Tetrahedron Letters,Vol.27,No.12, pp 1395-1398,1986 0040-4039/86 $3.00 + .00
Printed in Great Britain

PHOTOREACTIONS OF *(E)*- and *(Z)*-2,5-DIMETHYLHEXATRIENE FORMATION OF A CYCLOPROPENE DERIVATIVE: A NOVEL REACTION IN TRIENE PHOTOCHEMISTRY

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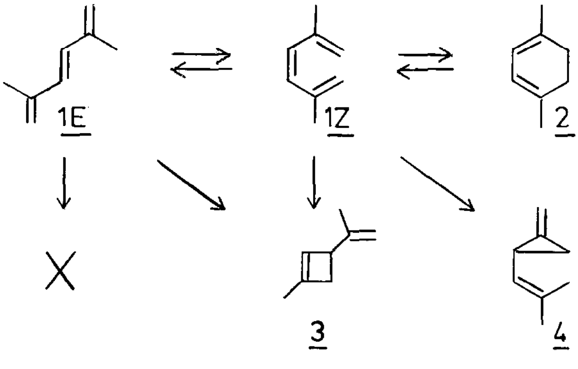
The products obtained upon direct irradiation of 2,5-dimethylhexatriene at 254 nm have been reinvestigated. The previously observed short-wavelength irradiation product has been identified as 1-methyl-2-(2-methyl-2-propenyl)cyclopropene 6. The proposed intermediacy of a vinylcarbene in the formation of this novel type of product is supported by independent synthesis.

The solution photochemistry of the isomeric 2,5-dimethyl-1,3,5-hexatrienes, 1E and 1Z, was first described by Vroegop *et al.*[1] After prolonged irradiation (λ > 225 nm) the vinylcyclobutene derivative 3 (major product) and 1-methylene-2-(2-methyl-1-propenyl)cyclopropane 4 were isolated, while evidence was obtained for the presence of a small amount of 1,4-dimethylcyclohexadiene 2 in the irradiation mixture. The triplet-sensitized photochemistry of 1E/1Z was shown[1] to involve only E ⟶ Z isomerization.

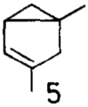
A few years later Gielen *et al.*[2] demonstrated the strong influence of the irradiation wavelength on the primary photoproduct composition of 1E and 1Z, thus providing strong evidence for the validity of the NEER principle.[3] During this study a novel product X was detected by GC analysis. It was produced specifically in short-wavelength irradiation (λ ≦ 254 nm) and appeared to originate from 1E. Scheme 1 summarizes the known photoreactions of the 2,5-dimethylhexatrienes.



Scheme 1. Photoreactions of *(E)*- and *(Z)*-2,5-dimethyl-1,3,5-hexatriene.[1,2]

As part of a more general investigation[4] into the wavelength and conformation effects on the photoreactivity of substituted trienes, we decided to reinvestigate the product mixture resulting from irradiation of 1E in n-pentane at 254 nm, aiming in particular at the isolation and identification of product X. The known products 3 and 4 were isolated and characterized by NMR and IR.[4] In corroboration of its structure assignment compound 4 was synthesized *via* an independent route and compared to some variously substituted methylene cyclopropanes.[4] This established the structure of 4 beyond doubt.

