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DEUTERIUM ISOTOPE EFFECTS IN THE PHOTOCHEMISTRY OF 2,5-DIMETHYL- AND 2,5-DI-*tert*-BUTYL-1,3,5-HEXATRIENES

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Summary

Deuterium isotope effects on the efficiencies of light-induced rearrangements of 2,5-dimethyl- and 2,5-di-*tert*-butylhexatrienes are reported. The 4π electrocyclizations show an inverse secondary isotope effect, in agreement with the existence of the theoretically predicted barrier on the potential energy surface of the excited state. In the formation of allylcyclopropene derivatives isotope effects provide evidence for a mechanism involving a biradical intermediate. The surprisingly large decrease in the efficiency of *E-Z* isomerizations in *E*- and *Z*-2,5-di-*tert*-butyl-1,3,5-hexatrienes after deuteration of the central double bond is ascribed to a reduced frequency of the hydrogen out-of-plane deformation which initiates the reaction.

1. Introduction

Mechanistic studies of the chemistry of the singlet excited states of conjugated hexatrienes and other polyenes have, in general, been based on comparative product analyses (at best at the level of quantum yields) of structurally related compounds [1 - 6]. Valuable insight into structure-reactivity relations has been obtained, but knowledge of the shape of the potential energy surfaces of the excited states and of their dynamics is still scarce. Spectroscopic studies have given information on the initial events in the vertically excited state [7 - 9]. The present picture of the overall shape of the excited state potential energy surface is based mainly on theoretical considerations and calculations (for a review on polyenes, see ref. 10; see also ref. 3). The application of time-resolved techniques in this field has been hampered by the non-fluorescence of most trienes [11, 12].

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The use of isotope effects is a well-established, though complicated, method of probing the role of certain modes of vibration in the reaction process. Following its fruitful applications in ground state chemistry (see, for example, ref. 13), it is now finding its way into the field of organic photochemistry (for some recent examples, see refs. 14 - 16; see also refs. 17 - 20).

In this paper we report the deuterium isotope effects observed in the photochemical isomerizations of the 2,5-dimethyl- and 2,5-di-*tert*-butyl-1,3,5-hexatrienes shown in Fig. 1 [4 - 6].

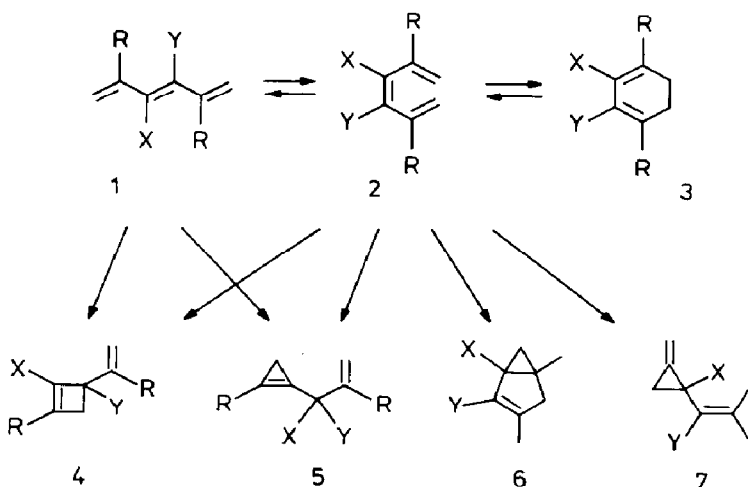


Fig. 1. Photochemical isomerizations of the compounds under investigation: a, R = Me, X = Y = H; b, R = Me, X = D, Y = H; c, R = Me, X = H, Y = D; d, R = Me, X = Y = D; e, R = *t*Bu, X = Y = H; f, R = *t*Bu, X = Y = D. 6 and 7 are formed only when R = Me.

2. Methods

The syntheses of the deuterated trienes are based on the introduction of deuterium at positions 3 and 4 by reduction of the appropriate 2,5-dialkyl-3-hexyne-2,5-diols with LiAlD_4 (LiAlH_4 for monodeuteration) and a D_2O work-up. The 3-(4)-(di)deuterated 2,5-dialkyl-2-hexene-2,5-diols thus obtained were dehydrated using anhydrous copper(II) sulphate, as described earlier [6]. Solutions (0.005 M in *n*-pentane) of *E*-2,5-dimethyl-1,3,5-hexatriene (1a) and of its deuterated analogues 1b (equivalent to 1c) and 1d were irradiated at 254 nm in a Rayonet RPR 200 reactor, in a room cooled to 4 °C [5]. Gas chromatography (using a fused silica column 25 m × 0.25 mm with chemically bonded polydimethylsiloxane at 25 °C with hydrogen carrier gas) was used to determine the product distributions. The deuterium distribution in 4b-4c and 7b-7c was measured by comparing integrated signal intensities in the 300 MHz ^1H nuclear magnetic resonance (NMR) spectra (Bruker WM 300, CDCl_3), measured with an appropriate relaxation delay, of d_0 and d_1 compounds. An average of six runs was used for this purpose. The case of 4 turned out to be particularly favourable since there is

