

CONFORMATIONAL EQUILIBRIUM AND PHOTOCHEMISTRY OF HEXA-1,3,5-TRIENES

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Abstract—Products found after photoisomerisation of some alkyl-substituted hexa-1,3,5-trienes were those predicted on the basis of the ground-state conformational equilibrium. Theoretical implications are briefly discussed.

INTRODUCTION

Some 10 years ago^{2,3} an endeavour was made to rationalize the photochemical and thermal isomerisation reactions of cyclohexadienes and hexa-1,3,5-trienes as established in the vitamin-D field,⁴ on the basis of essentially three categories of effects:

- (a) non-bonding interactions (steric hindrance)
- (b) π -electron interaction; orbital symmetry
- (c) influence of ground-state conformational equilibrium

Nowadays not only category (a) but also category (b)-effects can be considered as "classical", albeit that in the case of photoreactions the theoretical interpretation of (b) is still a matter of dispute. The third category (c) received less attention. Moreover, its theoretical implications, e.g. for the description of thermal relaxation and internal conversion, have scarcely been discussed.

For such compounds as hexatrienes, and polyenes in general, the principle (c) can be specifically formulated as follows: The various conformers, existing as an equilibrium mixture in the ground state, transform upon excitation into species which during their short (singlet excited) lifetime do not interconvert by way of rotation about the bonds, that—originally single—in the excited state possess considerable double bond character. (Partial rotations about the originally double bonds may be easier; they result in $E \rightleftharpoons Z$ interconversion). Accordingly, the various excited conformers should be considered as configurationally different compounds, each giving rise to specific products at their return to the ground-state. In the relative article² this hypothesis was used i.e. to argue that the quantum yield of cyclisation of previtamin D could not be high since this reaction would depend on a conformer present in small percentage.

In order to test the general validity of the principle and to explore its scope and predictive value we have investigated a series of alkyl substituted hexa-1,3,5-trienes with regard to their conformational characteristics and their photoreactions. This

was deemed all the more important since systematic experimental data in this field may reveal what happens during thermal relaxation of excited molecules in the liquid phase, what geometrical changes and perhaps even what chemical processes may take place and what factors govern internal conversion. These are all questions that are fundamental to many aspects of photochemistry and that still remain largely unanswered. Alkyl groups were chosen as substituents because their polar effects are small and their steric requirements are known.

For hexa-1,3|Z|,5-trienes, in principle three (four) planar conformations are to be envisaged: tZt, cZt and tZc, cZc. Depending on the nature and positions of the substituents mostly one of these will predominate in the equilibrium mixture.

RESULTS

Fig 1 gives the UV characteristics and some relevant NMR data as well as what we conclude to represent the preferred conformation of the compound concerned.

Although owing to steric crowding several of the hexatrienes cannot be planar, the extinction coefficients show clear regularities, the values of ϵ_{\max} for the compounds with predominantly tEt, tZt, cZt and "cZc" conformation being $\sim 50\cdot000$, $40\cdot000$, $22\cdot000$ and $10\cdot000$, respectively. All data of Fig 1 seem to fit into a consistent pattern and offer a solid basis for the discussion of the reactions and products observed upon irradiation.

The simplest picture describing the results of our irradiation experiments conforms to the original principle (c), i.e. the product composition is determined by the conformational equilibrium. The main products formed from a given compound are geometrically related to and easily derived from the major conformer. If the tZt form predominates (e.g. hexa-1,3,5-triene, $\epsilon \sim 40\cdot000$, Fig 2) the main reaction is $Z \rightleftharpoons E$ isomerisation ($\phi_{E \rightarrow Z} = 0\cdot034$, $\phi_{Z \rightarrow E} = 0\cdot016$; other products are formed with small quantum yields only.

