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FLUOROCYCLOPENTANES—VI[1]

1H- AND 2H-PENTAFLUOROCYCLOPENTADIENE

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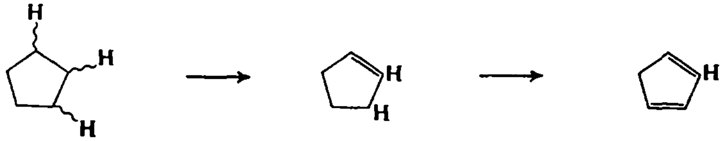
Abstract—Dehydrofluorination of 1H:5H-hexafluorocyclopentene with molten potassium hydroxide gives 2H-pentafluorocyclopentadiene, which dimerizes readily. Dehydrofluorination of 3H/4H-hexafluorocyclopentene gives a mixture of the 1H- and 2H-pentafluorocyclopentadienes. The 1H-diene also dimerizes.

IN PART II[2] of this series, we reported that hexafluorocyclopentadiene was formed when 3H- or 4H-heptafluorocyclopentene were dehydrofluorinated by passage through molten potassium hydroxide (no diene could be detected in aqueous alkali dehydrofluorinations; only a very slow reaction to give water-soluble materials occurred). We have now extended this reaction to the preparation of the 1H- and 2H-pentafluorocyclopentadienes in low yield.

If the possibility of rearrangement is discounted, the 2H-compound is the only diene that can be formed by the dehydrofluorination of 1H:5H-hexafluorocyclopentene with molten potassium hydroxide. The 1H:5H-compound can itself be readily prepared in good yield by the dehydrofluorination (aqueous alkali) of any of the 1H:2H:3H-heptafluorocyclopentanes.[3]



(all unmarked bonds are joined to fluorine)

The 2H-diene dimerized extremely rapidly—much more so than hexafluorocyclopentadiene—and because of this we have been unable to study it. Gas chromatography showed that the dimeric product consisted of at least three compounds, one of which comprised some 80–90% of the mixture. If this major dimer is the product of a Diels–Alder self-condensation like that from cyclopentadiene itself—and this is probable because hexafluorocyclopentadiene forms a dimer which is almost certainly a Diels–Alder product[2]—then eight structural formulae are possible. IR spectroscopy indicated that there were —CF=CF— and —CH=CF— double bonds in the major dimer and this reduces the number of possible structures to four, I and II and their *endo*-isomers. Further support for these structures came from NMR measurements; proton resonance showed one olefinic proton and one non-olefinic, and fluorine resonance three tertiary fluorines. These spectroscopic measurements do not, of

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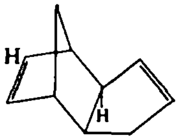
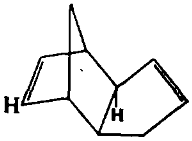
[1] Part IV. A. Bergomi, J. Burdon, T. M. Hodgins, R. Stephens and J. C. Tatlow, *Tetrahedron* **22**, 43 (1966).

[2] J. Burdon, T. M. Hodgins, D. R. A. Perry, R. Stephens and J. C. Tatlow, *J. Chem. Soc.* 808 (1965).

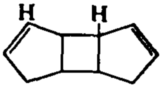
[3] J. Burdon, T. M. Hodgins, R. Stephens and J. C. Tatlow, *J. Chem. Soc.* 2382 (1965).



I



II



III

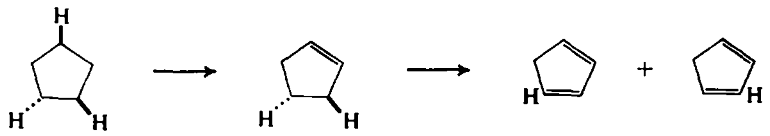
(all marked bonds are joined to fluorine)

course, rule out structures of type III; further evidence from the fluorine resonance spectrum does render such structures rather implausible, however, since two AB patterns with $J_{AB} = 180$ c/s and $J_{AB} = 252$ c/s were discernable. Such large coupling constants can only arise from geminal fluorines and it is hard to see why the two —CF_2-groups on III should give rise to the very different coupling constants observed. Both structures I and II, however, have two very different types of —CF_2-group; those at positions 5 (in 5-membered ring) and 10 (—CF_2-bridge).

The four possible structures (I and II and their *endo*-isomers) would be rather difficult to distinguish and we have not attempted to do so. When more ^{19}F NMR spectra of such compounds have been measured it may be possible to analyse the ^{19}F spectrum more fully to obtain the true structure.

