.** It was shown that treatment of the 1,1-diphenylindene solution and the photolysis cell with either acid (3 N H_2SO_4) or base (3 N NaOH) prior to flash photolysis did not affect the decay times of the transients.

The nature of the rate-determining step in the removal of the isoindene was investigated by studying the rate constants for the decay of **5a** and **5b** (2-H and 2-D). The rate constants for **5a** were $k_H = 42\ s^{-1}$ and $k_D = 6.5\ s^{-1}$ (23.4 °C) while for **5b,** $k_H = 3.1\ s^{-1}$ and $k_D = 0.84\ s^{-1}$. Thus the kinetic isotope effects (k_H/k_D) are 6.5 and 3.7 under these conditions and the 1,5-hydrogen shift is determining the kinetics of the decay of the isoindene. The primary isotope effect is within the range of values observed in symmetry allowed, concerted sigmatropic rearrangements.[23] The rate constant for **5a** (3-D) was 40 s^{-1} (23.4 °C) showing that the secondary isotope effect is very small.

Further information on the nature of the species involved in the rearrangement can be deduced from measurements on the series of diphenylindenes (**3a,c–e**) which involve different substituents on one of the phenyl rings. On irradiation of these indenes, the substituted phenyl group migrates (Scheme I). The first-order rate constants observed for the decay of the isoindene in deoxygenated hexane at 20 °C follow: 1,1-diphenylindene (**3a**), 36 s^{-1}; 1-*p*-cyanophenyl-1-phenylindene (**3c**), 14 s^{-1}; 1-*p*-bromophenyl-1-phenylindene (**3d**), 27 s^{-1}; and 1-*p*-methoxyphenyl-1-phenylindene (**3a**), 44 s^{-1}. Figure 2 shows the appropriate linear free energy plot, in which the logarithm of the decay rate constant for the substituted isoindene is plotted vs. σ^n. The σ^n values for the aryl moiety are taken from the literature.[24] The small negative slope ($\rho = -0.6$) of the line indicates that the transition state for the 1,5-hydrogen shift is electron deficient at C-2 of the five-membered ring (the migration start), and that the migrating hydrogen has a slight "hydride ion" character. The extent of electron withdrawal from C-2 is rather small, as evidenced by the small negative value of ρ. This value of -0.6 is similar to ρ for the decomposition of *tert*-butyl perbenzoates (-0.5 to -0.9), a reaction in which charged species are not formed, but much less than ρ for quaternarization of anilines (-3.0 to -4.0).

The rate constants increase with temperature, and can be interpreted in terms of the Arrhenius equation. The values of the Arrhenius parameters for 1,1-diphenylindene are $E_a = 13.1 \pm 0.5$ kcal mol^{-1} and $\ln A = 26.0 \pm 0.8$. This corresponds to an entropy of activation, $\Delta S^{\circ\ddagger}$, of -8.9 cal K^{-1} mol^{-1} evaluated using $A = (ekT/h)e^{\Delta S^{\circ\ddagger}/R}$. The corresponding values for 1,1,3-triphenylindene are $E_a = 14.4 \pm 0.6$ kcal mol^{-1}, $\ln A = 20.5 \pm 1.0$, and $\Delta S^{\circ\ddagger} = -19.7$ cal K^{-1} mol^{-1}. The low values of the activation energies and the negative activation entropy again support a concerted mechanism for the 1,5-hydrogen shift. These values for the phenyl-substituted isoindenes can be compared with the data on the 1,5-formyl shift in methyl-substituted indenes. Field, Jones, and Kneen[17] have reported $\Delta H^{\circ\ddagger} = 22.1$ kcal mol^{-1} and $\Delta S^{\circ\ddagger} = -11.4$ cal K^{-1} mol^{-1} for the 1,5-formyl shift in 1-formyl-1,3-dimethylindene in diphenyl ether solution. The results of Roth[25] on the hydrogen shift in 5*H*-perdeuteriocyclopentadiene give a value of $\Delta S^{\circ\ddagger} = -12$ cal K^{-1} mol^{-1}, while those of McLean and Haynes[26,27] on the hydrogen shift in 1-methylcyclopentadiene and 1,5-dimethylcyclopentadiene yield values of -10 and -4 cal K^{-1} mol^{-1}, respectively. Even more directly related to our experiments are the data of Miller and Boyer[10] on the H shift in 1-phenylindene. They showed that the hydrogen shift in diphenyl ether as a solvent had an entropy of activation of -2.3 cal K^{-1} mol^{-1}. All the activation entropies are negative values, but the magnitudes differ markedly in the various molecules. All the molecules in which hydrogen shifts occur are effectively planar, yet the activation entropies are still very sensitive to the specific substitution in the system. It is possible that the large negative $\Delta S^{\circ\ddagger}$ for **4b** is due to freezing of rotational motion in the substituent phenyl groups at the transition state.

