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VALENCE-BOND ISOMER CHEMISTRY. PART 12 [1]. PYROLYSIS OF THE HEXAFLUOROBICYCLO[2.2.0]HEXA-2,5-DIENE-DIAZOMETHANE ADDUCT. SIGMATROPIC FLUORINE SHIFTS AND ELIMINATION OF DIFLUOROCARBENE FROM HEXAFLUOROCYCLOHEPTATRIENES

M.G. BARLOW, R.N. HASZELDINE and C.J. PECK

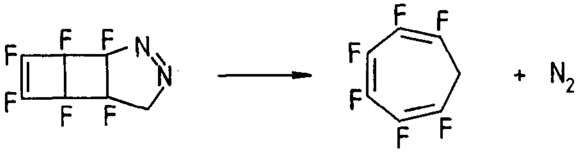
Chemistry Department, The University of Manchester Institute of Science and Technology, Manchester M60 1QD (Great Britain)

SUMMARY

Flow pyrolysis of the title adduct yields tetrafluoroethylene and all three tetrafluorobenzenes.

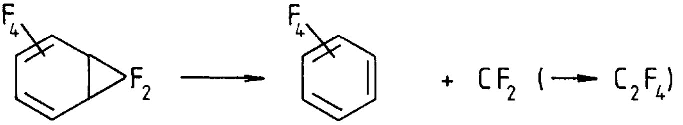
DISCUSSION

Hexafluorobicyclo[2.2.0]hexa-2,5-diene is a reactive dipolarophile, forming 1:1- and 1:2-adducts with many 1,3-dipoles [2]. The phenyl azide adduct loses nitrogen on heating, forming hexafluoro-1-phenylazepine [3], and this prompted a study of the diazomethane adduct as an analogous source of hexafluorocycloheptatriene:



Rapid passage of the vapour of this adduct at ca. 0.15 mmHg through a silica tube heated to 450 °C resulted, unexpectedly, in the formation of tetrafluoroethylene (52%), 1,2,3,4-, 1,2,3,5-, and 1,2,4,5-tetrafluorobenzenes (95% on the converted adduct) in the ratio 8:36:56, and recovered adduct (17%).

Thermal [1,5] sigmatropic shifts of hydrogen occur readily in cycloheptatriene [4]. For fluorine, both [1,3] and [1,5] shifts are allowed processes [5]. Cheletropic elimination of difluorocarbene from a suitable norcaradiene:



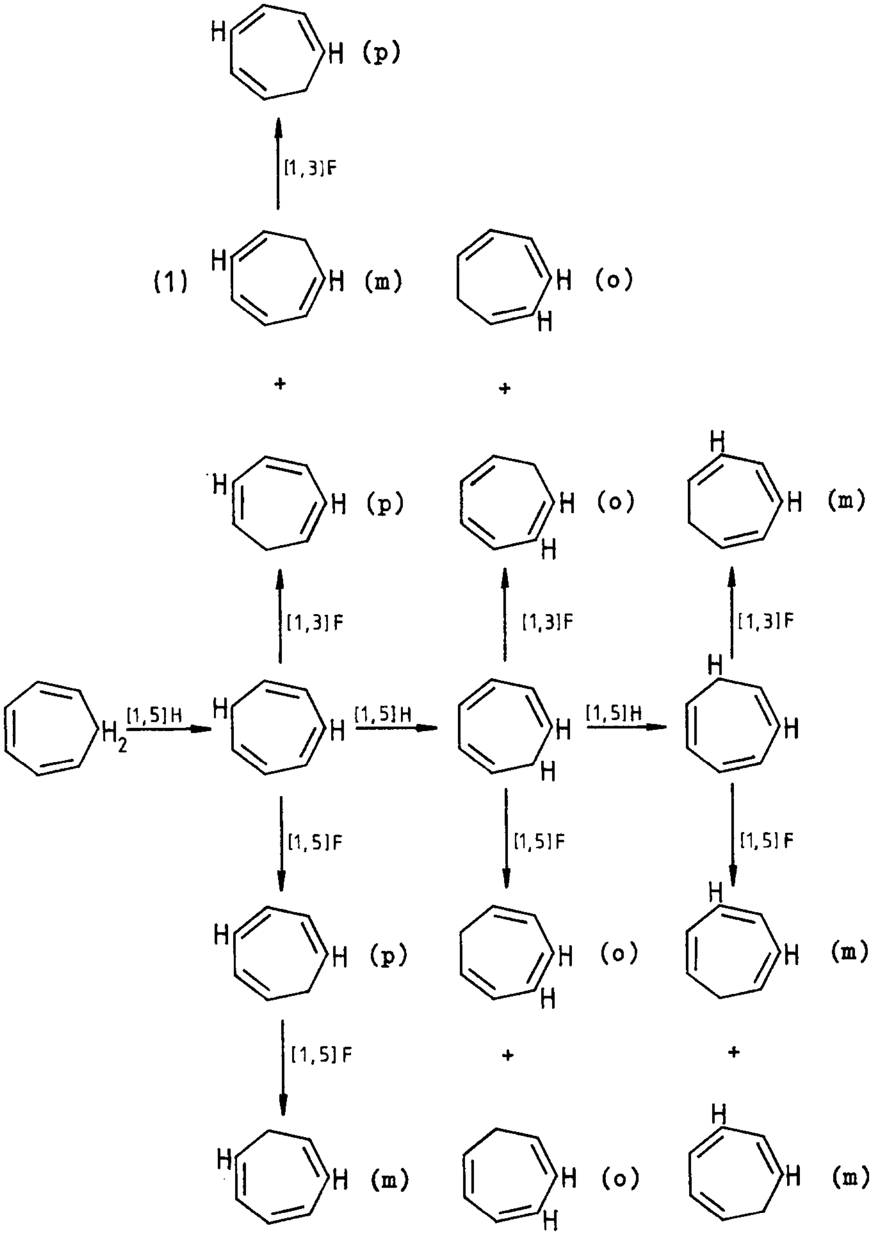
would provide a source for the tetrafluoroethylene and the tetrafluorobenzenes. The cycloheptatriene-norcaradiene equilibrium is well known [6].