no overlap of signals or disturbance by impurities. The average normalized intensity per proton of the seven signals of 4a was 1.000 ± 0.014 , which allowed accurate determination of the ratio of 4c to 4b as 1.11, with an estimated accuracy of ± 0.02 . The amount of 6b and 6c isolated was too small to permit accurate measurements of the deuterium distributions. In the case of 7b and 7c the accuracy was limited by the large width of the signals and the presence of impurities. The quantum yields of rearrangements of the 3,4-dideutero-2,5-di-*tert*-butyl-1,3,5-hexatrienes 1e and 2e at 254 nm were determined as described previously [6].

3. Results and discussion

The product distributions of the 2,5-dimethylhexatrienes are listed in Table 1. The results of quantum yield measurements on the di-*tert*-butyl compounds are presented in Table 2. To facilitate comparison the data on the d_0 compounds [4 - 6] have been included.

TABLE 1

Product distribution of deuterated *E*-2,5-dimethylhexatrienes at 80% conversion

Starting material	Product				
	4	5	6	7	X ^a
1a	70.8	12.3	4.8	8.5	3.5
1b-1c	73.0 ^b	9.0	4.5	8.7 ^c	4.8
1d	73.9	6.7	4.6	9.5	5.3

^aUnidentified, unstable product.

^b[4c]:[4b] = 1.11 ± 0.02 .

^c[7b]:[7c] = 0.99 ± 0.04 .

TABLE 2

Quantum yields of product formation from the 2,5-di-*tert*-butylhexatrienes 1e and 2e and from their 3,4-dideutero analogues 1f and 2f

Starting material	Product				
	1	2	3	4	5
1e		0.046	—	0.029	0.006
1f		0.028	—	0.032	0.003
2e	0.052		0.46	0.0040	0.0011
2f	0.032		0.45	0.0044	0.0006

3.1. 4π electrocyclizations

A clear deuterium isotope effect on the triene 4π electrocyclization[†] is observed on irradiation of 3-deutero-2,5-dimethylhexatriene (**1b**) (see Table 1). Integration of the peaks of H-2 and H-3 in the ¹H NMR spectrum revealed that the vinylcyclobutene derivatives **4b** and **4c** are formed in a ratio of 1:1.11 (Fig. 2). Thus ring closure towards the deuterated site is favoured. The quantum yield data on the 2,5-di-*tert*-butyl compounds confirm this observation (Because of the relatively large error limits associated with the determination of absolute quantum yields ($\pm 10\%$) the intramolecular competition experiment on **1b** is more reliable. For the dideuterated compounds an *intermolecular* competition experiment would offer more reliable information than the separately determined quantum yields.) . Theoretical studies of the disrotatory interconversion of *s-cis*-butadiene and cyclobutene [21 - 23] have predicted the presence of a small barrier on the excited state surface, where the lowest B excited state, populated by the absorption of light, meets the descending surface of the A state. The observed inverse α -deuterium isotope effect can be associated with the (adiabatic) crossing of this barrier. The situation is analogous to ground state reactions involving a hybridization change from sp^2 to sp^3 . In that case an inverse α -deuterium isotope effect is often found [13, 16, 17] though not always [15, 17, 24].

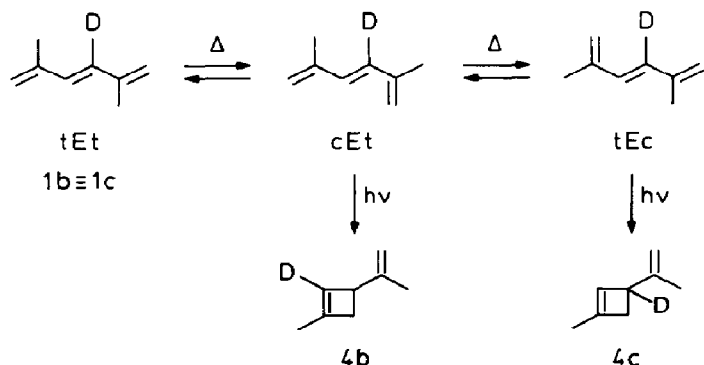


Fig. 2. Formation of vinylcyclobutenes **4b** and **4c** from *E*-2,5-dimethylhexatriene **1b**.

