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[4+2]-CYCLOADDITION OF SINGLET OXYGEN TO CONJUGATED ACYCLIC HEXADIENES : EVIDENCE OF SINGLET OXYGEN INDUCED cis ⇌ trans - ISOMERIZATION

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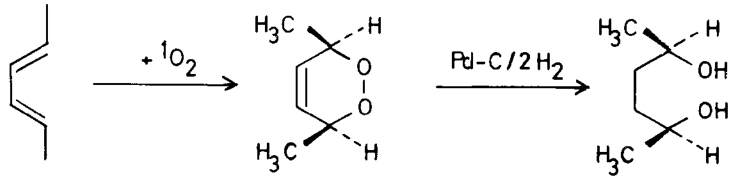
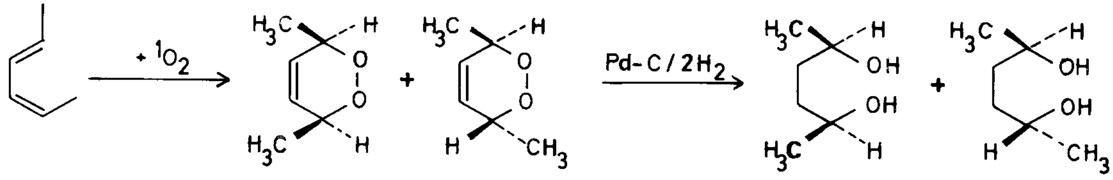
Summary Addition of singlet oxygen to trans,trans-2,4-hexadiene (1) occurs stereospecifically to give endoperoxide 2. With cis,trans-2,4-hexadiene (4), however, a mixture of diastereomeric endoperoxides, 2 + 5, is observed. Evidence of a singlet oxygen - induced cis ⇌ trans - isomerization is gained by competitive Diels-Alder reaction of 4 with singlet oxygen / diethyl diazenedicarboxylate.

trans,trans-2,4-Hexadiene (1) irradiated in O_2-saturated CCl_4-solution at 13° C in the presence of tetraphenylporphin (TPP) absorbs one molecule of oxygen [1]. After removal of CCl_4 at 10° C / 10 Torr followed by distillation of the residue at 35-40° C / 0.1 Torr, endoperoxide 2 is obtained as the sole product [3]. Catalytic hydrogenation of the distillation product yields meso-2,5-hexanediol (3), free of traces of the d,l-isomer 6 [4].

Under identical irradiation conditions and work-up procedures, cis,trans-2,4-hexadiene (4) absorbs one molecule of oxygen, but yields a mixture of endoperoxides, 2 and 5 [6], in a ratio of 83 : 17, as revealed by ^{1}H-n.m.r.-analysis of the endoperoxide mixture as well as by vpc - determination of the mixture of diastereomeric 2,5-hexanediols (3 + 6), obtained after catalytic hydrogenation.



1 2 3



4 2 5 3 6

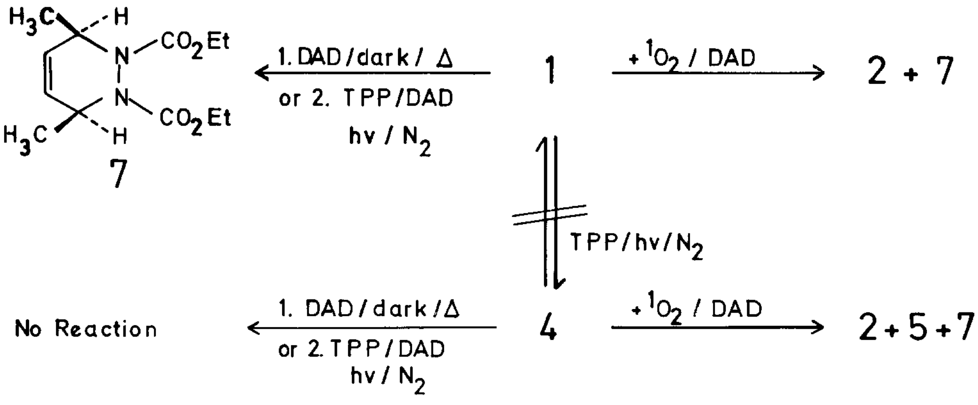
TPP-photosensitized cis ⇌ trans-isomerization of the starting 2,4-hexadienes is excluded since neither 1 nor 4 gives the other isomer when irradiated in oxygen-free CCl_4-solutions in the presence of TPP.

