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PHOTOCHEMISTRY OF 2,5-DIMETHYL- AND 2,5-DI-*tert*-BUTYL-1,3,5-HEXATRIENES: CONFORMATION AND REACTIVITY — A QUANTITATIVE STUDY

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Summary

The quantum yields of isomerization upon direct irradiation at 254 nm of 2,5-di-*tert*-butyl- and 2,5-dimethyl-1,3,5-hexatrienes have been determined using a novel simulation method for the time evolution of the composition of the reaction mixture under irradiation. Two factors controlling the efficiency of photochemical rearrangements in 1,3,5-hexatrienes are identified: for certain bond-forming processes particular conformations are required, as dictated by the non-equilibration of excited rotamers principle; the efficiencies of *E-Z* interconversion and allylcyclopropene formation from *E*-trienes are enhanced by non-planarity.

1. Introduction

In the photochemistry of polyenes wide variations in efficiency of rearrangement are encountered. Some dienes and trienes have disappearance quantum yields of about 0.01 [1 - 3] or less [4]. In contrast, quantum yields up to 0.7 are found for vitamin D isomers [5, 6], in cyclic dienes and trienes [7, 8], and in the *E-Z* isomerization of rhodopsin to bathorhodopsin, the primary event in the photochemistry of vision, with a quantum yield of 0.67 [9]. With respect to their photochemistry the conjugated hexatrienes are probably the most thoroughly investigated polyenes [10 - 12]. Nevertheless, only a small amount of quantitative information concerning their photochemical reactivity and the factors controlling it is available.

We wish to report here on a quantitative study of the effect of the conformation of the trienes in the ground state on the efficiency of their photochemical rearrangements. For this purpose we compare quantum yield data

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Fig. 1. Photochemical reactions of 2,5-dimethyl-1,3,5-hexatrienes.

for the 2,5-di-*tert*-butylhexatrienes irradiated at 254 nm with data for the 2,5-dimethylhexatrienes [4, 13]. The isomerization pathways common to both systems are illustrated in Fig. 1 for the 2,5-dimethylhexatrienes. The trienes are drawn in the conformations which are the most stable [13, 14]: *tEt* for 1a and *cZt* for 2a.

In addition to the reversible interconversions of *E*-triene 1, *Z*-triene 2 and 1,3-cyclohexadiene 3, irreversible 4π electrocyclization of 1 and 2 to vinylcyclobutene derivatives 4 and formation of allylcyclopropene derivatives 5 are observed.

2. Methods

2.1. Syntheses

E-2,5-Di-*tert*-butyl-1,3,5-hexatriene (1b) was prepared by reduction of 2,2,3,6,7,7-hexamethyl-4-octyne-3,6-diol [15] with lithium aluminium hydride and subsequent dehydration using anhydrous copper(II) sulphate [16]. Sensitized isomerization with fluorenone afforded a mixture of 1b and the *Z* isomer 2b (about 1:9), from which the *E* isomer was removed by Diels–Alder reaction with 4-phenyl-1,2,4-triazoline-3,5-dione. Thermal isomerization of 2b yielded 1,4-di-*tert*-butyl-1,3-cyclohexadiene (3b). Compounds 1b and 2b are shown in Fig. 2 in their most stable ground state conformation, *cEc* and *cZc* respectively [14].

Fig. 2. Predominant conformations of the 2,5-di-*tert*-butylhexatrienes.

2.2. Determination of quantum yields

For each of the light-absorbing components in the reaction mixture the rate of conversion (expressed in terms of the concentration c) is

$$\frac{dc_i}{dt} = A \left(\sum_{i \neq j} \Phi_{ji} \alpha_j - \sum_{i \neq j} \Phi_{ij} \alpha_i \right) \frac{dI}{Vdt} \quad (1)$$

Here Φ_{ij} denotes the quantum yields of the reaction $i \rightarrow j$, dI/dt is the photon flow and V the volume of the sample. Rate equation (1) contains the fraction A of the incident light absorbed by the sample, and the fractional absorbances α . These are given by eqns. (2) and (3):

$$A = 1 - 10^{-\sum_p c_p \epsilon_p d} \quad (2)$$

$$\alpha_i = \frac{c_i \epsilon_i}{\sum_p c_p \epsilon_p} \quad (3)$$

Here we have assumed monochromatic irradiation for convenience. This is often preferable from an experimental point of view as well. The equations can easily be generalized for polychromatic irradiation.