If the preferred form is the cZt conformer

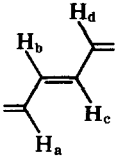

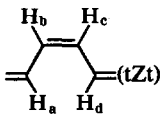
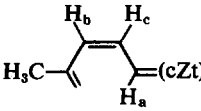
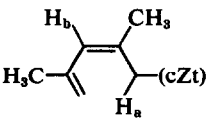
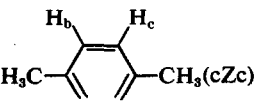
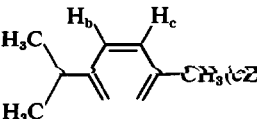
	main conformation	$\epsilon(\lambda_m)$	$\delta H_a, \delta H_d$	$\delta H_b, \delta H_c$
(E)hexa-1,3,5-triene	 (tEt)	51700 (256)	6.0-6.5	
[E.E.E.] okta-2,4,6-triene		55000 (263)	5.7-6.2	
(Z)hexa-1,3,5-triene	 (tZt)	41000 (254)	6.3-7.1	5.6-6.2
2 methyl-(Z)-hexatriene	 (cZt)	22400 (259)	6.7-7.2	5.7-6.2
2,4 di methyl-(Z)-hexatriene	 (cZt)	23900 (255)	6.7-7.2	5.73
2,5 di methyl-(Z)-hexatriene	 (cZc)	12300 (237)	—	5.87
2 methyl-5-propyl-(Z)-hexatriene	 (cZc)	8700 (245)	—	6.8

Fig 1. UV extinction coefficients (at λ_{max}), characteristic NMR data and the preferred conformation of some hexa-1,3,5-trienes. The data on the unsubstituted E and Z hexatriene are from l.c. 5)

(example 2-methyl-(Z)-hexa-1,3,5-triene, $\epsilon \sim 22\cdot000$, Fig 3) we find the photoproducts [3.1.0] bicyclohex-(2)-enes ($\pi_s^4 + \pi_a^2$ cycloaddition), vinyl cyclobutenes (cyclisation of the cisoid butadiene moiety, which may also occur with the E isomer) and 1,2,4 hexatrienes (1,5 H-shift).

Finally, in the 2,5 substituted hexatrienes ($\epsilon \sim 10\cdot000$; Figs 4 and 5) the molecules are far from planar but the situation resembles the cZc form most (and the cZt form to a less extent); here one

finds besides vinyl cyclobutenes a considerable amount of the cyclohexa-1,3-diene derivatives. This then constitutes the analogy to the photocyclisation of pre-vitamin D, now realised with the simplest possible model compounds*. A survey of our results and interpretation is offered in Figs 5 and 6. It is noteworthy that with α terpinene we find that opening of the cyclohexadiene system and formation of the [2.2.0] bicyclohexene system occur at similar rates. The novel methylene vinyl cyclopropanes found can be thought of as arising from 1,4 addition of the $-\text{CH}_2-\text{H}$ grouping to the cisoid butadiene part of a cZt conformer probably present to a minor extent.

*Comparable results with other model molecules are presented in the interesting recent publication of Dauben *et al.*⁶

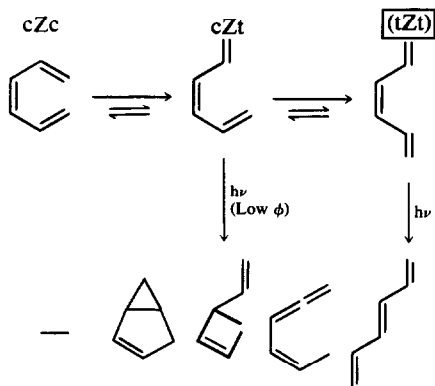


Fig 2. (Z)-hexa-1,3,5-triene; $\epsilon = 41\,000$ (254 nm) Conformations and photoproducts (confer Ic 5).