Another possible origin of the isotope effect is in the ground state conformational equilibrium, *i.e.* the *tEc* (*tZc*) rotamer of **1b** (**2b**) leading to **4c** may be preferred to the other rotamer producing **4b**. Such an equilibrium isotope effect is not expected to be large enough to be the only cause of the isotope effect observed on the product distribution. Equilibrium isotope effects comparable in magnitude with the effect reported here are found when deuterium is partitioned over sites with different hybridizations

[†]This process occurs in both **1a** and **2a**. The major part of **4a** (about 60%) originates from **1a** [5].

[25 - 27]. When the sites are only conformationally different, *e.g.* axial and equatorial positions in cyclohexanes [28, 29], the isotope effect is smaller. Moreover, the effect is likely to be unimportant in the di-*tert*-butyl compounds, which exist mainly in *s-cis* conformations.

The present interpretation of the inverse secondary isotope effect in 4π electrocyclozation is in agreement with the theoretically predicted barrier on the potential energy surface. In order to substantiate this interpretation additional evidence for the existence of the barrier is required. Determination of reaction rates at various temperatures would be very useful.

3.2. The formation of allylcyclopropenes

In the formation of allylcyclopropenes **5** from trienes a relatively large deuterium isotope effect is found. We have discussed [5, 30] two possible pathways for the overall process of allylcyclopropene formation, differing in the order of 1,2-hydrogen migration and ring closure, as shown in Fig. 3.

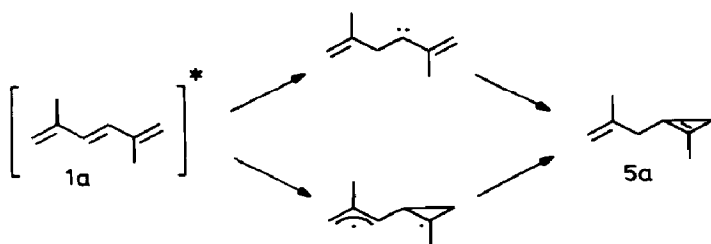


Fig. 3. Two pathways for the formation of allylcyclopropene **5a** from *E*-2,5-dimethylhexatriene **1a**.

In either mechanism the hydrogen shift can be associated with a primary kinetic isotope effect (related to the migrating nucleus) and a secondary α effect (at the accepting carbon atom). The latter is expected to contribute to a small preference for migration towards the deuterated site, thereby reinforcing the primary kinetic isotope effect. The data in Tables 1 and 2 reveal the presence of a normal isotope effect, $\Phi_{\text{H}}/\Phi_{\text{D}}(1 \rightarrow 5) \approx \Phi_{\text{H}}/\Phi_{\text{D}}(2 \rightarrow 5) \approx 2$ (for the d_2 compounds), showing that hydrogen migration is involved in the yield-determining step.

The decrease in the yield of **5** on going from **1a** to **1d** (the allylcyclopropenes **5** originate mainly from the *E*-trienes **1** [4 - 6]) is accompanied by a clear increase in the yield of the, unfortunately still unidentified, unstable compound **X**. This suggests that **5** and **X** have a common precursor. A significant increase in the yield of **X** from an intermediate state or intermediate species, when the rate of hydrogen migration leading to **5** is decreased, is possible only if the efficiency of formation of **5** from the intermediate (state) is high enough. Otherwise there would not be a sufficient increase in the lifetime of the intermediate (state). Since the quantum yield of the conversion of **1** (and **2**) to **5** is consistently very low [6] we conclude that the hydrogen shift is not the primary process in the excited triene leading to **5**. This lends support to the alternative mechanism, in which a three-membered ring is formed as the primary process (Fig. 4).

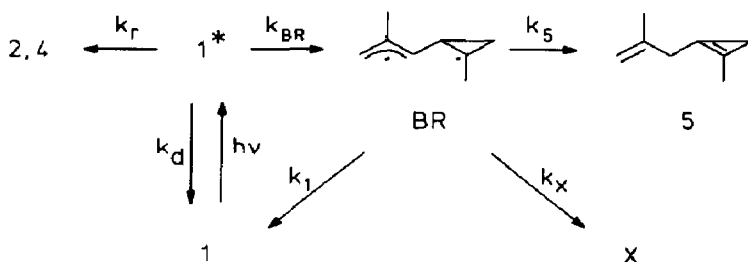


Fig. 4. Proposed reaction scheme involving a biradicaloid (BR) intermediate.