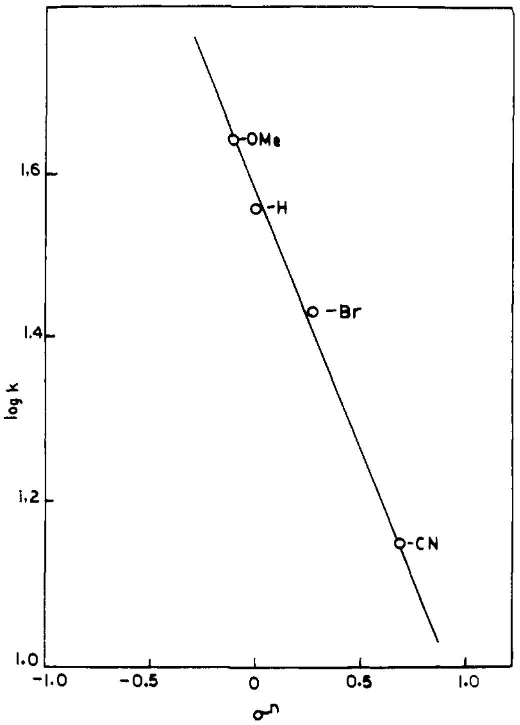


Figure 2. Correlation of rates of rearomatization of isoindenes **5e**, **5a**, **5d**, and **5c** with σ^n.

The activation energy data reported above for the decay of the isoindenes are very interesting, in that they can be used with literature data to estimate, for the first time, the difference in energy between an isoindene and an indene. Miller and Boyer[10] report an activation energy at +33.2 kcal mol^{-1} for the thermal conversion of 1-phenylindene to the isoindene. One can obtain the ground state energy of the isoindene with respect to that of the indene from the difference in the activation energies of the forward and reverse reactions. The compound chosen to model the reverse reaction should have a phenyl group at the 1 position since Miller and Boyer[10] found that the substitution of a phenyl group for a hydrogen atom at the start position of an H migration in the thermal reaction increases the rate by about 130 (owing to the change in the conjugation of the phenyl group at the 1 position from nonconjugated in the reactant to conjugated in the isoindene, and so to conjugated in the transition state). We have chosen 1,2-diphenylindene as the model compound, and have assumed that the activation