Products 3 and 4 account for 75 and 9%, respectively, of the product mixture at 90% conversion of the E-triene.[5] The proportion of 1Z present in the pseudo-equilibrium 1E $\rightleftarrows$ 1Z never exceeds 3%; at 90% conversion its amount is negligible. The cyclic isomer 2 is not observed at all under the present conditions of irradiation. According to Gielen *et al.*[2] its concentration should be less than 0.2% throughout.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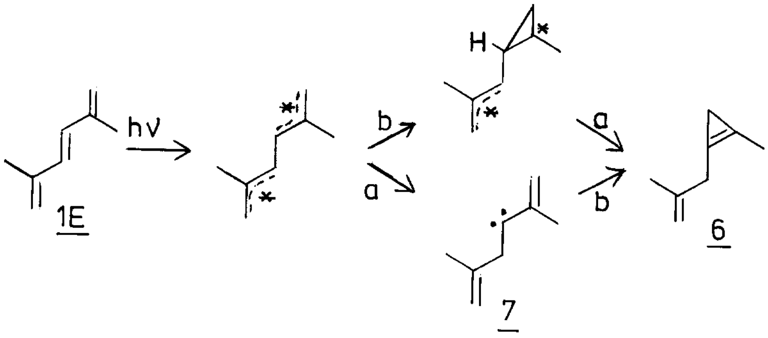
GC shows the presence of two more products, 5 and 6, in the irradiation mixture, accounting for 5 and 12%, respectively. The former compound has escaped attention in earlier studies; it can only be observed separate from 3 by using well-optimized GC conditions.[6] Samples of 5 obtained by preparative GC invariably contained considerable amounts of 3. In spite of this the signals due to 5 can easily be recognized in the ^{1}H NMR spectrum of the mixture, and allow the identification of 5 as 1,3-dimethyl(3.1.0)bicyclohex-3-ene.[7] It must have been formed from 1Z by intramolecular (4 + 2) cycloaddition, a well-known type of reaction in triene photochemistry.

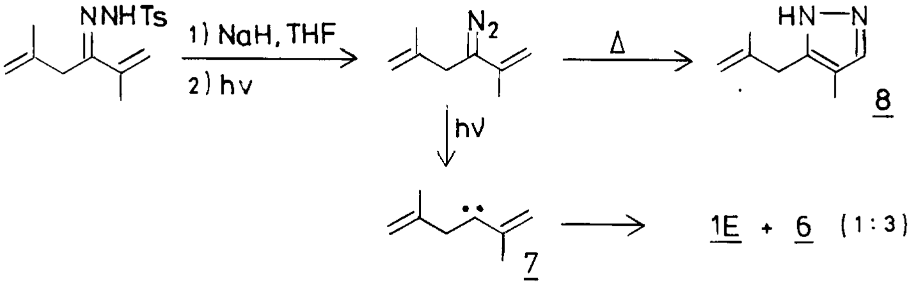
The second novel photoproduct 6 probably is to be identified with product X in the earlier studies.[2] It was initially characterized by its ^{1}H NMR spectrum.[8] A conspicuous feature is the absence of large H-H couplings indicating five separate groups of (nearly) equivalent protons. The chemical shifts and coupling patterns are in favour of the assignment as 1-methyl-2-(2-methyl-2-propenyl)cyclopropene.

The mechanism of the transformation 1E $\rightarrow$ 6 must account for (1.3) bond formation and (1.2) hydrogen shift along the central double bond. Such a rearrangement has not been observed before in triene photochemistry.[9] The formation of cyclopropenes from butadienes is thought to occur via (1.3) ring closure followed by a (1.3)H shift.[10] That mechanism clearly does not apply to the present rearrangement. Two conceivable routes to the cyclopropene, both involving the twisted bisallyl species but differing in the order of ring closure and hydrogen shift, are depicted in scheme 2.

The sequence a,b implies the intermediacy of carbene species 7. The occurrence of carbenes in the photochemistry of alkenes is well-documented.[11] Vinylcarbenes have been proposed as intermediates in allene and cyclopropene photoreactions.[12] To investigate the possible intermediacy of the vinylcarbene 7 it was generated independently by photolysis of the appropriate tosylhydrazone sodium salt[13] as outlined in scheme 3.



Scheme 2. Possible pathways of the transformation 1E ⟶ 6 (a: (1.2)H-shift; b: (1.3)bonding).



Scheme 3. Generation and rearrangement of vinylcarbene 7.

The products 1E and 6 obtained proved to be identical (GC, ^{1}H NMR) to those isolated from the triene photoproduct mixture.

A stepwise mechanism whereby hydrogen migrates along the central double bond followed by cyclization of the vinylcarbene intermediate (scheme 2, sequence a,b) thus adequately accounts for the overall photorearrangement to cyclopropene 6. The feasibility of this route is of interest in view of a recent theoretical treatment[14] of polyene photoisomerization processes, where hydrogen (pseudo)migration has been invoked to explain the fast diabatic transitions between excited and ground states.