In the Scheme are represented possible [1,5] sigmatropic shifts of hydrogen, and some of the alternative [1,3] or [1,5] shifts of fluorine. The three possible tetrafluorobenzenes obtained are represented by o, m, or p, for the 1,2,3,4-, 1,2,3,5-, or 1,2,4,5-isomers, respectively.

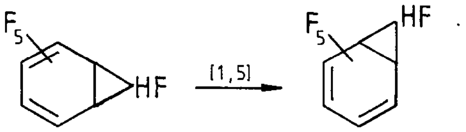
The 1,2,3,4-tetrafluorobenzene is a minor product and its production requires two hydrogen shifts, which indicates that fluorine shifts are faster. It is difficult to distinguish between the alternative [1,3] and [1,5] fluorine shifts, since both predict 1,2,4,5-tetrafluorobenzene as the preferred isomer, its proportion depending upon how successfully cheletropic elimination of CF_2 competes with the second fluorine shift.

The 1,2,4,5- and 1,2,3,5-tetrafluorobenzenes are produced in the ratio 60:40; there are two explanations for this. If the two initial [1,3] fluorine shifts are equally possible, 20% of the heptatriene molecules (1) undergo a second [1,3] shift. This requires that CF_2 elimination be some four times faster than fluorine shift. Alternatively, 40% of the molecules underg two [1,5] fluorine shifts, implying that CF_2 elimination is only slightly faster.

[1,5] hydrogen shifts have activation energies of 135 kJ mol^{-1} in 7-methylcycloheptatriene, but this falls to 108 kJ mol^{-1} in the 7-methoxy derivative [7], and a relatively

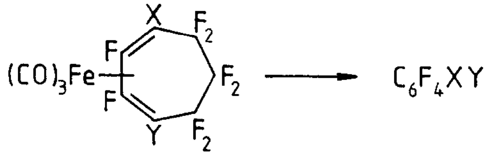


SCHEME Sigmatropic Hydrogen and Fluorine Shifts in Hexafluorocycloheptatrienes (Fluorine Substituents not Shown) low value may well apply here. The cycloheptatriene-norcaradiene equilibrium should be fast [8], and [1,5] alkyl shifts in the norcaradiene [9]:



should not be a complication since, in general, alkyl shifts have activation energies some 80 kJ mol^{-1} higher than hydrogen shifts [10]. The elimination of the stabilised CF_2 carbene [11] has an analogy in the allowed elimination of CF_2 from hexafluorocyclopropane, where the activation energy is 161 kJ mol^{-1} [12], but here the activation energy should be lower since an aromatic molecule is produced. However, no clear cut distinction is possible at this stage between [1,3] and [1,5] fluorine shifts, which must await a study of individual cycloheptatrienes under conditions where CF_2 elimination is not complete.

(Polyfluorocyclohepta-1,3-diene)iron tricarbonyls produce fluorobenzenes on pyrolysis [13]:



X = Y = F or H;

X = F, Y = H.

It was suggested that these arose <u>via</u> difluorocarbene elimination from a norcaradiene. Sigmatropic shift of hydrogen, but not of fluorine, at the cycloheptatriene stage was considered since the 1<u>H</u>,4H-compound produced both 1,2,3,5- and 1,2,4,5-tetrafluorobenzenes.

Sigmatropic shifts of fluorine have rarely been reported and examples have been confined to five- [14] and six-membered [15] rings, where, apparently, [1,5] are favoured, and the [1,3] shifts seen in cyclohexadienes possibly fluoride-ion catalysed [16]. They may be rather easier than hitherto suspected.

Pyrolysis of 1,2,3,4,5,6-Hexafluoro-7,8-diazatricyclo[4.3.0.0^{2,5}]-nona-3,7-diene

The title compound [2] (0.36 g, 1.6 mmol) was sublimed *in vacuo* at 60 °C and *ca*.0.15 mmHg through a silica tube (heated length 40 cm x 1.2 cm i.d.) at 450 °C, and the products (0.258 g) which condensed at -196 °C were fractionated by trap-to-trap distillation to give: (i) tetrafluoroethylene (34 mg, 0.34 mmol, 52% upon the adduct converted), which condensed at -196 °C; (ii) a mixture of 1,2,4,5- (0.106 g, 0.70 mmol, 52%), 1,2,3,5- (68 mg, 0.45 mmol, 34%), and 1,2,3,4-tetrafluorobenzenes (15 mg, 0.10 mmol, 7%), which condensed at -78 °C and was identified by ^{19}F n.m.r. spectroscopy; and (iii) starting material (60 mg, 0.26 mmol, 17%), which condensed at 0 °C, together with a trace of tarry residue (1 mg).

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