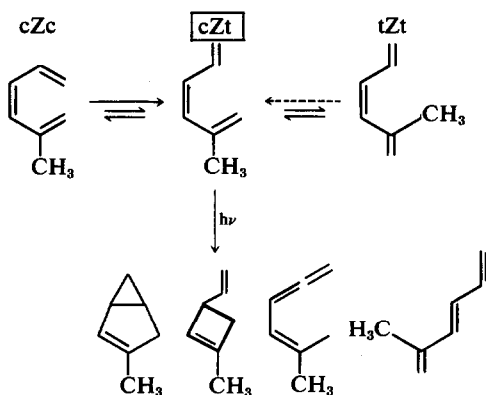


Fig 3. 2-methyl-(Z)-hexa-1,3,5-triene; $\epsilon = 22\,400$ (259 nm) Conformations and photoproducts.

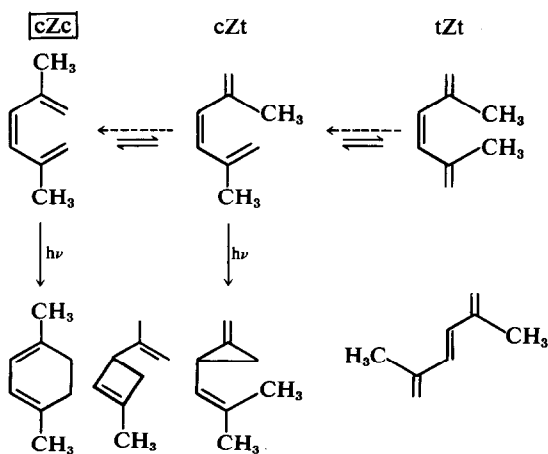


Fig 4. 2,5-dimethyl-(Z)-hexa-1,3,5-triene; $\epsilon = 12\,300$ (237 nm). Conformations and photoproducts.

Another valuable analogy between simple alkyl hexatrienes and compounds in the vitamin-D field is observed with 2-methyl and 2,4-dimethylhexa-1,3,5-triene and (Δ^5 Z) vitamin D itself. That the

latter compound exists in solution for the greater part in the cZt form is deduced from its extinction coefficient ($\epsilon_{\max} = 19\,000$). The detailed geometry was revealed by X-ray analyses.^{7,8} Recently it was found in this laboratory that vitamin D upon irradiation yields just those isomers, that should be expected on the basis of the results reported here for 2-methyl and 2,4-dimethyl hexatrienes.⁹

DISCUSSION

The results presented follow a clear and relatively simple pattern consistent with our original idea implying that the various conformers of the ground state upon absorption of UV light yield different excited species which do not interconvert during their short (singlet excited) lifetime. Each of these excited species transforms into specific products when returning to a ground state. However, this simple picture considered from a theoretical point of view gives rise to a series of questions.

The main difficulty lies in the assumption that a molecule, brought into a vibrationally excited state by absorption of a short wavelength quantum, will during thermal relaxation not be able to overcome the rotational barriers preventing it from equilibrating with its cousins. One might consider the influence of the solvent cage that could oppose to drastic geometric changes within a very short time (10^{-12} sec.). However we know of no experimental data indicating whether such an effect of the solvent cage could be of substantial influence. We should therefore keep an open mind to alternative mechanisms that may explain the experimental results. Assuming that equilibration between the various conformers in the excited state can take place and that this equilibration during thermal relaxation results in a mixture of the various (excited) conformers similar to that of the conformational equilibrium in the ground state, then—in fact—the photoproduct composition might conform to predictions on the basis of principles formulated at the beginning of this article. Such an assumption would seem not unrealistic since comparable steric effects may be operative in the excited state and the ground state. Still, for the moment we feel somewhat in favour of the original alternative, i.e. the non-interconversion of excited conformers. Further study is clearly needed, and coordination of various experimental methods—flash techniques, variation of wavelength of the excited light, temperature and viscosity of the medium—as well as systematic variation of molecular structure is essential to obtain insight into the detailed behaviour of molecules in the excited state and the factors governing the regularities observed in photoisomerisations.