The general kinetic equations expressed in eqn. (1) cannot be solved analytically except for special experimental conditions (explicit solutions for particular cases have recently been worked out: see ref. 17). A commonly used method is that in which dc/dt is made essentially constant by starting from the pure component i , implying $\alpha_i = 1$, and keeping the conversion so low that $\alpha_i = 1$ remains a valid approximation, while the fraction A of the incident light absorbed is constant. Determination of the quantum yields Φ_{ij} then only requires measurement of dc/dt for the starting material and each product (from linear regression of the concentration c vs. the irradiation time), the photon flow per unit volume dI/Vdt and A . We used this approach to determine the quantum yields of reactions of 1b and 3b, at less than 3% conversion.

Although eqn. (1) cannot be solved explicitly it can be used very easily to perform a numerical simulation of the time dependence of the composition of the multicomponent reaction mixture. Values of molar absorption coefficients at the wavelength of irradiation (or equivalent measures of the absorbance of the components) are now required. For a proper simulation the changes in the fractional absorbance α_i of each component over each time interval, in which dc/dt is assumed to be constant, must be sufficiently small. The same requirement applies to the light absorption A of the sample as a whole. To carry out the simulation we developed a computer program in TURBO PASCAL for use on an IBM (or compatible) personal computer. (The program is available from A.M.B. on request.)

The method presented here avoids the experimental problems associated with analyses at low conversion, facilitating accurate determination of the reaction rates.

3. Results

The quantum yields of the reactions of **1a** have been derived using the known quantum yields of the reactions of its *Z* isomer [13] and data from experiments in which the trienes were irreversibly converted for about 80% [4]. The final distribution of the products and the pseudostationary *E/Z* ratio were the criteria used to judge the correctness of the parameters involved in the simulation.

Similarly we carried out simulations of the evolution of the composition of the reaction mixture in the 2,5-di-*tert*-butylhexatrienes/1,4-di-*tert*-butylcyclohexadiene system. In this case the *Z* isomer **2b** could not be obtained in a pure form: it invariably contained its thermal isomerization product **3b**. Since the latter was easily purified and investigated spectroscopically, the UV absorption spectrum of the *Z*-triene could be obtained by deconvolution [13]. Irradiations of mixtures containing mainly the *Z*-triene **2b** and some cyclohexadiene **3b** were carried out up to about 25% conversion. At this stage the photoequilibration between the two was virtually complete. The simulation of this reaction, using the separately determined quantum yields of isomerizations of the *E*-triene **1b** and of the ring opening of the cyclohexadiene **3b**, allowed the simultaneous determination of the very small quantum yields of formation of the vinylcyclobutene **4b** and allylcyclopropene **5b** and the large quantum yield of formation of **3b** from the *Z*-triene **2b**.

The quantum yields determined are presented in Table 1.

TABLE 1

Quantum yields of formation of products at 254 nm

Starting material	Product					$\Sigma\Phi$
	1	2	3	4	5	
1a ^a		0.004	—	0.001	0.0001	0.005
1b		0.046	—	0.029	0.006	0.081
2a ^b	0.37		0.014	0.04	^c	0.42
2b	0.052		0.46	0.004	0.001	0.52
3b	—	0.54		—	—	0.54

^aSee ref. 4.

^bActually measured at 248 nm, see ref. 13.

^cLess than 0.005. This is an upper limit estimated from the lowest quantum yield that could be determined [13] and an estimate of the detection sensitivity of **5a**.

4. Discussion

The principle of non-equilibration of excited rotamers (NEER) [11] allows us to identify the ground state conformations that are required for

efficient production of certain products. The dramatic difference between the quantum yields for ring closure of the *E*-triene **1a** and **1b** to vinylcyclobutenes **4** is readily explained in the context of the NEER principle: **1b** exists predominantly in the *cEc* conformation, while in the mixture of conformational isomers of **1a** only small amounts of cisoid rotamers are present. One *s*-cis linkage is clearly required for the electrocyclic process. Similar considerations apply to the 6π electrocyclization of *Z*-trienes: **2b**, obviously existing mainly in the *cZc* conformation [13, 14], is well suited for conversion to the cyclohexadiene **3b**, while **2a**, which exists predominantly as the *cZt* rotamer [13], is not.

