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SIGMATROPIC 1.5-HYDROGEN SHIFT AND CONCOMITANT CYCLOPROPANE BOND CLEAVAGE ON THERMOLYSIS OF trans-1-ISOPROPENYL-4-METHYLENE spiro[2.x]ALKANES INTO 1-METHYLENE-(3'-METHYLBUT-2'-ENYL)-CYCLOALK-2-ENES

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Summary. Thermolysis of several *trans*-1-isopropenyl-4-methylene-*spiro*[2.x]-alkanes (x = 4,5) in xylene solution at 130° causes quantitative rearrangement to 1-methylene-2-(3'-methylbut-2'-enyl)cycloalkanes (3 - 4).

The thermal "homo-Cope rearrangement", which takes place with a sigmatropic [3,3] shift and concomitant cyclopropane bond cleavage, has been well documented for flexible geometric isomers of 1.2-dialkenylcyclopropanes.[1] The thermolysis of 1.2-dialkenylcyclopropanes constrained in rigid systems is still largely unexplored. This study aimed at exploring preferences in sigmatropic shifts during thermolysis of *trans*-1.2-dialkenylcyclopropanes constrained into *spiro*[2.x]-alkane systems.

When a solution of 1a in xylene was heated to 130° for 6 h. and then chromatographed by VPC,[2] the Cope reaction product 7 was not obtained. Instead, a single isomeric C_6H_{18}-compound was obtained in 83% yield, b.p. 74-76° (0.03 mm Hz). It was assigned the 1-methylene-2-(3'-methylbut-2'-enyl)-cyclohex-2-ene structure (3) on the basis of its spectroscopic properties (UV, NMR and MS) and its catalytic hydrogenation to the hexahydro derivatives (8 and 9). Similarly, the thermolysis of (1b) yields(81%) the homologous 1-methylene-2-(3'-methylbut-2'-enyl)-cyclohept-2-ene (4), b.p. 121-122° (26 mm Hz).

The UV spectra of (3) and of (4) in C_6H_{12} exhibited absorption bands at 234 mμ (ε 12000) and 239 (ε 12000), respectively, which are characteristic for conjugated cyclodienes comprising an *endo* and an *exo*-cyclic double-bond whithin their framework as present in structures (3) and (4).[3]

The mass spectrum of (3) exhibited a molecular-ion at m/e 162 (6%) and peaks at m/e 147 (9%), 119 (100%), and 91 (53%), corresponding to loss of CH_3, C_3H_7, and C_5H_{11}. The mass spectrum of (4) exhibited peaks at 176 (M^+, 11%), 161 (13%, M-CH_3), 133 (95%, M-C_3H_7), 119 (95%, M-C_4H_9) and 91 (100%, M-C_6H_{13}) which corresponds to the highly stable tropylium ion $C_7H_7^+$.

The 270 MHz ^{1}H-NMR spectrum of (3) in $CDCl_3$ indicated the disappearance of the cyclopropane proton resonances at δ 0.6 and 0.87 in (1a) and the appearance instead of new resonances assignable to structure (3), as follows : two singlets at δ 1.63 (3H, H^a) and 1.719 (3H, H^b), and signals at δ 1.69 (2H, q,J 6.21 Hz, H^c), 2.12 [2H, dt, H^d, collapsing to triplet on irradiation at δ 5.67 (assigned to H^j)], 2.35 (2H, t, H^e), 2.86 [2H, d J 7.02 Hz, H^f, collapsing to singlet on irradiation at 5.18 (assigned to H^i)], 4.74 (1H, s, H^g), 4.89 (1H, s, H^h), 5.18 [1H, t, H^i, collapsing to singlet on irradiation at 2.86 (assigned to H^f)] and 5.67 (1H, undeveloped t, H^j, collapsing to singlet on irradiation at 2.12 (assigned to H^d)].

The proton resonances assignable to structure (4) were as following : δ 1.60 (3H, s, H^a), 1.70 (3H, s, H^b), 2.0-2.30 (4H, m, H^c), 2.30 (4H, t J 6.0 Hz, H^{d+e}), 2.84 (2H, d J 8.0 Hz, H^f), 4.88 (2H, s, H^{g+h}), 5.12 (1H, double t, J 8.0 Hz, H^i) and 5.59 (1H, t, J 6 Hz, H^j).

Whereas the absorption of the first two moles of hydrogen by (3) or by (4) was rapid in presence of 10%-Pd/C in EtOH, the absorption of the third mole of H_2 was very slow indeed.[4] The separation of the reaction mixture after 20 h by VPC[2] yielded 45% of the tetrahydro product (10, ret. time: 27.7 min.), 28% of the *cis* (ret. time: 22.4 min.), and 27% of the *trans* (ret. time: 18.7 min.) hexahydro products, 9 and 8, respectively. The structures of 8 - 10 were elucidated from their NMR and MS analyses.

