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INFLUENCE OF WAVELENGTH ON THE PHOTOCHEMISTRY OF E- AND Z-HEXA-1,3,5-TRIENES

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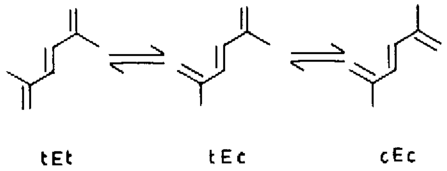
In order to understand why with conjugated trienes the nature and the relative amounts of the various photoproducts seem to parallel the composition of the conformational equilibrium one may have recourse to the old idea of non-interconversion of the species originating upon $\pi \rightarrow \pi^*$ excitation of the s-trans and s-cis conformers of such molecules.[1-3] Predictions along this line have proven to be remarkably effective e.g. in the vitamin D field.[4-8]

An alternative would be to assume that equilibration between excited conformers occurs all right, and that the ensuing equilibrium composition is similar to that of the ground state, the factors governing the equilibrium being comparable in the two states. If one makes the additional assumption that the rates of product formation from the various excited conformers are not too different then the conformational equilibrium in the excited state will result in a product composition that is similar to the one predicted from the ground state conformational equilibrium.

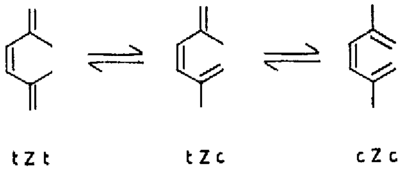
In a previous publication[4] it was indicated that discrimination between the original hypothesis of non-interconversion of rotamers upon excitation and the alternative mentioned may be arrived at by careful analysis of the influence of variation of wavelength on product composition. In the case of non-equilibration of rotamers in the $\pi \rightarrow \pi^*$ excited singlet state the product composition should reflect the relative amounts of the various conformers in the ground state and their extinction coefficients. However if the electronically excited conformers do interconvert and reach a quasi-equilibrium then there should be no or little influence of λ_{irr}

Now it has to be realised that wavelength-dependent product composition need not necessarily be the result of the effect considered here, but may also originate from other causes, e.g. from the photosensitivity of the product components in combination with the often strongly different ratios of their extinction coefficients at various wavelengths. This effect has been known for a long time in the photochemistry of the pro- and previtamins D where it appears to be largely responsible for the synthetically important feature that upon irradiation of ergosterol at λ > 300 nm a considerable yield of lumisterol is obtained whereas at shorter wavelengths the amount of this compound in the reaction mixture is practically negligible. In order to distinguish between the alternative assumptions mentioned above one should therefore determine the product composition as a function of time and at low degrees of conversion. Extrapolating towards zero time then may give the required information.

I



II



In this publication we report the results of an extended investigation of the E/Z-isomeric 2,5-dimethyl-1,3,5-hexatrienes (I and II). These compounds were chosen because they represent the simplest hexatriene where the conformational equilibrium may be expected to contain significant amounts of each of the three more or less planar conformers.[2] Moreover the symmetrical structure reduces the number of possible photoisomers, facilitating the often difficult analyses of the irradiation mixtures. Lastly the methyl groups may be assumed to have little direct influence on the triene chromophore (of course these groups have an indirect effect through steric crowding resulting in non-planarity of the chromophore in a number of conformations).

Irradiations of the carefully purified isomers[9] were carried out with solutions in pentane (conc. 2-5 g/l; temp. 18° C) at 313 nm and at 254 nm (suitably filtered radiation from HBO 1000 W and Hanau TNN 15/32 mercury lamps, respectively). Samples were taken at regular time intervals and analysed by GC (20 m x 0.4 mm capillary column coated with squalane; column temp. 50° C; Vidar 6300 Digital Integrator). Table I gives the percentages of the various photopro-

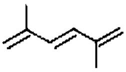
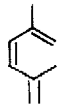
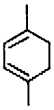
PRODUCTS	Z - TRIENE		E - TRIENE	
	313 NM	254 NM	313 NM	254 NM
	1.13	8.05		
			6.23	4.55
	0.01	0.93	0.59	3.50
	8.85	0.75	0.34	0.15
	0.01	0.27	—	0.54
X	—	—	—	0.20

Table I.
Composition (in %) of the irradiation mixtures of E- and Z-2,5-dimethyl-1,3,5-hexatriene at 10% conversion.

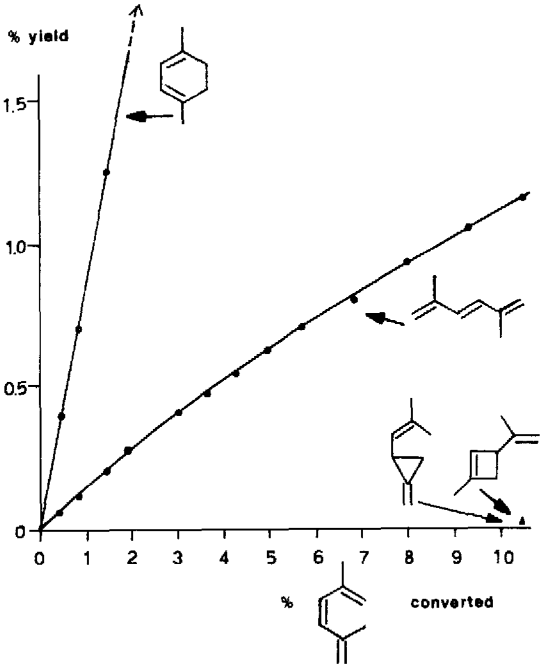


Fig. 1. Irradiation of Z-2,5-dimethyl-1,3,5-hexatriene at λ 313 nm.

