Tetrahedron Letters No. 32, pp. 2751-2754, 1970. Pergamon Press. Printed in Great Britain.

THERMOLYSIS OF SPIRO[2.4]HEPTADIENE-4,6

*J.M.E.Krekels, J.W. de Haan and **H.Kloosterziel

*Laboratory of Instrumental Analysis and **Laboratory of Organic Chemistry

University of Technology, Eindhoven, The Netherlands.

(Received in UK 29 May 1970; accepted for publication 10 June 1970)

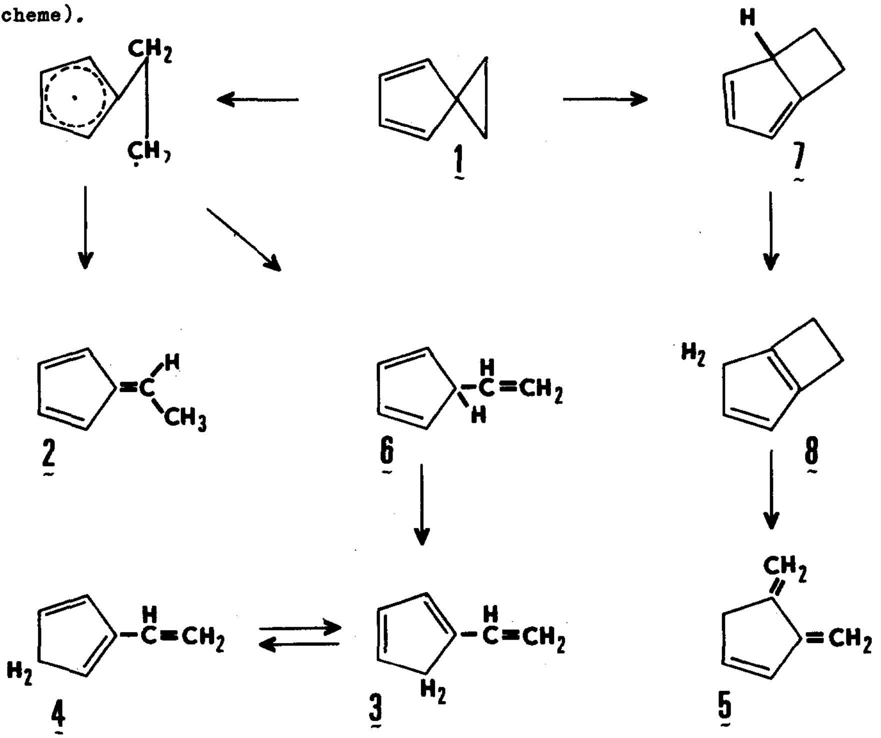
Geminal dimethylcyclopentadienes upon heating isomerize to vicinal dimethylcyclopentadienes by a suprafacial sigmatropic 1,5 shift of a methyl group (1). This and the succeeding letter concern other geminally substituted cyclopentadienes : spiro compounds.

Spiro[2.4]heptadiene-4,6 (**1**) **isomerizes at 345-400°C (diluted with nitrogen in a flow system) by first-order kinetics (log A = 12.89 (s^{-1}); E_a = 43.6 kcal/mole). For all but one (vide infra) of many columns tried the gas-liquid chromatogram (GLC) of the product consists of two peaks.**

One (2) is 6-methylfulvene (**2**): **m/e = 92; ^{1}HNMR = three proton doublet at δ= 2.13 and five proton multiplet at δ= 5.9-6.5 ppm; λ_{max}nm (logϵ) = 254.5 (4.85), 259.5 (4.85), 269 (4.63); hydrogenation (3) yields ethylcyclopentane = A (2, 4).**

The other component (2) readily polymerized (no effect of inhibitors). GLC on a 30 m x 0.25 mm capillary column coated with octadecene effected at 25° separation into three major (3, 4, 5) and one minor (< 2%; unidentified) peaks. These properties precluded individual isolation. The NMR spectrum consists of signals in three regions: δ= 2.9-3.2(=C-CH_2-C=C); δ= 4.8-5.1(=CH_2) and δ= 5.8-6.8(=CH-C). Hydrogenation (3) yields A, cis- (=B) and trans-1,2-dimethylcyclopentane (=C) (2, 4). The amount of 3 + 4 corresponds with A; that of 5 with B + C. Taking into consideration all possible C_7H_8 compounds containing a five-membered ring, the combined GLC, NMR and hydrogenation data for widely varying compositions lead to the assigned structures for 3, 4 and 5

(see scheme).