Although *s*-cis rotamers predominate in **1b** (*cEc*) and in **2a** (*cZt*) the quantum yields of the 4π electrocyclic ring closure are quite low. Theoretical calculations [18 - 20] on the parent system *s*-cis-1,3-butadiene have revealed the presence of a small barrier on the surface of the excited state leading to cyclobutene. Deuterium isotope effects [14] are in accord with the existence of such a barrier in the case of the 2,5-dimethyl- and di-*tert*-butylhexatrienes. Clearly this renders the ring closure too slow to compete effectively with other modes of deformation of the initially prepared excited state, which lead to other reactions or to decay to the ground state.

The quantum yields for the 6π cyclization of **2b** and of the *cZc* rotamer of **2a** (selectively excited at 303 nm [13], $\Phi = 0.42$) are similar to those reported for conformationally restricted cyclic *cZc* trienes [7]. The ground state structure of the *cZc* rotamers is probably helical. The interaction of the p_z lobes at the terminal carbon atoms, revealed by the significant red shift of the origin of the absorption band [7, 10, 14], allows easy formation of the new C—C bond. The high quantum yield, with the concomitantly reduced yields of other processes (notably *Z*—*E* isomerization), suggest that the 6π electrocyclization occurs rapidly, not hampered by a significant potential energy barrier.

E—*Z* interconversion and the formation of allylcyclopropene derivatives **5** are, in principle, possible in any conformation. It is of particular interest to see how the ground state conformation affects the efficiencies of these conformationally unrestricted processes. It turns out that in *E*-2,5-dialkylhexatrienes both reactions are significantly enhanced when the conformation is changed from predominantly *tEt* (**1a**) to *cEc* (**1b**). A similar phenomenon was observed in a series of *E*-2-methyl-5-alkyl-1,3,5-hexatrienes, in which the reactivity increases with increasingly bulky 5-alkyl groups, that is with an increasing proportion of non-planar *cEt* rotamers present in the ground state equilibrium [4, 14]. The photoisomerization of trienes to allylcyclopropenes will not be discussed in detail here. However, it is of interest to note that in the present work we show for the first time that allylcyclopropenes can originate both from *E*- and *Z*-trienes [4, 14].

The planar *tEt* hexatrienes such as **1a** can be compared with *E*-1,3,5-hexatriene. The modes of deformation active in the vertically excited state of *E*-hexatriene have been derived from the vibrational structure of the UV absorption spectrum [21, 22] and from the pre-resonance Raman spectrum

[23]. It was concluded that only in-plane displacements are coupled to the electronic transition, showing that the vertically excited species deforms to a stable planar structure, close to the initially prepared state. In simple alkenes, however, there is a spontaneous twist in the S_1 state [24]. Recent calculations [25] support the qualitative notion that accommodation to the excitation by in-plane distortion (mainly changes in the bond lengths) is more facile as the chain length is increased.

Thus, planar hexatrienes such as **1a** and the parent hexatrienes [2] remain planar in the 1^1B_u excited state, and show surprisingly little photochemical reactivity. However, the lack of fluorescence [26] (all our attempts to observe fluorescence of 2,5-dialkylhexatrienes in hydrocarbon glasses at 77 K were unsuccessful) points to a rapid decay of the excited state. The large line width of the vibrational bands in the electronic absorption spectrum measured in a supersonic jet may be due to a very short lifetime of the Franck-Condon state [22]. From the observation of concentration-dependent behaviour in the photochemistry of 2,5-dialkylhexatrienes [4] and dienes [1] it has been concluded that long-lived species are probably formed upon direct excitation. In view of the very low quantum yields of isomerization, intersystem crossing to the lowest triplet state, which is known to lead to relatively efficient *E-Z* interconversion, can be excluded.