Diethyl diazenedicarboxylate (DAD) undergoes a thermal Diels-Alder reaction at 13° C with the trans,trans-isomer 1 in CCl_4 to give cycloadduct 7[7]; with the cis,trans-isomer 4, however, no cycloaddition product is observed even after double the reaction time necessary for quantitative formation of 7 from 1.

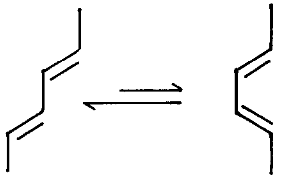
Execution of the DAD-reaction in the presence of TPP and light in oxygen-free CCl_4-solution leads to the same results: only 1 reacts with DAD to give 7, whereas 4 remains inert.

However, if the DAD-reaction is performed in O_2-saturated CCl_4-solution in the presence of TPP and light, the DAD-cycloadduct 7 is obtained from 1 as well as from 4, besides the expected endoperoxides 2 (from 1) and 2 + 5 (from 4). Furthermore, if the ratio of the starting concentrations of DAD and 4 is increased from 1 : 1 to 2 : 1, the ratio of the endoperoxides 2 : 5 is decreased from 69 : 31 to 57 : 43, respectively, as was shown by ^{1}H-n.m.r.-analysis of the endoperoxide mixtures as well as by vpc-determination of the hydrogenation products 3 and 6.

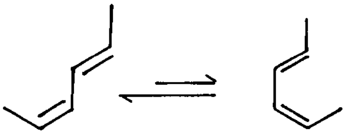
In our opinion, the experimental results are only compatible with the assumption of a singlet oxygen - induced cis ⇌ trans - isomerization of 4 ⟶ 1.



1 as well as 4 constitute s-trans ⇌ s-cis equilibria in solution, with 1b and 4b being present to about 1 % or less at room temperature[9]. 1b and 4b are the conformational isomers necessary if the Diels-Alder reactions occur in a concerted fashion. In accord with the concerted nature of the [4 + 2]-cycloaddition of 1b + $^1O_2$ is the fact that the ß-value[10] of 1 is rather large (under the reaction conditions in CCl_4 ß = 0.040 mol/l),



1a 1b



4a 4b

i.e., the rate constant k_r of 1b + $^1O_2$ is rather small, k_r = $3\cdot10^4$ l/mol·sec[11]. However, these values are obtained by using the concentration of 1 rather than that of 1b in the kinetic analysis. If about 1% of 1 is in the s-cis conformation at 13°C, k_r should be about $3\cdot10^6$ l/mol·sec, a value comparable to the k_r-value obtained for 1,3-cyclohexadiene (= $9.7\cdot10^5$ l/mol·sec) under the same reaction conditions[12].

The assumption seems warranted that whereas interactions of $^1O_2$ with 1b and 4b yield endoperoxides 2 and 5, respectively, interactions of $^1O_2$ with 1a and 4a may result in the formation of exciplexes (1a···$^1O_2$) and (4a···$^1O_2$), respectively. Although the formation of endoperoxides 2 and 5 from the corresponding exciplexes cannot be rigorously excluded, the main reaction of the exciplexes is their decomposition into oxygen and 1 from (1a···$^1O_2$), into oxygen and 1 + 4 from (4a···$^1O_2$). Whether the oxygen molecule remains in the singlet state or is (at least partly) deactivated to its triplet ground state during the exciplex decomposition remains to be investigated.