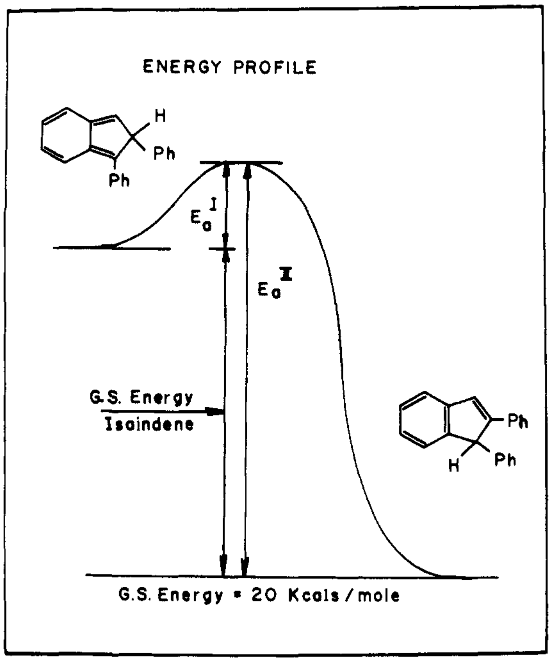


Figure 3. Energy vs. reaction coordinate profile for the 1,2-diphenylisoindene to 1,2-diphenylindene conversion. E_a^{II} is the corresponding literature value[10] for 1-phenylindene conversion.

energy, E_a^{II} of Figure 3, for the thermal conversion of the diphenylindene is the same as that measured by Miller and Boyer[10] for 1-phenylindene. This leads to a value of about 20 kcal mol^{-1} for the difference in the energies of 1,2 diphenylindene and 1,2-diphenylisoindene.

As the value reported above for the energy difference between the diphenylisoindene and the diphenylindene is the only value available that is based on experimental data, it was worthwhile to estimate that energy difference using other techniques. The experimental value was determined using hexane as a solvent. However, Miller and Boyer[10] have shown that the 1,5-hydrogen shift in 1-phenylindene does not depend on the identity of the solvent, in agreement with results on other 1,5-hydrogen shifts.[28,29] Thus the solvent, in this instance, appears to fill the role of merely occupying space, rather than being directly involved in the solvation of the reactant or the transition state. Accordingly, the techniques proposed by Benson[30,31] to estimate the differences in the enthalpies of species in the gas phase, using group additivity methods, might be relevant to the case of the isoindene–indene conversion in solution. Initially the standard enthalpy change at 298 K was estimated for the conversion of the unsubstituted indene to the isoindene from the values for the standard enthalpies of formation, 42.0 and 68.6 kcal mol^{-1}, respectively. In this case all the group additivity values were available and the estimate led to a value of $\Delta H = 26.6$ kcal mol^{-1}. Not all the group additivity values were available to estimate directly the standard enthalpies of formation of 1,2-diphenylindene and 1,2-diphenylisoindene, but one could estimate a value by assuming that $C\text{-}(C_d)_2(C_B)(H) \simeq -1.5$ and $C\text{-}(C_B)_2(C_d)(H) \simeq -1$. This approximation led to an estimate of 26 kcal mol^{-1} for the difference in enthalpies of 1,2-diphenylindene and 1,2-diphenylisoindene. The estimate from the group additivity method for calculating enthalpies of formation in the gas phase is thus in reasonable agreement with the value, 20 kcal mol^{-1}, calculated from the experimental data in solution. Part of the discrepancy could be due to the use of the activation energy of 1-phenylindene as a model for the diphenylindene thermal conversion. It would be expected that the activation energy of the diphenylindene thermal conversion would be greater than that for the 1-phenylindene conversion (because of the loss of conjugation of the phenyl group at the 2 position).

Conclusion

These studies have shown that isoindenes can be generated as transients by aryl migration in the photolysis of suitable indenes. The transients can be investigated by various physical techniques (NMR and visible spectrophotometry), and the lifetimes are in a range where the kinetics can be determined by flash photolysis experiments. The difference in the energies of 1,2-diphenylindene and 1,2-diphenylisoindene has been estimated as 20 kcal mol^{-1}

Experimental Section

Materials. All solvents were reagent grade and were distilled before use. Hexane was purified by stirring for 24 h with fuming sulfuric acid (30% SO_3) followed by washing with water, sodium bicarbonate solution, and water. The hexane was dried over sodium sulfate and distilled. 1,1,3-Triphenylindene, 2-deuterio-1,1,3-triphenylindene, and the deuteriodiphenylindene were prepared by the procedures of Miller and Boyer.[32] The diarylindenes (**3c–e**) were prepared as described.[18] ^1H NMR spectra were obtained at 100 MHz on the Varian HA-100 spectrometer, and ^{13}C NMR spectra at 22.62 MHz on a Bruker WH-90 Fourier transform spectrometer.

