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WAVELENGTH EFFECT ON THE PHOTOCHEMICAL REACTIONS OF *(Z)*-2,5-DIMETHYL-1,3,5-HEXATRIENE: SELECTIVE EXCITATION OF ROTAMERS.

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The UV absorption spectrum of Z-2,5-dimethyl-1,3,5-hexatriene 1 is typical of a cZt triene, but the long wavelength tail indicates the presence of the (minor) cZc rotamer. The sudden change in the photoreactivity of 1 around 290 nm is in agreement with selective excitation of these rotamers. No indication is obtained for an intrinsic excitation energy dependence of the photoreactivity of the individual rotamers.

Selective excitation of different ground state rotamers has been invoked by several authors to explain the wavelength dependent photochemistry of conjugated hexatrienes [1]. In an earlier study the dramatically different photochemistry of Z-2,5-dimethyl-1,3,5-hexatriene 1 at 254 nm and 313 nm [1a] was attributed to selective excitation of its cZt and cZc rotamers. These results confirmed that no equilibration between rotamers occurs in the excited state (NEER-principle [2]). Unfortunately no independent evidence has hitherto been presented for the actual occurrence of the two rotamers.

Little is known about the population of rotamers in conformational equilibrium mixtures of trienes. The properties of the individual rotamers are not well known either. Therefore the occurrence of *exclusive* conformational control could not be demonstrated and additional (or alternative) causes of the wavelength effect have been considered, in particular the involvement of different electronically or vibrationally excited states. This would imply violation of the rules of Kasha and Vavilov, extended to photochemical reactions [3]. Not many indisputable examples of such violations are known [3,4]. In general, the photoreactions have to be very fast in order to compete successfully with internal conversion. Some of the reactions of dienes and trienes may fulfil this requirement [5].

Dauben and Phillips [1e] studied the wavelength dependence of the quantum yields of the photochemical reactions of previtamin D_3. A rather sudden change in the quantum yields of ring closure to lumisterol and 7-dehydrocholesterol (Provitamin D_3) was observed in a small wavelength region at the long wavelength tail of the absorption band of previtamin D. The authors argued that it would be unlikely that the relative extinction coefficients of the cZt and cZc rotamers, thought to be predominantly responsible for Z-E isomerization and ring closure reactions, respectively, would change so drastically in so small a wavelength range. It was therefore concluded that excited state properties are responsible for the wavelength effect. A similar conclusion had been reached earlier in the case of Vitamin D [1d].

As part of an extensive study [6] of the photochemistry of 2,5-dialkyl-1,3,5-hexatrienes we have reinvestigated the wavelength effect on the photochemistry of Z-2,5-dimethyl-1,3,5-hexatriene 1 in n-pentane. Product distributions (representing relative quantum yields) were measured at low conversion, and extrapolated to zero conversion, at wavelengths between 248 and 313 nm. The results are shown in Figure 1. Absolute quantum yields, determined at three wavelengths, are listed in the table.

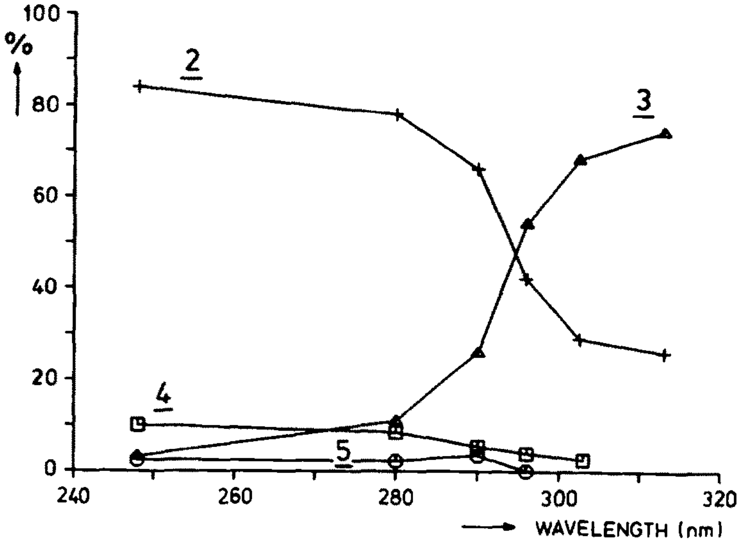

Figure 1 . Distribution of photochemical reaction products of 1.