EXPERIMENTAL

Syntheses of hexatrienes. Most trienes were prepared following the method described by Hwa e.a. for hexa-1,3,5

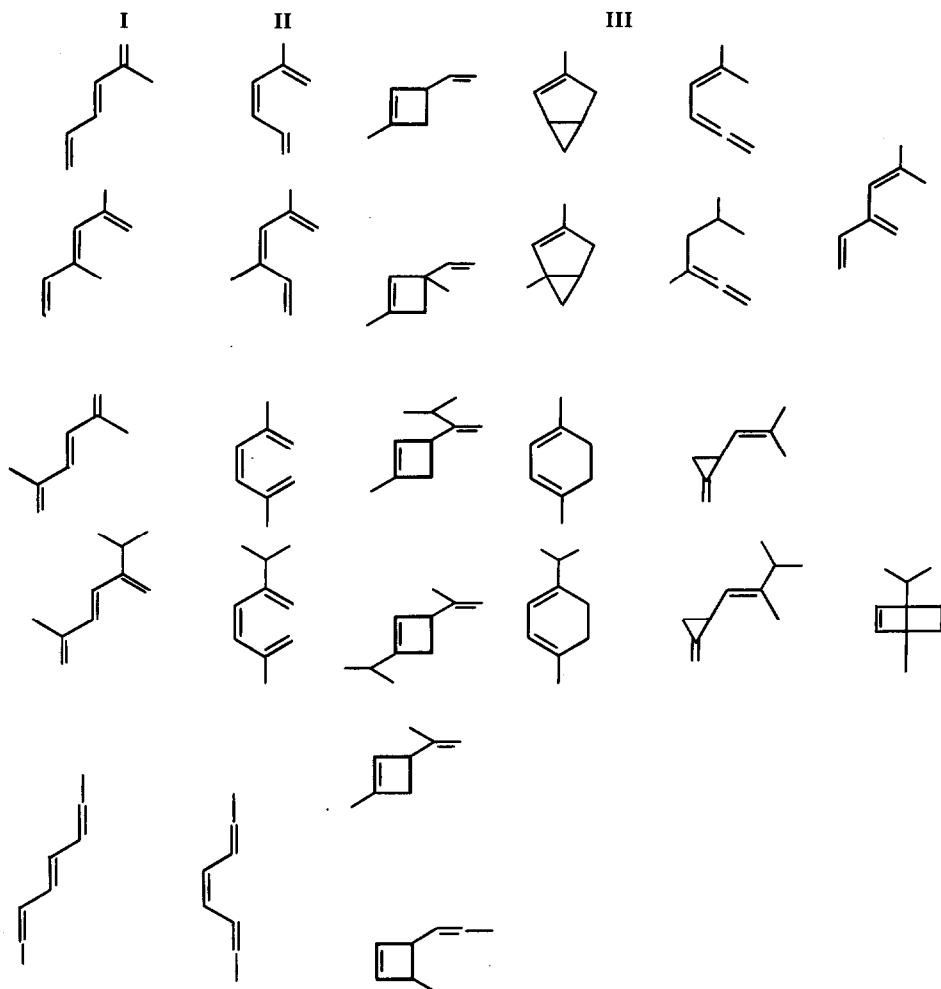


Fig 5. Irradiation of various alkyl-substituted hexatrienes. Main conformers of $\Delta^3[E]$ (Column 1), $\Delta^3[Z]$ (Column 2) isomers and photoproducts isolated (Column 3)

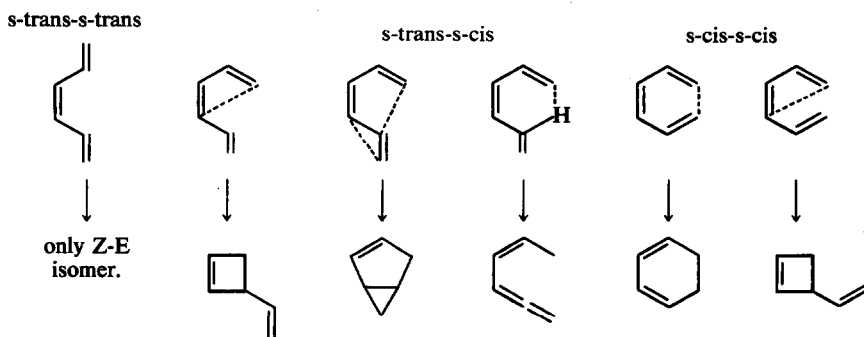


Fig 6. The three planar conformations of the (Z)-hexa-1,3,5-trienesystem and the corresponding photoproducts. Formation of the $\Delta^3[E]$ isomer is omitted from the representation.