The meaning of the symbols used is self-explanatory. On the basis of this scheme the kinetic isotope effects k_5^0/k_5^1 and k_5^0/k_5^2 can be derived from the ratios of the yields Y_5/Y_X , with the additional assumption that k_1 and k_X are not subject to an isotope effect:

$$\frac{\Phi'_X}{\Phi_X^0} = \frac{\tau'_{BR}}{\tau^0_{BR}} \frac{\Phi'_{BR}}{\Phi^0_{BR}} \quad (1)$$

$$\frac{\Phi'_5}{\Phi_5^0} = \frac{k'_5 \tau'_{BR}}{k_5^0 \tau^0_{BR}} \frac{\Phi'_{BR}}{\Phi^0_{BR}} \quad (2)$$

$$\frac{k_5^0}{k'_5} = \frac{\Phi_5^0}{\Phi'_5} \frac{\Phi'_X}{\Phi_X^0} = \frac{Y_5^0}{Y'_5} \frac{Y'_X}{Y_X^0} \quad (3)$$

Here $\tau_{BR} = (k_1 + k_X + k_5)^{-1}$. The superscripts indicate the number of deuterium atoms, the prime representing either 1 or 2. This analysis leads to $k_5^0/k_5^1 = 1.9$ and $k_5^0/k_5^2 = 2.8$. These values agree very well: neglecting secondary isotope effects, a kinetic isotope effect of 2.8 should apply to only 50% of the monodeuterated molecules of 1b. The effective kinetic isotope effect of 2.8 is in the range reported for other light-induced 1,2-hydrogen shifts [18 - 20], the small value being typical of a non-linear transition state. The isotope effect on the relative efficiencies P_n of formation of products ($n = 5, X$ or 1) from the BR is related to the kinetic isotope effect by

$$\frac{P_n^0}{P_n'} = \frac{k_5^0}{k'_5} + P_n^0 \frac{k'_5 - k_5^0}{k'_n} \quad (4)$$

This is easily derived from the relationships $P_n^0 = k_n^0/(k_5^0 + k_X + k_1)$ and $P_n' = k_n'/(k_5' + k_X + k_1)$. Neglecting differences in Φ_{BR} we can estimate the efficiency of the hydrogen shift in the BR intermediate. With $P_5^0/P_5' = 2$ (Table 2) and $k_5^0/k_5^1 = 2.8$ we obtain $P_5^0 \approx 0.44$. Then, from the product ratio we find $P_X^0 \approx 0.13$. This implies that a significant fraction (43%) of the BR decays to triene, but since the efficiency of formation of the BR is very low this does not constitute an important decay channel of the excited *E*-triene.

3.3. Other irreversible rearrangements

There appear to be no significant isotope effects on the rearrangements of *Z*-2,5-dimethyl-1,3,5-hexatriene **2a** to bicyclohexenes **6** and methylenecyclopropanes **7**. We would expect to find small secondary isotope effects only. In these cases our measurements are not sufficiently accurate.

3.4. *E-Z* isomerization

Surprisingly large isotope effects are found in *E-Z* interconversion of the 2,5-di-*tert*-butylhexatrienes. The efficiencies of these processes are reduced by about 40% on deuteration. It is unlikely that a shortening of the excited state lifetime is responsible for this phenomenon, since the quantum yields of the ring closure processes are not lowered. The efficiency of *E-Z* isomerization relative to those of other processes seems to be determined in a very early stage of the evolution of the electronically excited state, competing modes of deformation leading *irreversibly* to different regions of the space of nuclear coordinates. The onset of *E-Z* isomerization involves an out-of-plane motion of the hydrogen atoms attached to the central C=C bond, in opposite directions. Such a deformation can be enhanced in the vertically excited state by an appropriate non-planar conformation of the triene. As we have proposed earlier [6], the out-of-plane motion which leads to a perpendicular excited state, giving rise to relatively efficient *E-Z* isomerization, competes with other deformations. For example, in *E*-trienes most excited molecules decay to a non-reactive near-planar relaxed species (*cf.* Fig. 4 in ref. 6), and in *cZc* trienes ring closure is the preferred pathway (*cf.* Table 2). Within this framework we can attribute the deuterium isotope effect on *E-Z* interconversion to the reduced frequencies of the initial deuterium out-of-plane motion compared with those of a hydrogen out-of-plane motion. As the twisting motion is slower a larger fraction of the excited molecules relaxes towards other decay channels.

As far as we are aware this is the first example of this type of kinetic isotope effect in photochemistry. It is completely different in nature from known isotope effects in thermal chemistry, which are mainly determined by the zero-point energy differences of initial and transition states.

If early dynamics are really so important for determining the fate of the excited species, then one might expect that the amount of excitation energy could play an important role, leading to wavelength-dependent photochemistry. Dramatic wavelength effects have indeed been observed in the photochemistry of hexatrienes, *e.g.* **2a**. However, we have shown that in the case of **2a** this is caused by selective excitation of rotamers, rather than by a dependence of the excited state properties on the excitation energy [4].

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