Ø	wavelength (nm) 248	290	303
1→2	0.37	0.35	0.19
1→3	0.014	0.14	0.42
1→4	0.04	0.03	--
1→5	0.01	0.02	--

Table. Quantum yields of reactions of 1.

It is seen that at short wavelength Z-E isomerization yielding E-2,5-dimethyl-1,3,5-hexatriene 2 is the major process, while at longer wavelength ring closure to 1,4-dimethyl-1,3-cyclohexadiene 3 is more efficient, in agreement with earlier results [1a]. Dramatic changes in the product distribution occur around 290 nm, reminiscent of the behaviour of previtamin D [1e]. The relative yields of 1-methyl-3-(2-propenyl)cylobutene 4 and 1-methylene-2-(2-methyl-1-propenyl)cyclopropane 5 decrease in parallel to that of 2 . This suggests that they have a common precursor, namely the cZt rotamer. A plausible reaction scheme, which incorporates earlier results [1a], is shown in Figure 2.

The quantum yields are quite high, in contrast to those of 2 [6b,7] or of E- and Z-1,3,5-hexatriene [8]. The steric strain present in the ground state of 1 can be relieved after excitation by twisting of the weakened central double bond. This initial deformation, which seems not to occur in planar hexatrienes [6b,9], appears to be important for efficient Z-E isomerization.

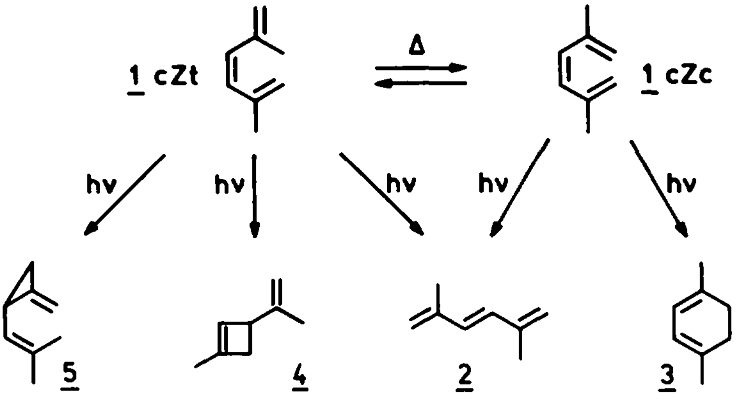

Figure 2. Photochemical reactions of the rotamers of 1.

Simultaneously we have addressed the problem of ground state conformational isomerism in 1. Although NMR data [7] do not allow quantitative conclusions, they provide strong indications for the presence of cZt and cZc rotamers, the former being the more abundant. IR and Raman spectra of 1 [7] show a large number of bands compared to those of the highly symmetrical 2 [10]. This points to the occurrence of multiple or at least asymmetrical species, but the interpretation is far from straightforward. Attempts to determine the structures and energies of stable ground state rotamers using the semi-empirical theoretical methods MNDO and QCFF/PI, were unsuccessful. The presence of several intimately coupled 'soft' modes of deformation (single bond twisting, angle bending) precludes the reliable localization of true minima on the potential energy surface [11].

In order to obtain insight into the characteristic spectroscopic properties of simple alkylated cZt and cZc trienes we prepared Z-2-t-butyl- and Z-2,5-di-t-butyl-1,3,5-hexatrienes 6 and 7 [6b,7]. Their UV absorption spectra are shown together with that of 1 in Figure 3. NMR studies [7] confirm our expectations with regard to the ground state conformation of these compounds.