triene itself.¹⁰ For the synthesis of (E, E, E)-octa-2,4,6-triene the description given by Brandsma *et al.* was followed.¹¹ All reactions were carried out in a N₂ atm. The E-trienes were isolated by preparative GLC or fractional crystallisation from pentane at -60°. The Z-trienes were prepared starting from the E-isomers by sensitized isomerisation in pentane (1 g triene and 0.25 g fluorenone per 100 ml pentane) A Hanau S'1200 Watt Hg lamp was used as a light source with a satd soln of ammonium ferric sulphate in 2N H₂SO₄ as a filter absorbing light with $\lambda < 380$ nm. When the photostationary state had been reached the irradiation was stopped and pentane and fluorenone were removed. The E and Z isomers were separated by preparative GLC, fractional crystallization from pentane at -60° or by Diels-Alder reaction of the E isomer with maleic anhydride. 2,5-dimethylhexa-1,3,5-triene was prepared in a pure state also by direct synthesis as described (*l.c.* 5).

The Z-hexatrienes obtained had a better than 99% purity. The Z-configuration was confirmed by the facile thermal ringclosure to the corresponding cyclohexa-1,3-diene and by IR and UV data.

The NMR spectra were recorded with a Varian H.A. 100, a Jeol NMR-MH 60 and a Jeol PS 100; CDCl₃, CCl₄ and C₆D₆ were used as solvents, TMS as internal reference. For the structure elucidation of photoproducts double resonance techniques were applied.

UV spectra were recorded with Cary 14 and Cary 15 spectrometers. IR spectra were obtained from the neat liquids with a Beckman IR 10 apparatus.

Data on the synthesized trienes

(E)-2-methylhexa-1,3,5-triene (containing 5% [Z]-isomer). NMR (δ values, CDCl₃, 100 MHz): 6.1-6.6 (m, 3H); 4.9-5.4 (m, 4H); 1.90 (s, 3H) IR: 3080, 3040, 3020, 2970, 2940, 2905, 1790, 1615, 1450, 1430, 1370, 1155, 990, 940, 880 cm⁻¹; UV (heptane): $\epsilon = 35\text{--}000$ (268 nm), 43-000 (258), 31-000 (248). $n_D^{25} = 1.5138$.

(Z)-2-methylhexa-1,3,5-triene. NMR (CDCl₃, 100 MHz): 6.9 (triplet, 1H, $J = 16.4$ and 10.4 Hz); 5.7-6.2 (AB, 2H, $J = 11.0$); 4.9-5.5 (m, 4H); 2.00 (s, 3H). IR: 3080, 3000, 2960, 1810, 1605, 1580, 1450, 1365, 1280, 1245, 1230, 1125, 995, 955, 885, 805, 790, 715, 670, 630 cm⁻¹; UV (heptane): 16-600 (269), 22-400 (259), 18-800 (249). $n_D^{24} = 1.4925$.

^d(E)-2,5-dimethylhexa-1,3,5-triene. NMR (CCl₄, 60): 6.33 (s, 2H); 5.05 (s, 4H); 1.91 (s, 6H). IR: 3080, 3020, 2970, 2940, 2910, 1770, 1615, 1450, 1430, 1370, 1305, 1250, 1000, 950, 875 cm⁻¹; UV (heptane): 33-900 (270), 43-400 (260), 31-900 (250); $n_D^{21} = 1.5123$.