Irradiation of 1,1,3-Triphenylindene. A solution of 1,1,3-triphenylindene (45 mg, 0.13 mmol) in hexane (150 mL) was irradiated at −78 °C, under argon, with Hanovia type L 100-W mercury lamp in a centrally placed quartz immersion well. The latter was double walled, and the space between the walls was evacuated. The lamp was cooled with a current of air. The irradiation was continued for 15 min, and the resulting orange solution was warmed to room temperature and left for 3 h. Analysis by VPC (5% of QF-1 on 60/80 Chromosorb W at 220 °C) showed that 90% of the 1,1,3-triphenylindene had reacted, and a single product had been formed. The solvent was distilled and the mixture was chromatographed on 4.0 × 35 cm of silica gel, slurry packed in hexane. Elution was with 10% benzene–hexane and 75-mL fractions were collected. Fractions 7–10 contained 1,2,3-triphenylindene, mp 132–134 °C (lit.[32] 132–134 °C), from ethanol, yield 78%.

Low-Temperature NMR Spectra. A solution of 1,1,3-triphenylindene (10 mg) in ca. 0.7 mL of cyclopentane was transferred to a quartz NMR tube (tube no. 703 PQ, Wilmad Glass Co., Inc., Buena, N.J.). The ^1H NMR spectrum of the solution was run at −78 °C on the HA-100 spectrometer. The solution was then purged with argon for 10 min at room temperature, and was cooled again to −78 °C in a bath of ethanol. The ethanol was contained in a partly silvered, quartz Dewar, and was cooled with a "Flexi-Cool" refrigeration system (FTS Systems, Inc., Stone Ridge, N.Y.). The cold sample was irradiated in the cooling bath for 40 min in a Rayonet photoreactor, using nine RPR 2537 Å lamps.

The sample was quickly transferred to the precooled probe of the spectrometer, and the spectrum of 1,2,3-triphenylisoindene was taken. Finally, after warming to room temperature, the spectrum of the product solution was obtained at −78 °C. In all of the above, the singlet resonance of the solvent (cyclopentane) at δ 1.51 served as reference and lock. The spectra of irradiated 2-deuterio-1,1,3-triphenylindene were obtained similarly. The spectra are shown in Figure 1.

Low-Temperature Visible Absorption Spectrum. A solution of 1,1,3-triphenylindene (3.0 mg) in cyclopentane (~0.7 mL) was irradiated at −78 °C for 5 min, as described above for the NMR experiments. The irradiated solution was poured into a vacuum-jacketed absorption cell, of 4.5-cm path length containing 70 mL of isopentane at −78 °C. The absorption spectrum was taken on the Cary 14 spectrometer. The spectrum had λ_{max} 478 nm, approximate log ϵ 4.6.

Fluorescence Spectra. A sample of **3a** or **3b** in cyclopentane in the NMR tube was irradiated as described for the absorption spectrum. The sample was kept at −78 °C using the quartz Dewar, normally used for phosphorescence spectra, which contained dry ice–methanol. The fluorescence spectrum was obtained with the Aminco-Bowman spectrofluorimeter. Excitation was at 546 or 436 nm for **3b** and at 436 nm for **3a**.