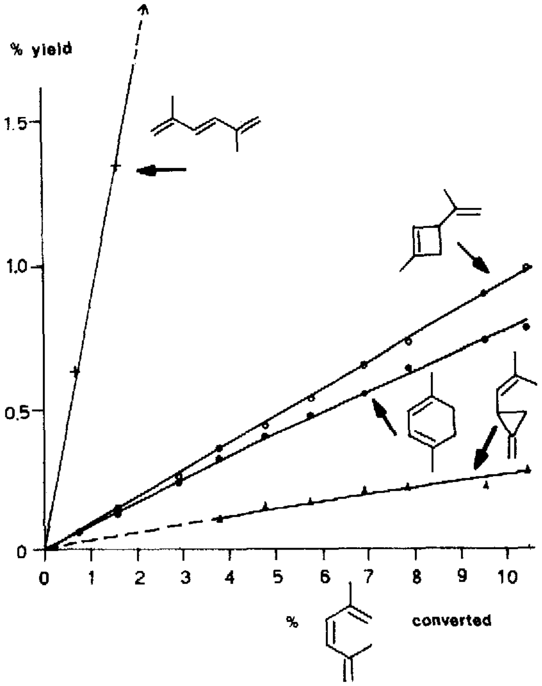


Fig. 2. Irradiation of Z-2,5-dimethyl-1,3,5-hexatriene at λ 254 nm.

ducts present after 10% conversion of starting material. Figures 1 and 2 illustrate for the Z-isomer the composition of the irradiation mixture at increasing degrees of conversion.

The results disclose a pronounced influence of the wavelength of irradiation on the ratios of products formed. In the case of the Z-hexatriene photocyclization to the cyclohexadiene is the major process and there is relatively little Z→E isomerization when radiation of λ 313 nm is used. At λ 254 nm the situation is reversed, Z→E isomerization being the strongly predominant process.

With the E-hexatriene the influence of wavelength of irradiation on product composition is also striking, but here the picture is complicated by the effect mentioned earlier; the rate of photoreaction of the E-isomer is much slower (10-100 times, depending on the wavelength used) than that of some of its photoproducts, notably the Z-isomer. Even at very low degrees of conversion this leads to a product composition that can not be interpreted in a straightforward manner. However, extrapolation to zero time clearly shows that upon irradiation both at 313 nm and at 254 nm the E-hexatriene gives rise to the Z-isomer and the vinylcyclobutene as primary photoproducts. Formation of the latter compound is in agreement with recent findings.[7] Short wavelength irradiation, however, gives an additional as yet unidentified isomer X, also produced directly from the E-hexatriene and probably originating from a higher excited state.

The clearcut effects of λ_{irr} on the formation of primary photoproducts from these simple hexatrienes is difficult to reconcile with the occurrence of an equilibrium between rotamers in the excited singlet state.[10] It seems reasonable therefore to drop this alternative hypothesis and retain the old line of thought implying the non-equilibration of rotamers upon excitation.[1] This however does not yet prove that product composition is governed solely by the composition of the ground state equilibrium of conformers in conjunction with their extinction coefficients at the wavelengths of irradiation. In order to conclude on this point one should know the absorption curve of each of the separate conformers, and preferably also determine the conformational equilibrium by an independent method (e.g. NMR). Occasionally one encounters the view that the absorption of the curled cZc form is shifted to longer wavelengths compared to that of the tZt hexatriene rotamer. However as far as we can see there are no experimental data or calculations of sufficient exactness to warrant such a conclusion where in practice we have to do with sterically crowded non-planar conformers.

Therefore we have to leave open the question whether the different ratios of light absorption at the two wavelengths by the individual conformers are the main cause for the observed phenomena. One should certainly also consider the possibility that the pathways and pattern of relaxation of one and the same conformer may strongly depend on the energy of the absorbed light quantum, resulting in wavelength dependency of photoproduct composition.[12,13]

At this stage the following conclusions can be formulated.

1) The old hypothesis of the non-equilibration of $\pi \rightarrow \pi^*$ excited rotamers of conjugated trienes now seems to be satisfactorily established.

2) The preceding conclusion implies that the conformational equilibrium in the ground state is reflected in the photoproduct composition, each type of rotamer upon excitation yielding its own specific product(mixture).

3) Variation of product composition as a result of variation of wavelength of irradiation will occur as a consequence of point 2), the absorption curves of the various rotamers generally being different. Besides, one and the same conformer may yield different products upon excitation by light quanta of different energy. Probably both effects will be operative, their relative importance varying with the structure of the compound exposed to irradiation.

Notes and References

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9. The E-isomer contained no detectable impurity (GC). The Z-isomer could not be obtained without a trace (< 0.3%) of the cyclization product 1,4-dimethylcyclohexa-1,3-diene.
10. In a communication on the photochemistry of 2,6-dimethylhepta-1,3,5-triene Courtot and Rumin report substantial differences in the composition of the mixtures obtained by irradiation at λ 254 nm and λ > 280 nm (ref. 11). Probably analysis of the composition at varying low degrees of conversion will indicate a situation analogous to the one described in this publication.
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