The preparation of 6 according to scheme 3 afforded sufficient quantities to record ^{13}C NMR[15] and Raman[16] spectra which gave further support for the structure assignment. Unfortunately we were unable to cool the irradiation mixture sufficiently to prevent the (thermal) ring closure of the diazo intermediate leading to pyrazole 8.[17]

At present we are extending these studies to a range of 2,5-dialkylhexatrienes.[4]

Notes and References

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2. J.W.J. Gielen, H.J.C. Jacobs and E. Havinga, Tetrahedron Lett. 3751 (1976); J.W.J. Gielen, Ph.D. Thesis, Leiden 1981.

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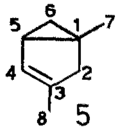
4. A.M. Brouwer, Ph.D. Thesis, Leiden, to be published.

5. Substance 4 is photochemically labile. When the conversion of 1E exceeds about 90% 4 (ε_{254} 100) is no longer protected by the internal filter effect of the strongly absorbing triene and rapidly disappears from the reaction mixture. Its fate is as yet unknown.

6. 30 m OV101 capillary column, 25°C; hydrogen proved to be irreplaceable as a carrier gas.



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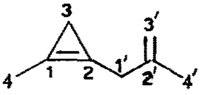
7. ^{1}H NMR (300 MHz, Bruker WM300, $CDCl_3$, chemical shifts in ppm relative to internal TMS): CH_2-2 2.27 (m) (partly obscured by signals of 3); H4 5.49 (quin, $J_{4-8} = J_{4-5} = 1.7$ Hz); H5 1.39 (m, $J_{5-6exo} = 7$ Hz, $J_{5-6endo} = 3.4$ Hz); H6exo 0.66, H6endo 0.06 ($^2J = 3.4$ Hz); CH_3-7 1.27 (s); CH_3-8 1.63 (q).



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8. ^{1}H NMR: CH_2-3 0.83 (s); CH_3-4 2.07 (t, $J_{4-1'} = 1.6$ Hz); CH_2-1' 3.11 (bs); CH_2-3' 4.77, 4.79 (m); CH_3-4' 1.78 (t, $^4J = 1.2$ Hz).

9. It now appears to be general in 2,5-dialkylhexatrienes (ref. 4).

10. R. Srinivasan and S. Boué, Tetrahedron Lett. 203 (1970); S. Boué and R. Srinivasan, J. Am. Chem. Soc. 92, 3226 (1970).

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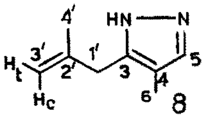
14. I. Ohmine, J. Chem. Phys. 83, 2348 (1985).

15. 6: ^{13}C NMR (75 MHz, Bruker WM300, solvent $CDCl_3$, chemical shifts relative to TMS, multiplicity with respect to $^1J_{CH}$): C-1 and C-2 107.9 (s), 106.8 (s); C-3 8.4 (t, J = 167 Hz); C-4 22.6 (q, J = 125 Hz); C-1' 34.7 (t, J = 127 Hz); C-2' 142.6 (s); C-3' 111.2 (t, J = 154 Hz); C4' 11.5 (q, J = 123 Hz).

16. 1650 cm^{-1} (s): methylene C=C stretch; 1875 cm^{-1} (vs): cyclopropene C=C stretch. We thank Drs. D.J. Stufkens and Th.L. Snoeck (University of Amsterdam) for recording the Raman spectrum.

17. 3-(2-Methyl-2-propenyl)-4-methylpyrazole 8:
^{1}H NMR: H5 7.32 (bs); CH_3-6 2.00 (d, $J_{6-5} = 0.6$ Hz); CH_2-1' 3.32 (bs); $H_t3' = 4.82$ ($J_{t-1'} = 0.8$ Hz, $J_{t-4'} = 1.1$, $J_{c-t} = 2.0$ Hz); H_c3' 4.70 ($J_{c-1'} = 1.5$ Hz, $J_{c-4'} = 0.8$); CH_3-4' 1.71 (dd).
^{13}C NMR: C-3 and C-4 113.1 and 116.4 (s); C-5 134.0 (d, J = 182 Hz); C-6 8.1 (q, J = 127 Hz); C-1' 33.9 (t, J = 127 Hz); C-2' 142.6 (s); C-3' 111.7 (t, J = 156 Hz); C-4' 22.1 (q, J = 126 Hz).



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(Received in UK 2 January 1986)