Trapping of 1,2,3-Triphenylisoindene. A solution of 4-phenylurazole (500 mg) in methylene chloride (25 mL) was cooled to −3 °C and treated with 2.0 g of lead tetraacetate (Alfa Inorganics, containing 10% of acetic acid).[22] After stirring for 3 min, the red solution was cooled to −78 °C. Triphenylindene (100 mg) in tetrahydrofuran (distilled from $LiAlH_4$) (125 mL) was purged with argon for 15 min, cooled to −78 °C, and irradiated with the 100-W Hanovia lamp and vacuum jacketed immersion well described above, for 30 min. The cold solution of dienophile was then added, and the mixture was kept at −78 °C for 2 h and then was warmed to room temperature. Evaporation gave a brown solid which was washed with successive 25-mL portions of water, 0.1 N HNO_3, and 0.1 N NaOH. The solid was dissolved in acetone, boiled with charcoal, and filtered through Celite. Evaporation and recrystallization from methanol gave white crystals (50 mg), mp 268–269 °C. Anal. Calcd for $C_{35}H_{25}N_3O_2$: C, 80.90; H, 4.85; N, 8.09. Found: C, 80.74; H, 4.78; N, 8.19.

Preparation of 1,3-Diphenyl-2,2-dimethylisoindene (6). This isoindene was prepared by the method of Alder and Fremery.[5] A yellow oil was obtained on evaporation of the filtered reaction mixture, as reported. This showed three methyl group resonances at δ 1.74, 1.70, and 1.68 (100 MHz, $CDCl_3$ solvent). In an attempt to purify **6** by distillation, it was heated to ca. 240 °C at 10^{-4} Torr, and the distillate (166–168 °C) was collected. The NMR spectrum showed that the resonance at δ 1.70 had disappeared completely, while those at δ 1.74 and 1.68 remained. The latter are attributed to **7**, formed from **6** by a methyl group shift.[19b]

Flash Photolysis. All flash measurements were made using cylindrical, jacketed Vycor cells of 25 cm path length and 50 mL capacity. Temperature control (±0.1 °C) was achieved by circulating water or methanol using a Forma Scientific Inc. constant-temperature bath. Solutions of the various indenes (2×10^{-4} M) were deoxygenated using oxygen-free nitrogen immediately prior to being flashed.

An energy input of 750 J/flash was discharged through a cylindrical flash lamp, 70 cm long and containing xenon at 100 Torr, which was parallel to the long axis of the photolysis cell. The excitation flash lamp had a half-life of 30 μs. The absorption spectra of the transients were obtained after a predetermined delay. Light from the monitoring flash (180 J) was dispersed in a medium quartz spectrograph (Hilger E 498.7) and recorded on photographic film.

Decay of the isoindene intermediates was followed quantitatively by monitoring the transmittance of the light filtered from a continuous xenon lamp (Oriel Corp., Model 6137) placed in front of the photolysis cell. A Jarrell-Ash Model 82-410 monochromator and a 1P 28 photomultiplier connected to a Biomation Model 805 Waveform Recorder permitted the recording of the transmittance at a particular wavelength as a function of time. The data were transferred from the Waveform Recorder to punched tape and processed on the CDC 6400 computer. The decays followed first-order kinetics, and the rate constants were determined at temperatures in the range 0–40 °C. The errors in the activation energy and the preexponential factor were propagated in the usual manner[33,34] and were significantly greater than the precision of the data.

Investigation of Effect of Acid and Base on Decay Time. A stock solution (200 mL) of 1,1-diphenylindene in purified hexane (5 mg indene/100 mL) was prepared. This was divided into three equal portions. One of these was used as a control sample. The second portion was shaken with 3 N H_2SO_4 (2×20 mL), separated, and dried. This was flashed in the usual cell which had been rinsed with 3 N H_2SO_4 and dried. The third portion was similarly treated with 3 N NaOH and flashed in a base-treated cell. Good first-order decay plots were obtained from all three solutions. The rate constants (22 °C, deoxygenated solution) follow: control, 38 s^{-1}; acid treated, 35 s^{-1}; base treated, 35 s^{-1}.

Acknowledgment. We thank the National Research Council of Canada for financial support.

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