We propose the following hypothetical explanation, which accounts for the observations mentioned above. Let us assume that the 2^1A_g state is energetically below the 1^1B_u state in all all-trans planar polyenes [27 - 29], with an energy gap which decreases with decreasing chain length. Internal conversion from the initially prepared 1^1B_u to the 2^1A_g state could then become very rapid in hexatriene and even more so in butadiene [22], causing uncertainty broadening of the absorption bands. The 2^1A_g species cannot rapidly decay by fluorescence because the radiative transition to the ground state is forbidden. If this conjecture is true a long-lived transient species should exist, detectable by absorption spectroscopy, probably at quite a long wavelength. To our knowledge no attempts to detect such a transient have been reported.

In contrast to **1a** the non-planar **1b** has immediate access to out-of-plane motions, enabling more efficient photochemical reaction. Twisting of the central double bond (which, at an early stage, involves nothing more than a hydrogen out-of-plane motion [30]) in the non-planar excited state is driven by the increased bond order of the formerly single bonds. The consequences of the availability of out-of-plane distortions are demonstrated nicely in the UV absorption spectra displayed in Fig. 3.

The diffuse shape of the spectrum of **1b** is presumably caused by the activity of vibronic transitions corresponding to low-frequency modes. Model calculations of 1,3-butadiene [31] exemplify the relationship between the shape of the surface of the excited state and the appearance of the UV absorption spectrum.

The quantum yields of reaction of **1b** are greater by at least an order of magnitude than those of **1a**. Still, the disappearance quantum yield of

Fig. 3. UV absorption spectra of *E*-2,5-dimethylhexatriene 1a and *E*-2,5-di-*tert*-butylhexatriene 1b.

1b is not large. A tentative explanation can be put forward. If the vertically excited species decays irreversibly to structures of lower energy on the excited state surface, then the initial gradients of the potential energy along various internal coordinates will be decisive for the choice among reaction paths. The antibonding interactions introduced into the 6π system by $1\ ^1A_g \rightarrow 1\ ^1B_u$ excitation are mainly localized at the central bond, and will provide a driving force for twisting and for changes in bond lengths. In a (near-)planar geometry the initial gradient along the torsional coordinate is quite small compared with the gradients along the bond lengths. Thus, the system is pushed towards a metastable (near-)planar geometry and not towards the twisted minimum, even though the latter may represent a deeper well in the potential energy surface. The twisted minimum may well be inaccessible from the near-planar geometry. This concept, schematically depicted in Fig. 4, is corroborated by the results of semiempirical calculations of Dinur *et al.* [31] on butadiene. These workers have shown that a significant energy gain is obtained by twisting one of the double bonds of butadiene at fixed bond lengths, whereas a barrier to twisting arises when relaxation of the bond lengths is allowed.

Although a non-planar initial geometry certainly helps to increase the out-of-plane gradient, an additional driving force appears to be required for efficient *E-Z* interconversion in hexatrienes and longer polyenes. Steric hindrance (see below) or environmental interactions (*e.g.* in retinal-proteins) may serve this purpose.

Irrespective of the electronic nature of the relaxed (near-)planar excited state the identification of its radiationless decay channel remains a central

Fig. 4. Schematic representation of the potential energy as a function of two modes of deformation in an alkene (polyene).

issue in the study of the excited state behaviour of trienes and other polyenes. It is worthwhile to continue these investigations looking for more reactive *E*-trienes. *E*-3-*tert*-Butylhexatriene may be an interesting candidate [32].

The *Z*-trienes **2a** and **2b** are significantly distorted from planarity, with the expected consequences for their UV band shapes and photochemical reactivity [13]. Twisting of the central double bond provides a massive relief of steric strain in the vertically excited state, whatever its nature, 2^1A_g - or 1^1B_u -like. This is undoubtedly the cause of the high quantum yield of *Z*-*E* isomerization of *cZt*-**2a**. The *cZc* species **2b** and the *cZc* rotamer of **2a** [13] show less efficient *Z*-*E* isomerization, probably because the very efficient ring closure constitutes the major decay channel to the ground state surface.