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References and Footnotes

1. Standard reaction conditions and 15 ml irradiation unit with automatic O_2-consumption recording system, see ref. 2. A 150 W Halogen-Bellaphot-lamp (Osram) and a band filter (transparent between 480 and 570nm) (Hoya) was used for electronic excitation of tetraphenylporphin ($2\cdot10^{-4}$ mol/l) in CCl_4.
2. H.Paur, Dissertation, Univ. München, 1982.
3. a) Elemental analysis and spectroscopic data are in accord with the structures described. b) 2: 85% yield of isolated yellowish oil; b.p. 35-40°C / 0.1 Torr; mol.wt.: 114 (theor.), 119 (osmometric in acetone); ^{1}H-n.m.r. (CCl_4, 80 MHz): δ = 1.28 (d, 2 CH_3), 4.60 (q, 2 tert. H), 5.82 (s, 2 -CH=); ^{13}C-n.m.r. ($CDCl_3$, 80 MHz): δ = 18.476 (q, CH_3), 74.208 (d, tert. C), 128.667 (d, C=C).
4. Vpc separation of meso- and d,l-hexanediols, prepared after ref. 5, is performed by using a 50 m polypropylene glycol glass capillary column at 90°C.
5. R.M.Dodson, V.C.Nelson, J. Org. Chem. 33 (1968), 3866.

6. 72% of isolated mixture of **2** + **5**; **5**: yellowish oil; b.p. 32-37° C / 0.1 Torr; ^{1}H-n.m.r.: δ = 1.17 (d, 2 CH_3), 4.55 (q, tert. H), 5.74 (s, -CH=); ^{13}C-n.m.r.: δ = 17.476 (q, CH_3), 73.875 (d, tert. C), 128.879 (d, C=C).
7. **7**: colorless oil[8]; ^{1}H-n.m.r.: δ = 1.23 (t, 2 $\text{-CH}_2\text{-C}\underline{\text{H}}_3$, J = 6 Hz), 1.28 (d, 1 CH_3, J = 6 Hz), 1.50 (d, 1 CH_3, J = 6 Hz), 4.1 (m, 2 $\text{-C}\underline{\text{H}}_2\text{-CH}_3$), 5.38 (m, 2 tert. H), 5.73 (m, 2 olef. H). In a fixed conformation of **7**, the two ring-methyl groups assume different (equatorial and axial) positions. The large difference of these two groups is even more striking in the ^{13}C-n.m.r. spectrum: δ = 18.022 and 21.020 (q, 2 ring-CH_3), 61.365 and 62.244 (d, 2 tert. C), 129.031 and 130.182 (d, 2 -C=), 155.715 and 156.200 (s, 2 carbonyl-C), 50.401 and 51.824 (t, 2 $\text{-}\underline{\text{C}}\text{H}_2\text{-CH}_3$), 14.539 (q, 2 $\text{-CH}_2\text{-}\underline{\text{C}}\text{H}_3$).
8. S.G.Cohen, R.Zand, *J. Am. Chem. Soc. 84* (1962), 586.
9. 1,3-Butadiene and isoprene represent s-*trans* / s-*cis* equilibria of greater than 95:5 at room temperature: a) R.S.Liu, N.J.Turro, G.S.Hammond, *J. Am. Chem. Soc. 87* (1965), 3406; b) J.C.Tai, N.L.Allinger, *J. Am. Chem. Soc. 98* (1976), 7928.
10. K.Gollnick, *Adv. Photochem. 6* (1968), 1.
11. $\tau(^1O_2)$ in CCl_4 = $7\cdot10^{-4}$ sec : P.B.Merkel, D.R.Kearns, *J. Am. Chem. Soc. 94* (1972), 7244.
12. In chloroform, the corresponding rate constants increase by about one order of magnitude: B.M.Monroe, *J. Am. Chem. Soc. 103* (1981), 7253.

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