A kinetic study using a micro flowreactor linked up with the capillary GLC column revealed (a) a temperature independent ratio 2 : 3 : 4 (0.49 : 0.40 : 0.11) and (b) an increasing ratio (2+3+4) : 5 with increasing temperature. The activation parameters are for 1 → 2+3+4 : log A = 13.84, E_a = 47.1 kcal/mole, $\Delta S^{\neq}$= +3 cal/mole.degr, $\Delta H^{\neq}$ = 45.8 kcal/mole and for 1 → 5 : log A = 10.98, E_a = 38.1 kcal/mole, $\Delta S^{\neq}$ = -15 cal/mole.degr, $\Delta H^{\neq}$ = 36.8 kcal/mole.

The conversion of 1 to 2 is analogous to the cyclopropane-propene rearrangement, which is believed to occur in two steps via a biradical (5). Although other mechanisms can be envisaged, we conclude from a that 3 and 4 arise from this common intermediate. The alternative second step leads to 5-vinylcyclopentadiene (6), which will by rapid 1,5 shifts of hydrogen (6) isomerize to 1- and 2- vinylcyclopentadiene (3 and 4).

The ratio 2 : (3+4) = 0.49 : 0.51 shows that the two reactions 1 → 2 and 1 → 6 have equal probabilities.

The difference between $\Delta H^{\neq}$ for the reaction cyclopropane → propene (65 kcal/mole) (5) and for the reaction 1 → 2+3+4 (47 kcal/mole) compares well with the difference in the bond dissociation energies D of CH_3CH_2-H = 98(7) and of C_5H_5-H = 70 - 75 kcal/mole (8).

From b it follows that 5 is formed via a more rigid transition state in the rate-determining step. As such we propose the (one-step) sigmatropic 1,5 shift of an alkyl group in 1 to give 7. Rapid 1,5 shift of hydrogen (6) will convert 7 to 8 and subsequent electrocyclic opening of the cyclobutene ring (9) leads to the observed 3,4-dimethylidene cyclopentene (5).

The rates of reaction 1 → 5 and the methyl shift of geminal dimethylcyclopentadienes are comparable: $\Delta G^{\neq}$ at 600°K = 46 and 40 - 42 kcal/mole respectively (though the values for $\Delta H^{\neq}$ differ more : 36.8 and 42 - 45). If both processes occurred by way of dissociation into radicals the estimated difference (10) is 27.6 (ringstrain of cyclopropane (11)) plus 6 (a methyl versus a primary radical) = 33 kcal/mole. If sigmatropic processes are involved about one half of the difference in ring strain of cyclopropane (27.6) and of cyclobutane (26.2) emerges into the comparison. The near-equality of the rates thus confirms the conclusion that the ring expansion 1 → 5 and the methyl shift (12) are both sigmatropic reactions.

REFERENCES AND NOTES

1. J.W. de Haan and H.Kloosterziel, (a) Rec.trav.Chim. 84, 1594 (1965);
   (b) Ibid 87, 298 (1968).
2. Isolated by preparative GLC.
3. 1 atm. H_2; PtO_2; roomtemperature; in cyclohexane.
4. Identified by comparison of NMR and IR spectra.
5. For leading references see H.M.Frey, Adv. Phys. Org. Chem. 4, 147 (1966).
6. W.R.Roth, Chimia 20, 229 (1966).
7. J.A.Kerr, Chem.Rev. 66, 465 (1966).
8. E.Hedaya, D.W. Mc Neil, P.Schissel and D.J. Mc Adoo, J.Am.Chem.Soc. 90, 5284 (1968).
9. R.W.Carr and W.D.Walters, J.Phys.Chem. 69, 1073 (1965).
10. Assuming that recombination of radicals is a non-activated process.
11. E.L.Eliel, Stereochemistry of Carbon Compounds, New York 1962, p.188.
12. From $D(CH_3CH_2-CH_3)$ = 85 kcal/mole one estimates $D(C_5H_5-CH_3)$ = 72.5(± 2.5) - 98 + 85 = 60 kcal/mole, which is appreciably higher than the observed value for $\Delta H^{\neq}$(40 - 45 kcal/mole) for the methyl shifts (1). This confirms the previous rejection of a free radical mechanism.