5. Experimental details

5.1. Syntheses

Intermediate products in the syntheses were characterized by ^1H NMR spectrometry using a Jeol PS100 spectrometer operating at 100 MHz. A mixture (1:1) of CDCl_3 and CCl_4 was used as solvent, tetramethylsilane ($\delta = 0$) as internal reference. Detailed spectroscopic studies of the trienes are reported elsewhere [14].

1b was prepared as follows. Treatment of acetylene–dimagnesium bromide (from ethylmagnesium bromide and ethyne) with 3,3-dimethylbutan-2-one afforded 2,2,3,6,7,7-hexamethyl-4-octyne-3,6-diol (melting point, $81 - 82^\circ\text{C}$ — ^1H NMR δ 1.95, OH; 1.44, CH_3 ; 1.06, *t*-Bu). This diol (2.9 g, 0.013 mol) was added in small portions to a magnetically stirred solution of LiAlH_4 (1 g, 0.025 mol) in dry tetrahydrofuran (THF) (100 ml) as quickly as permitted by the foaming caused by hydrogen evolution. The flask was tightly stoppered. After stirring overnight the mixture was cautiously quenched by dropwise addition of a small amount of water, just

enough to decompose the aluminate intermediate and to destroy the excess hydride. This left a clear THF solution and a crystalline precipitate. Filtration, washing of the residue with ether and evaporation of solvents under reduced pressure gave *E*-2,2,3,6,7,7-hexamethyl-4-octene-3,6-diol (^1H NMR: 5.87, CH; 1.28, CH_3 ; 0.98, *t*-Bu). For dehydration, three bulbs were fitted together and placed in a bulb-to-bulb distillation apparatus. The first contained the diol (2 g, 0.009 mol) and CuSO_4 (1.0 g), the second CuSO_4 (0.5 g) and the third a few crystals of hydroquinone. Pressure was reduced to 12 mm and the first bulb heated gradually to 120 °C. When a distillate formed in the second bulb, this bulb was also moved into the heating compartment. When no more distillate formed in the collecting bulb the apparatus was cooled and dismantled. The organic distillate was carefully removed from the water that had co-distilled, with the aid of a small amount of *n*-pentane. Pure 1b was obtained by filtration of the pentane solution over SiO_2 , and removal of the solvent. The product yield after reduction and dehydration was 61%.

For the fluorenone-sensitized isomerization, an argon-purged solution of fluorenone (0.25 g) and 1b (0.25 g) in *n*-pentane (100 ml) was irradiated at 350 nm, using four Sylvania F8T5 lamps, for about 10h. An equilibrium mixture containing about 90% 2b was obtained. After filtration of the solution over SiO_2 (0.2 - 0.5 mm) and evaporation of the solvent the residue was taken up in acetone (2 ml) and treated with a solution of 4-phenyl-1,2,4-triazoline-3,5-dione (about 10 mg) in acetone (1 ml). After concentration the solution was filtered over SiO_2 with pentane. Gas chromatography evinced the removal of 1b. The thermal isomerization of 2b to 3b was accomplished by preparative gas chromatography (GC) (6 m 20% squalane on Chromosorb) at 140 °C. The cyclohexadiene has a longer retention time than its isomers and was easily obtained in high purity (99.3%) (UV (cyclohexane) $\lambda_{\text{max}} = 263 \text{ nm}$, $\epsilon = 9000 \text{ l mol}^{-1} \text{ cm}^{-1}$).

5.2. Quantum yield measurements

Essentially monochromatic light at 254 nm was obtained from a Rayonet low pressure mercury lamp combined with a chlorine filter [33]. The samples, about 2.5 ml of 0.005 M solutions in spectroscopic grade cyclohexane (Merck), were stirred magnetically in a quartz cuvette of path length 1 cm. The photon flow was repeatedly measured using Actinochrome R 248/334 (from Photon Technology) [34]. It was typically $7 \times 10^{-10} \text{ einsteins s}^{-1}$ on an area of about 1 cm^2 . GC analyses of the reaction mixture, on a 25 m Alltech RSL-150 column, could be carried out at 60 °C without measurable disturbance by the conversion of 2b to 3b. The retention time of 2b was about 11 min.

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