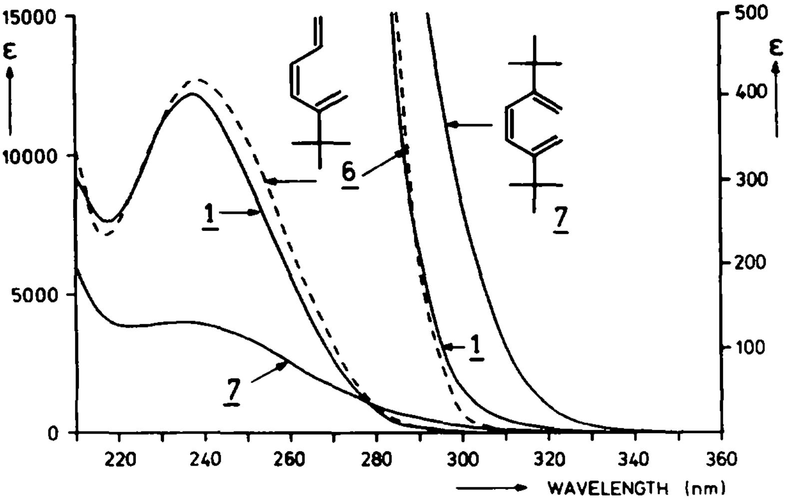

Figure 3. UV absorption spectra of Z-hexatrienes 1, 6 and 7.

Although one should keep in mind that conformations of different compounds that have the same conformational label (cZt or cZc) may still differ considerably in details of their geometries, the comparison clearly shows that 1 exists predominantly as the cZt rotamer. The long wavelength tail is attributed to the cZc rotamer. In view of the warning expressed above no attempt should be made to draw quantitative conclusions. Still, it is striking that the UV absorption spectrum of 1 can be simulated quite well by combining the spectra of 6 and 7 in a ratio of 9 to 1.

The relative extinction coefficients of 6 and 7 change drastically around 290 nm. At longer wavelength the ratio of absorbances of these species is doubled every 5 nm. Clearly the minor cZc rotamer of 1 is only excited to a significant extent at the long wavelength edge of the absorption spectrum, which explains the photoreactivity spectrum of 1 shown in Figure 1. For the case of previtamin D the change in relative extinctions of rotamers should be more rapid if selective excitation of rotamers would be the only cause of the wavelength effect reported by Dauben and Phillips [1e].

Z-2,5-di-t-butylhexatriene 7 undergoes efficient ring closure to the corresponding cyclohexadiene at 254 nm, little Z-E isomerization and undetectable vinylcyclobutene formation [6b,12], just like 1 when irradiated at long wavelength.

In conclusion our results establish the validity of the reaction scheme of Figure 2. There is no need to assume intrinsic dependence on the excitation energy of the photoreactivity of the individual rotamers in order to explain the observed wavelength effect.

EXPERIMENTAL SECTION [7]

Z-2,5-dimethyl-1,3,5-hexatriene was prepared following known procedures [7,13]. For irradiations degassed 0.01 M solutions in spectroscopic grade n-pentane (Janssen Chimica or Aldrich) were prepared in the reaction flask, a quartz cell of 1 cm pathlength. The solutions were stirred magnetically. Monochromatic light was obtained from a 1000 W Xe/Hg lamp (Hanovia) fitted with an Oriel grating monochromator (band width 5 nm) [13a]. The light was focussed on a small spot in the center of the reaction flask with the aid of quartz lenses. Light intensity was measured using Actinochrome R (248/334) (Photon Technology) [14]. Quantitative analysis was carried out by GLC (Hewlett Packard 5750, Alltech RSL-150 column (OV-101-like)). The conversion was less than 5 %. For UV spectroscopy a Cary 219 spectrometer was employed.

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