(Z)-2,5-dimethylhexa-1,3,5-triene. NMR (CCl₄, 60): 5.87 (s, 2H); 4.93 (s, 4H); 1.90 (s, 6H); IR: 3080, 2960, 2930, 2710, 1780, 1630, 1590, 1450, 1370, 1250, 1000, 890, 780, 730, 700 cm⁻¹; UV (heptane): 12-300 (237), $n_D^{20} = 1.4682$.

(E)-2,4-dimethylhexa-1,3,5-triene. NMR (CDCl₃, 60): 6.3 (d, 1H, $J = 10$, $J = 16$); 5.81 (s broad, 1H); 4.7-5.3 (m, 4H); 1.92 (s, 3H); 1.89 (s, 3H); IR: 3080, 3000, 2960, 2940, 2860, 2710, 1790, 1630, 1610, 1440, 1410, 1380, 1370, 1350, 1290, 1250, 1190, 1060, 980, 950, 890 cm⁻¹;

UV (heptane): (shoulder at 272), 22-200 (263), 22-200 (263), 23-400 (255); $n_D^{24} = 1.4995$

(Z)-2,4-dimethylhexa-1,3,5-triene. NMR (CDCl₃, 60): 6.9 (d, 1H, $J = 10$, $J = 18$); 5.8 (s broad, 1H); 4.7-5.4 (m, 4H); 1.89 (s, 3H); 1.86 (s, 3H); IR: 3080, 2970, 2940, 2910, 2850, 2720, 1810, 1590, 1625, 1440, 1370, 1260, 1200, 1060, 1030, 995, 980, 890, 850 cm⁻¹; UV (heptane): (shoulder at 272), 21-900 (262), 23-900 (255); $n_D^{25} = 1.4892$.

(E,E,E)-okta-2,4,6-triene. m.p.: 50-51°, NMR (CDCl₃, 100): 5.7-6.2 (m, 6H); 1.70 (d, 6H, $J = 6$); IR (KBr disc.): 3005, 2950, 2900, 1630 (weak), 1430, 1370, 980, 790 cm⁻¹; UV (heptane): 44-400 (274), 55-000 (263), 31-000 (253).

Irradiation experiments

Analysis of products and identification of compounds. Solns of the trienes* in pentane (5-10 g/l) were irradiated in a N₂ atm. The soln circulated in an apparatus as described by Havinga and Bots.¹² The light from a Hanau S 1200 W HP Hg lamp passed through a Ni/Co sulphate soln ($\lambda' > 225$ nm). At regular intervals samples were taken and analysed by GLC. A Becker Multigraph or a Hewlett Packard F & M 5750 with flame detector and N₂ as carrier gas were used. (10% $\beta\beta'$ -oxydipropionitrile on chromosorb ϕ 80-100, 6 m steel column ($\phi = 3$ mm), column temp 50-70°, injection point 120°). After the irradiation the solvent was removed by careful distillation and the residue worked up applying preparative GLC.

Preparative GLC separations were carried out using a Becker preparative gaschromatograph (10% $\beta\beta'$ -oxydipropionitrile on chromosorb WAW 50-60, 6 m steel column ($\phi = 10$ mm), temps as in the analytical separation). Fractions were collected in vessels cooled to -60°.

Data on irradiation products

1-Methyl-3-vinylcyclobut-1-ene.

NMR (CDCl₃) signals: a b c d e f g h
 1H 1H 1H 1H 1H 1H 1H 1H
 ppm: 5.92 5.71 4.99 4.87 3.21 2.65 2.07 1.69

couplings: Jac 18.0, Jad 10.0, Jae 3.0, Jbh 1.3, Jcd 2.0, Jef 4.5, Jeg ~ 1, Jfg 14.0, Jfh 1.3, Jgh ~ 1.

IR: 3080, 3040, 2960, 2930, 2910, 1635, 985, 900, 830.

UV: no absorption maximum $\lambda > 220$ nm.

3-Methylbicyclo [3.1.0] hex-2-ene.

