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PHOTOCYCLIZATION OF AN (E) -HEXA-1,3,5-TRIENE

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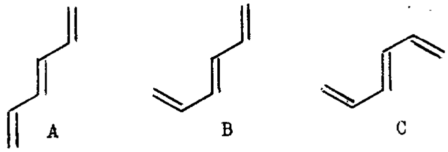
In the course of our studies on the photoreactions of simple hexatrienes[1] as well as in our recent study on the formation of so-called toxisterols and other products resulting from the irradiation of the Z/E isomeric previtamin D/tachysterol system[2] the question arose whether 'trans'-hexatrienes (i.e. (3E)-1,3,5-trienes) would have the capacity to undergo photocyclization. If one takes the conformational equilibrium in the ground state as a basis one would expect cyclobutene formation to occur, be it with a small quantum yield. Whereas the tEt conformation (A) certainly predominates in the mixture of conformers, and the cEc form (C) will be present to a small percentage only, the tEc form (B) may well occur to an extent that allows formation of a vinylcyclobutene in measurable quantity. In this paper we wish to report experimental evidence in support of this line of thought. Since an additional 2-alkyl group may be expected to increase the proportion of the tEc form, the experiments were carried out with (E)-2-methyl-1,3,5-hexatriene.



In a typical experiment a solution containing 2.9 g/l (E)-2-methyl-1,3,5-hexatriene in pentane was irradiated with light of λ ∿ 300 nm (mercury lamp, Bausch & Lomb monochromator). At regular intervals samples were taken and analysed by GC (35 m x 0.5 mm capillary column coated with OV-101). Some results are presented in Figure 1.

The figure clearly shows that in addition to the Z-isomer the methyl vinylcyclobutene is directly formed from the photoexcited E-triene. Other products (the bicyclohexene and the allene) evidently are formed only after a certain time-lag during which the proportion of the (Z)-hexatriene has increased to an appreciable level.

It can be concluded that (E)-2-methyl-1,3,5-hexatriene upon irradiation yields the Z-isomer and the cyclobutene derivative, the latter most probably originating from the tEc form (B). The Z-triene in turn yields the E-isomer, the bicyclohexene, the allene and the vinylcyclobutene (cf. ref. 1).

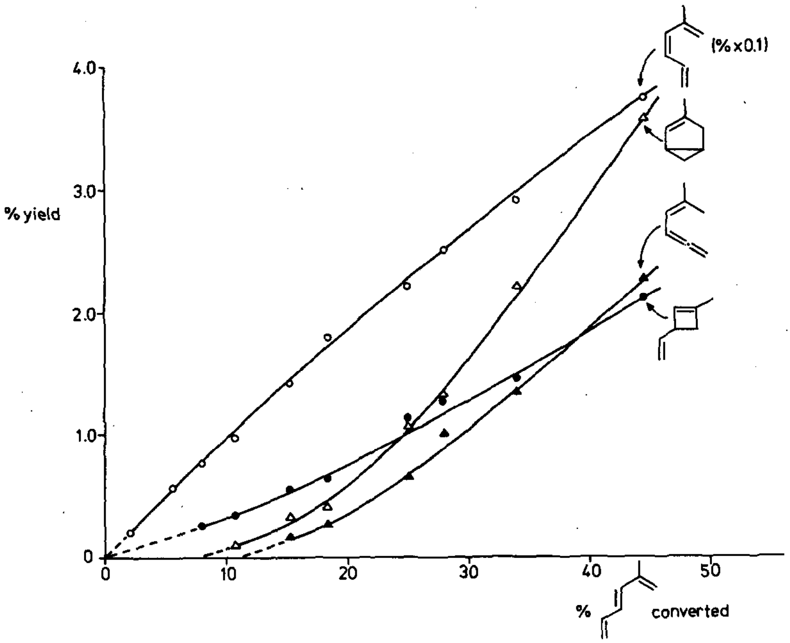


Fig. 1. Irradiation of (E)-2-methyl-1,3,5-hexatriene at $\lambda \sim 300$ nm

For the sake of completeness it should be added that the sensitive GC method used allowed to trace also a few very minor products. These possibly are cyclobutenes, bicyclohexenes and other products originating from species occurring to a minor extent in the mixture of (excited) conformers. That the diversity of products formed upon photoexcitation of 1,3,5-hexatrienes is large indeed became particularly clear in the recent investigation of the photoproducts of vitamin D[3] and previtamin D/tachysterol (toxisterols)[2,4]. The results of the present investigation formed an extra stimulus in the search for cyclobutenes among the photoproducts of tachysterols and previtamin D, which in the meantime has been succesful[4]. The recently determined structures of toxisterols A and B in turn challenge to trace analogous cyclopentene derivatives and solvent adducts among the photoproducts of simple model hexatrienes.

References.

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