Photochemistry of 2,5-dimethyl- and 2,5-di-tert-butyl-1,3,5-hexatrienes. Conformation and reactivity. A quantitative study
Brouwer, A.M.; Cornelisse, J.; Jacobs, H.J.C.

Published in:
Journal of Photochemistry and Photobiology A-Chemistry

Citation for published version (APA):
PHOTOCHEMISTRY OF 2,5-DIMETHYL- AND 2,5-DI-tert-BUTYL-1,3,5-
HEXATRIENES: CONFORMATION AND REACTIVITY — A
QUANTITATIVE STUDY

A. M. BROUWER†, J. CORNELISSE and H. J. C. JACOBS‡

Gorlaeus Laboratories, Leiden University, Department of Chemistry, P.O. Box 9502,
2300 RA Leiden (The Netherlands)

(Received July 16, 1987)

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 deter-
mined using a novel simulation method for the time evolution of the compo-
sition of the reaction mixture under irradiation. Two factors controlling the
efficiency of photochemical rearrangements in 1,3,5-hexatrienes are identi-
fied: 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 photo-
chemical reactivity and the factors controlling it is available.

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

†Present address: Laboratory for Organic Chemistry, University of Amsterdam,
Nieuwe Achtergracht 129, 1018 WS Amsterdam, The Netherlands.
‡Author to whom correspondence should be addressed.
Fig. 1. Photochemical reactions of 2,5-dimethyl-1,3,5-hexatrienes.

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

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

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

Here $\Phi_{ij}$ 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 $\alpha$. These are given by eqns. (2) and (3):

$$A = 1 - 10^{-\frac{c_i e_i e_p d}{C_p e_p}} \quad (2)$$

$$\alpha_i = \frac{c_i e_i}{\sum_p c_p e_p} \quad (3)$$

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 $Q_i = 1$, and keeping the conversion so low that $Q_i = 1$ remains a valid approximation, while the fraction $A$ of the incident light absorbed is constant. Determination of the quantum yields $\Phi_{ij}$ 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 $\alpha_i$ 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 la 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>
<thead>
<tr>
<th>Starting material</th>
<th>Product</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>ΣΦ</th>
</tr>
</thead>
<tbody>
<tr>
<td>laa</td>
<td>0.004</td>
<td>-</td>
<td>0.001</td>
<td>0.0001</td>
<td>0.005</td>
<td></td>
</tr>
<tr>
<td>lb</td>
<td>0.046</td>
<td>-</td>
<td>0.029</td>
<td>0.006</td>
<td>0.081</td>
<td></td>
</tr>
<tr>
<td>2ab</td>
<td>2b</td>
<td>0.37</td>
<td>0.014</td>
<td>0.04</td>
<td>c</td>
<td>0.42</td>
</tr>
<tr>
<td>2b</td>
<td>0.052</td>
<td>0.46</td>
<td>0.004</td>
<td>0.001</td>
<td>0.52</td>
<td></td>
</tr>
<tr>
<td>3b</td>
<td>-</td>
<td>0.54</td>
<td>-</td>
<td>-</td>
<td>0.54</td>
<td></td>
</tr>
</tbody>
</table>

*See 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 $6\pi$ electrocyclization of $Z$-triienes: 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 $4\pi$ 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 $6\pi$ 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 $6\pi$ 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 $Z$-triienes \[4, 14\].

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
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-\textit{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 \( 6\pi \) system by \( 1\text{ }^1\text{A}_g \rightarrow 1\text{ }^1\text{B}_u \) 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 \textit{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
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 \( E \)-triienes. \( E \)-3-\( \text{tert} \)-Butylhexatriene may be an interesting candidate [32].

The \( Z \)-triienes \( 2a \) 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 \( Z \rightarrow E \) isomerization of \( cZt-2a \). The \( cZc \) species \( 2b \) and the \( cZc \) rotamer of \( 2a \) [13] show less efficient \( Z \rightarrow E \) 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 \(^1\text{H} \) 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, tetramethysilane (\( \delta = 0 \)) as internal reference. Detailed spectroscopic studies of the trienes are reported elsewhere [14].

1b was prepared as follows. Treatment of acetylene-dimagnesium bromide (from ethymagnesium 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 °C - \(^1\text{H} \) NMR \( \delta \) 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. Filtra-
tion, 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 \( (^1H \text{NMR: 5.87, CH; 1.28, CH}_3; 0.98, t\text{-Bu}) \). For dehydration, three bulbs were fitted
together and placed in a bulb-to-bulb distillation apparatus. The first con-
tained 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 \( \text{SiO}_2 \), 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 solu-
tion over \( \text{SiO}_2 \) (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 \( \text{SiO}_2 \) with pentane. Gas chromatography
evined the removal of 1b. The thermal isomerization of 2b to 3b was ac-
complished 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 (cyclo-
hexane) \( \lambda_{\text{max}} = 263 \text{ nm, } \varepsilon = 9000 \text{ l mol}^{-1} \text{ cm}^{-1} \)).

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 cyclo-
hexane (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.

References

1 S. Boué, D. Rondelez and P. Vanderlinden, in B. Pullman and N. Goldblum (eds.),
126

8 A. Gottlieb, *Ph.D. Thesis*, University of California, Berkeley, 1985, cited in ref. 3.