Alkyl Shifts in Diradicals: Thermal Isomerization of Isopropenylspiropentane

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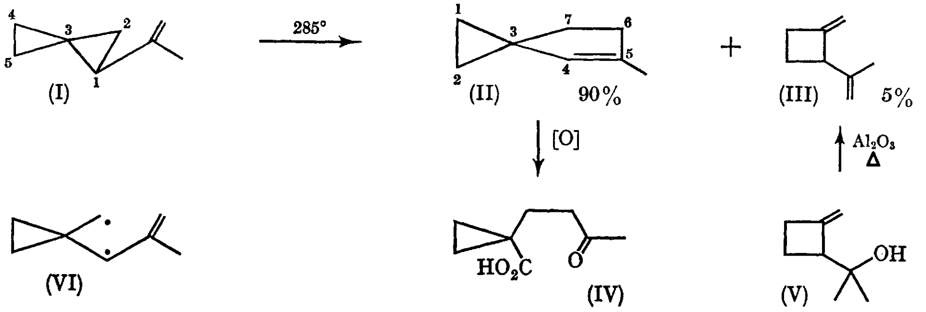
ISOPROPENYLSPIROPENTANE, (I), (99 + % homogeneous by capillary gas chromatography) when heated in a carefully neutralized, sealed tube at 285° for 1 hr. at a calculated internal pressure of one atmosphere gave two major compounds in yields of 5% and 90%. The main product was identified as 5-methylspiro[2,4]hept-4-ene (II) from spectral data; N.m.r. (100 Mc./sec.)[1] symmetrical multiplet at δ 0·5 (4H); quartet, $J = 1·3$ c./sec., at δ 1·7 (3H); unsymmetrical triplet with fine structure, $J = 7$ c./sec., at δ 1·85 (2H); unsymmetrical triplet with fine structure, $J = 7$ c./sec., at δ 2·35 (2H); sextet, $J = 1·3$ c./sec., at δ 4·74 (1H). Infrared spectra of (II): 3075, 3040, 3000, *etc.*, 6155, 1030, 1005, 990, 955, 855, and 820 cm.$^{-1}$; *M*, 108·0937 (calc. for C_8H_{12}, 108·0940). U.v. spectra: 212 mμ (ϵ, 5500). Further proof of the structure is shown by (II) being oxidized, in good yield, to a keto-acid whose spectroscopic properties are in accord with the structure (IV).

2-Isopropenylmethylenecyclobutane (III) was the minor product identified in the pyrolysis of (I). spectra: n.m.r. (60 Mc./sec.) of v.p.c. purified (III): triplet, $J = 1$ c./sec., at δ 1·7 (3H); broad multiplet from δ 1·7 to 2·8 (4H); broad multiplet from δ 3·3 to 3·8 (1H); multiplet at δ 4·75 (4H). Infrared: 3080, 2980, 2930, 1670, 1640, 1450, 1375, broad intense 880 cm.$^{-1}$; *M*, 108·0938 (calc. for C_8H_{12},



108·0940). Confirmation of the structure is shown by (III) being one of the major hydrocarbon products from the dehydration of dimethyl-(2-methylenecyclobutyl)methanol (V) at 190° over basic alumina in a flow system at 0·5 mm. Hg.

While no attempt was made to determine the kinetics of the reaction, it was found that isopropenylspiropentane isomerized only to the extent of 35% when heated at 245° for 65 min., indicating that the activation free energy for the process is in the neighbourhood of 41 kcal. This is about 8·5 kcal less than that for isomerization of vinylcyclopropane itself[2] and is probably due to the extra strain in the spiropentane system.[3] The ratio of (II) : (III) formed in the pyrolysis at 245° was 20 : 1 which is within experimental error of the ratio found in the 285° pyrolysis. With activation free energies of this magnitude, the only bond cleavage expected would be that of a bond to C-1 in (I), that is, to the carbon atom bearing the unsaturated side-chain.[4]

The two identified products from the isomerization, which represent 95% of the total product, are most economically derived by initial cleavage of the 1,2 or *peripheral* bond [resulting in the diradical (VI) followed by, or in concert with, an allylic rearrangement [to form (II)] or a methylene shift [to form (III)]. To the extent that the formation of (II) is a vinylcyclopropane rearrangement, the diradical intermediate (VI) is probably involved,[4]† and this same intermediate may be the precursor of (III). If initial cleavage of the 1,3 or *radial* bond of (I), were involved then 5-methylspiro[2,4]hept-5-ene and 3-isopropenylmethylenecyclobutane would have resulted. Thus, the formation of 2-isopropenylmethylenecyclobutane [*via* (VI)] in the pyrolysis of isopropenylspiropentane represents one of the first authenticated cases of a *vicinal* alkyl shift in cyclopropane thermolyses.[5] Whether or not this pathway represents that involved in the thermal rearrangement of spiropentane to methylenecyclobutane[3] has yet to be determined.

We thank the Petroleum Research Fund for partial support of this work and the National Science Foundation for a grant to Indiana University for the purchase of the A.E.I. MS-9 Mass Spectrometer used in this work.

(*Received, May* 31*st*, **1967**; *Com.* 535.)

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† Preliminary experiments reveal that partial pyrolysis of one of the four diastereomeric 1-isopropenyl-4-methylspiropentanes results in its interconversion with only one other of these diastereomers and not all three; moreover, the two interconverting isomers are epimeric only at C-1. Thus, diradicals are involved and result from peripheral-bond scission and not radial-bond cleavage since the latter pathway would serve to interconvert all four diastereomers prior to the structural isomerizations discussed.

[1] (a) We thank Prof. M. R. Willcott for this spectrum; (b) A Nuclear Overhauser Experiment (NOE) [see ref. 4c] suggested and performed by Prof. Willcott also points to the structure (II); thus, irradiation of the cyclopropyl proton resonances resulted in a 10—20% enhancement of the vinyl and the upfield set of methylene proton resonance signals relative to the remaining signals; (c) F. A. L. Anet and A. J. R. Borun, *J. Amer. Chem. Soc.*, 1965, **87**, 5250.

[2] M. C. Flowers and H. M. Frey, *J. Chem. Soc.*, 1961, 3547.

[3] (a) M. C. Flowers and H. M. Frey, *J. Chem. Soc.*, 1961, 5550; (b) P. J. Burkhardt, *Diss. Abs.*, 1962, **23**, 1524; (c) F. M. Fraser and E. J. Prosen, *J. Res. Nat. Bur. Stand.*, 1955, **54**, 143; (d) W. von E. Doering and J. C. Gilbert, *Tetrahedron*, Suppl. No. 7, 1966, 397.

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[5] (a) E. T. McBee, J. A. Bosome, and C. J. Morton, *J. Org. Chem.*, 1966, **31**, 768, found evidence for an alkyl shift in the liquid phase pyrolysis of 1,2,3,4-tetrachloro-6,6,7,7-tetramethylspiro[2,4]hept-1,3-diene; (b) Other reports of alkyl shifts in purported or possible diradical intermediates include: C. McKnight and F. S. Rowland, *J. Amer. Chem. Soc.*, 1966, **88**, 3179; H. Kristinsson and G. W. Griffin, *ibid.*, p. 378; D. E. McGreer, R. S. McDaniel, and M. G. Vinje, *Canad. J. Chem.*, 1965, **43**, 1389.