The mass spectrum of (10) exhibited the molecular-ion at m/e 166 (36%) and the base-peak at m/e 95, corresponding to a loss of the sidechain fragment C_5H_{11}. The 270 MH$_z$ ^{1}H-NMR spectrum of (10) showed no absorption below δ 2.0, indicating the absence of vinylic protons in consonance with structure (10). The isopropyl methyl proton resonances appear as a doublet at δ 0.88 (J 6.60 Hz) and the methyl protons as a singlet at 1.59, as expected.

The mass spectrum of (8) showed the molecular-ion at m/e 168 (9%), and the abundance of molecular-ion at m/e 168 in the MS of (9) was lower (6%), because the ionized *cis* molecule (9) is probably less stable than its *trans* ionized species (8).[5] The base peak, however, in the MS of both (8) and (9) appear at m/e 97, corresponding to losses of the sidechain fragment C_5H_{11}.

The events of cyclopropane ring-opening coupled with 1.5-hydrogen migration (1a→3, 1b→4), are most likely the consequence of stabilization of a transition-state for some concerted process.[6] Indeed, on examining the topologies of (1b) and (1a), one can see that the *axial* hydrogen on C-8 (as represented by 2) and C-9, respectively, are both properly aligned with, and in adequate proximity to the isopropenyl π-bond for concerted suprafacial 1.5-homodienyl hydrogen migration.[7] The inoperability of the conventional reaction mode, the homo-Cope rearrangement 1 → 9, appears to spring from the energetics of the non-concerted process.[8,9] It implies probably an initial homolytic cleavage of the cyclopropane bond to produce a biradical intermediate (5) followed by a high energy rotation of the allyl system and recyclisation to give the *cis*-isomer (6). The Cope-rearrangement of (6) into (7) must be very fast indeed.

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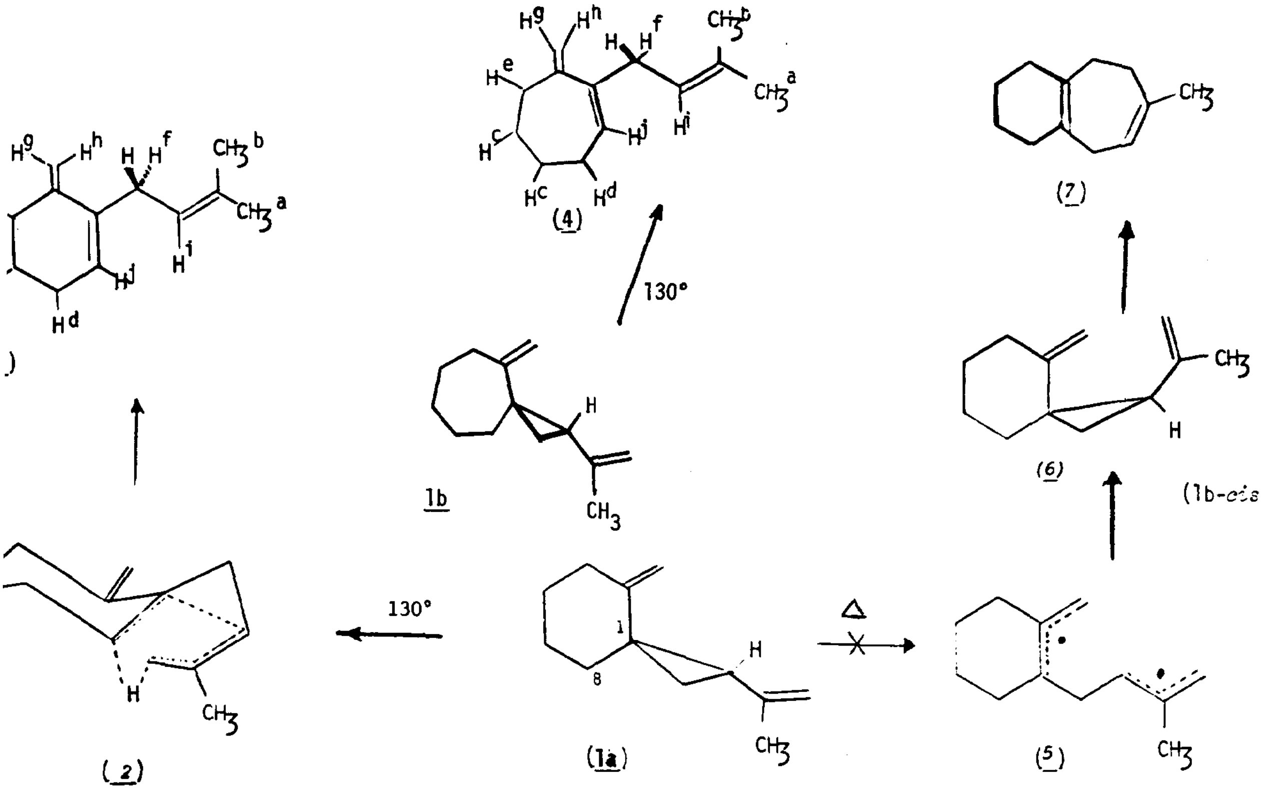
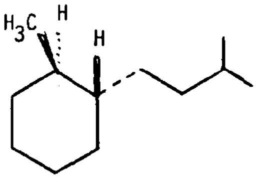