NMR (C₆D₆): a b c d e f g h
 1H 1H 1H 1H 1H 1H 1H 1H
 ppm: 5.49 2.48 2.01 1.57 1.50 1.45 0.71
 ab = 2.0 bc = 18.0 be = 7.0 dg = 7.5
 dh = 3.5 ef = 1.5 eg = 7.5 eh = 3.5
 gh = 3.5

IR: 3060, 3040, 2980, 2969, 2900, 2850, 2820, 1640, 1015, 835.

UV: no absorption maximum $\lambda > 210$ nm.

5-Methylhexa-1,2,4-triene

NMR (CDCl₃): a b c d e
 1H 1H 2H 3H 3H
 ppm: 5.99 5.88 4.85 1.74 1.69
 ab = 10.5 ac = 6.5 bd = 1.2 cd = 1.2
 UV (heptane): λ max 230 nm.

*We mostly started the irradiation experiments with solutions of the E isomers which were available in large quantities. That the isomerization products (Fig 5, III) generally originate from the Z triene can be deduced from the curves representing the concentration of the various compounds in the irradiation mixture as a function of time.

1,3-Dimethyl-3-vinylcyclobut-1-ene.

NMR (CDCl₃): a b c d e f g h
 1H 1H 1H 1H 1H 1H 3H 3H
 ppm: 6.04 5.81 4.98 4.88 2.27 2.27 1.72 1.27
 ac = 17.4 ad = 10.0 cd = 2.0
 bg = eg = fg = 1.5
 IR: 3080, 3040, 2960, 2920, 2860, 1635, 985,
 900
 UV: no absorption maximum at $\lambda > 210$ nm.

1,3-Dimethylcyclo[3.1.0]-hex-2-ene.

NMR (C₆D₆): a b c d e f g h
 1H 1H 1H 3H 4H 1H 1H
 ppm: 5.35 2.55 2.11 1.59 1.24 0.63 0.12
 ab = 2.0 ae = 1.6 bc = 17.0 be = 7.0
 eg = 8.0 eh = 3.0 gh = 3.0
 IR: 3050, 3030, 2980, 2860, 2830, 2720, 1635,
 1015, 840
 UV: no absorption maximum at $\lambda > 210$ nm.

3,5-Dimethylhexa-1,2,4-triene.

This compound showed fast thermal isomerisation to
 2,4-dimethyl-Z-hexa-1,3,5-triene
 IR: 1950 840
 UV (heptane) λ max 237 nm

2-Vinyl-4-methylpenta-1,3-diene.

NMR (CDCl₃): a b c d e f g h
 1H 1H 3H 3H
 ppm: 6.16 5.73 ~ 5.0 1.85 1.72
 ac = 18.0 ad = 10.5
 IR: 3100, 3010, 2970, 2920, 2830, 1810,
 1625, 1590, 985, 895, 840
 UV: no absorption maximum at $\lambda > 220$ nm.

1,4-Dimethylcyclohexa-1,3-diene.

could not be isolated from the irradiation mixture. The
 retention time was equal to that of an authentic sample on
 a $\beta\beta'$ -oxidipropionitrile column as well as on a carboxyl
 column.

1-Methyl-3-isopropenylcyclobut-1-ene.

NMR (CDCl₃): a b c d e f g h
 1H 2H 1H 1H 1H 6H
 ppm: 5.74 4.67 3.16 2.59 2.11 1.68
 ag \approx 1.5 bh = 1.5 de = 4.5
 df \approx 1.5 eg = 1.0 ef = 13.0
 fg = 1.5
 IR (solution in CCl₄): 3070, 3030, 2960, 2920, 2900,
 2860, 2820, 1775, 1635, 880.
 UV: no absorption maximum at $\lambda > 210$ nm.

1-Methylene-2-isobutenylcycloprane.

NMR (CDCl₃): a b c d e f g h
 2H 1H 1H 3H 3H 1H 1H
 ppm: 5.34 4.65 2.13 1.73 1.68 1.55 0.92
 ag = 2.0 ah \approx 2 bg = 2.0 bh = 2 cd = 9.0
 ce = 1 dg = 9.0 dh = 5.0 gh = 9.0
 IR: strong absorption at 3000 ~ 2900 and
 880.

1-Isopropyl-3-isopropenylcyclobut-1-ene and 1-methyl-3-(1'-isopropyl)vinylcyclobut-1-ene.

NMR (CCl₄): nearly identical NMR spectra. In C₆D₆ the
 signal of the methyl groups attached to the
 double bond can be separated in two peaks

(ratio 5:1, the same ratio is found in glc
 analysis)

: a b c d e f g h h' i
 1H 2H 1H 1H 2H 3H 3H 6H
 ppm: 5.70 4.77 3.12 2.46 2.06 2.04 1.64 1.52 0.91
 de = 4.3 ef = 12.0 gi = 7.0
 IR: 3080, 3040, 2960-2900, 2860, 1775, 1640,
 880, 830
 UV: no absorption at $\lambda > 210$ nm.

1-Methyl-4-isopropylbicyclo[2.2.0]hex-2-ene.

NMR (CCl₄): a b c d e f g h i j
 2H 3H 5H 3H 3H 3H
 ppm: 6.18 1.85 1.1 1.19 0.87 0.79
 the two methyl groups of the isopropyl
 group are magnetically non-equivalent.
 UV: no absorption maximum at $\lambda > 210$ nm.

1-Methylene-2-(2'-methyl-2'-isopropyl)vinylcycloprane.

NMR: a b c d e f g h i
 2H 1H 1H 1H 3H 1H 1H 6H
 ppm: 5.28 4.27 2.10 1.99 1.64 1.39 1.16 0.95
 ag or bg = 2 cf = 1.5 di = 7.0 eg = 8.0 gh = 8.0
 configuration around trisubstituted double bond is
 not known
 IR: 3070, 3040, 2960, 2920, 2860, 1775, 1640, 880,
 830 cm⁻¹

Z-3-Methyl-4-propenylcyclobut-1-ene.

NMR: a b c d e f g h
 2H 2H 1H 1H 3H 3H
 ppm: 6.09 ~ 5.70 3.92 3.11 1.06 1.01
 ce = 8.3 ef = 4.5 hf = 7.0

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REFERENCES

- ¹A detailed report in the Dutch language is given in P. J. Vroegop, Thesis Leiden (1972)
- ²E. Havinga and J. L. M. A. Schlatmann, *Tetrahedron* **16**, 146 (1961)
- ³E. Havinga, *Chimia* **16**, 145 (1962)
- ⁴G. M. Sanders, J. Pot and E. Havinga, *Fortschr. Chemie Org. Naturstoffen* (Editor L. Zechmeister) Vol **27**, p 131, Springer Verl. Wien (1969)
- ⁵N. G. Minnaard, Thesis Leiden (1970) and literature cited
- ⁶W. G. Dauben, J. Rabinowitz, N. D. Vietmeyer, P. H. Wendschuh, *J. Am. Chem. Soc.* **94**, 4285 (1972)
- ⁷D. Crowfoot-Hodgkin, M. S. Webster and J. D. Dunitz, *Chem. & Ind.* 1148 (1957)
- ⁸C. Knobler, C. Romers, P. B. Braun and J. Hornstra, *Acta Cryst* **B28**, 2097 (1972)
- ⁹S. A. Bakker, J. Lugtenburg and E. Havinga, *Rec. Trav. Chim.* **91**, 1459 (1972)
- ¹⁰J. C. H. Hwa, P. L. de Benneville, H. J. Sims, *J. Am. Chem. Soc.* **82**, 2537 (1960) J. C. H. Hwa and H. J. Sims, *Org. Synth.* **41**, 49 (1962)
- ¹¹J. P. C. M. van Dongen, A. J. de Jong, H. A. Selling, J. H. van Boom and L. Brandsma, *Rec. Trav. Chim.* **86**, 1077 (1967)
- ¹²E. Havinga, J. P. L. Bots, *Ibid.* **73**, 393 (1954)