(4) (7) 1b (6) (1b-*cis* (2) (1a) (5)



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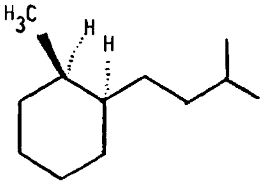

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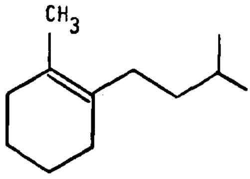


(10)

REFERENCES

1. (a) P.A. Wender, C.L. Hillman, and M.J. Szymanifka, *Tetrahedron Lett.*, 1980, pp. 2205; (b) E. Piers, I. Nagakura, and H.E. Morton, *J.Org.Chem.*, 1978, 43, 3630; (c) R.E. Moore, *Acc.Chem.Res.*, 1977, 10, 40; (d) M.P. Schneider and Csacski, *J.C.S. Chem.Comm.*, 1977, 330; *Angew.Chem.*, 1977, 89, 187; (e) D.L. Garin, *Tetrahedron Lett.*, 1977, 3035; (f) J.E. Baldwin and coworkers, *J.Amer.Chem.Soc.*, 1976, 98, 1593, 8283; 1974, 96, 1542; 1972, 94, 5910 and references cited therein; (g) J.A. Berson, P.B. Dervan, R. Malherbe, and J.A. Jenkins, *J.Amer.Chem.Soc.*, 1976, 98, 5937; A.N. Marvel and S.W. Almond, *Tetrahedron Letters*, 1979, 2777.

2. Column: 6'x¼, 5% OV 17 on G.C.Q. 100/120; temp., 80°C, 30 ml He/min.

3. Calcd. wavelength for such systems: 237 mμ.

4. (a) Murat, *Ann.Chim.Phys.*, [8] 16, 119 (1909) reported the reduction of (10) at 230-250° in presence of Nickel; (b) I.N. Nazarov, G.P. Kugatova, and V.V. Lutsenko, *Zhur.Obshchi Khim.*, 29, 1568 (1959), [*Chem.Abst.*, 54, 8669f (1959)] reported the production of (8) - (9) by catalytic reduction of 1-methyl-2-(3'-methyl-1-butadienyl)-cyclohex-3-ene first in presence of Pd and then with Pt.

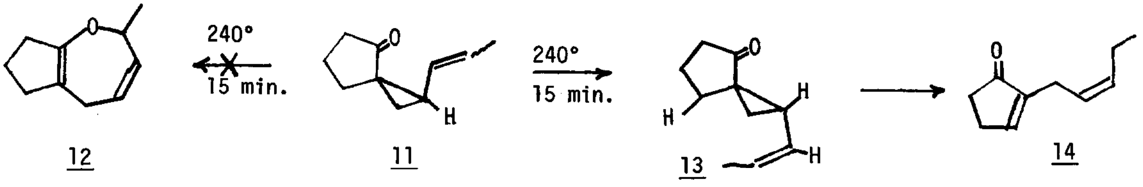
5. S.S. Berman, V.A. Zakharenko, and Al. A. Petrov, *Neftekhimiya*, 7, 703 (1967), [*Chem.Abstr.*, 68, 86737^j (1968)] have shown that *trans* 1,2-dialkylcyclohexanes are four times more stable than the *cis* isomer.

6. See, Ellis and H.M. Frey, *J.Chem.Soc.*, 1964, 5578.

7. (a) M.R. Detty and L.A. Paquette, *J.C.S. Chem.Comm.*, 1978, 365 and references cited therein; *J.Amer.Chem.Soc.*, 1977, 99, 821, 828, 834; M.R. Detty and L.A. Paquette, *Tetrahedron Letters*, 1977, 347; (b) G.V. Meehan, G.G. Pegg, and J. Taylor, *J.C.S. Chem.Comm.*, 1979, 709; (c) H.M. Frey and R. Walsh, *Chem.Revs.*, 1969, 69, 103; (d) W.R. Roth and J. König, *Annalen*, 1965, 688, 28; (e) M.J. Jorgensen and A.F. Tacher, *Tetrahedron Lett.*, 1969, 4651.

8. Compare, W. von E. Doering, and K. Sachdev, *J.Amer.Chem.Soc.*, 1974, 96, 1168.

9. Significantly, the heat induced sigmatropic change in the oxy-analogue of (1), 1-(*cis*-1- propenyl)-*spiro*[2,3]heptan-4-one (11), does not lead to the homo-oxy-Cope rearrangement product (12), but rather gives rise to an initial epimerization (11→13) followed by sigmatropic 1.5-hydrogen migration coupled with cyclopropane bond cleavage to form 2-(*cis*-2-pentenyl)-cyclo-2-pentenone (14): Y. Bahural, L. Cottier, and G. Descotes, *Synthesis*, 1974, 118.



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