An attempt to convert the dimer back into the monomer by heating it was largely unsuccessful. No reaction occured up to 500° and even at this temperature very little 2H-diene was formed; instead a more deep-seated decomposition appeared to be the main reaction from the number of products indicated by GLC. Decomposition to monomer was not observed[4] when the dimer of hexafluorocyclopentadiene was heated at 500° and above. Although the dimer of cyclopentadiene decomposes into the monomer at about its b.p. (170°), it appears[5] that halogen substitution increases the stability of such dimers. The dimers of hexafluoro- and 2H-pentafluorocyclopentadiene, however, appear to be the most stable of the compounds of this type yet reported.

1H-Pentafluorocyclopentadiene was prepared from 3H/4H-hexafluorocyclopentene by dehydrofluorination with molten potassium hydroxide. It was more stable than the 2H-diene which was also formed in the reaction and so could be separated by allowing the 2H-diene to dimerize. 3H/4H-hexafluorocyclopentene is easily prepared by the aqueous alkaline dehydrofluorination of 1H,4H/2H-heptafluorocyclopentane.[3] It is quite probable that a similar mixture of dienes would be obtained from 3H,4H/-heptafluorocyclopentene[3] as well.



(all unmarked bonds are joined to fluorine)

The 1H-diene does not undergo a Diels–Alder reaction with tetracyanoethylene or ethyl vinyl ether, but it does dimerize on being heated. Gas-chromatography

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[4] A. Bergomi, J. Burdon and J. C. Tatlow, unpublished.

[5] E. T. McBee and H. E. Ungnade, *Chem. Revs.* 58, 249 (1958); E. T. McBee, D. K. Smith and H. E. Ungnade, *J. Amer. Chem. Soc.* 77, 387 and 389 (1955).

showed that the dimer product contained at least two compounds, with the longer-retained one comprising about 70% of the mixture. It is probable, although not certain, that both dimers arise from the 1H-diene and are not cross-dimerization products of the 1H- and 2H-dienes because the major 2H-diene dimer (I or II or their *endo*-isomers) is completely absent from the mixture. Once again IR spectroscopy showed —CF═CF— and —CH═CF— double bonds in the mixed dimers and ^{1}H NMR, one olefinic proton; the ^{19}F NMR spectrum showed that the major isomer contained three tertiary fluorines and two very different types of —CF_2-groups (two AB patterns with J_{AB} = 270 c/s and 185 c/s). The major dimer at least, therefore, seems to be a Diels–Alder product with one of four possible formulae; those shown below and their *endo*-isomers.

(all unmarked bonds are joined to fluorine)

It is curious that when a mixture of the 1H- and 2H-dienes are allowed to dimerize, the same dimer of the 2H-diene and the same two dimers of the 1H-diene as are formed from the dienes alone are by far the major products; only very small amounts of other, possibly cross-dimerized substances, were formed.

We also attempted to isomerize the mixture of 1H- and 2H-pentafluorocyclopentadienes to their 5H-isomer with a view to the preparation of the pentafluorocyclopentadienide anion. However, the diene mixture was unaffected by passage over sodium fluoride at 200°. This is not perhaps surprising since the desired migration involves increasing the number of fluorine substituents on the double bonds and decreasing the hydrogen. We have previously observed[3,6] that migrations of double bonds in fluorohydro-olefins take place entirely in the opposite direction; that is, with an increase in the number of hydrogen substituents on double bonds.

EXPERIMENTAL

Dehydrofluorination of 1H:5H-*hexafluorocyclopentene*. The olefin[6] (1·1 g) was vaporized in a N_2 stream (2l./hr) and bubbled through molten KOH (50 g) at 210°. The products (0·3 g) were collected in a liquid air cooled trap. When the trap had warmed to about −10° an exothermic reaction (presumably the diene dimerizing) occurred. Separation by prep scale GLC (6′ × ½″ diam; packed with dinonyl phlthalate on Celite; temp 95°; N_2 flow-rate 9l./hr) gave 2H-pentafluorocyclopentadiene (trace), unreacted 1H-5H:hexafluorocyclopentene (0·05 g), a *dimer of* 2H-*pentafluorocyclopentadiene* (0·1 g), b.p. 135° (Found: C, 38·7; H, 0·8; top mass spectrum peak, 312. $C_{10}H_2F_{10}$ requires: C, 38·5; H, 0·6%; mol. wt 312) and two longer retained peaks (< 0·02 g combined). The dimer had ν_{max} at 1780 (CF═CF)[7] and 1670 cm^{-1} (CF═CH), and the monomer at 1780 and 1690 cm^{-1}. The ^{1}H NMR spectrum of the pure dimer showed two peaks of equal intensity at 5·3 (—CH═) (ca. 20 c/s broad) and 3·4 (⪖C—H) (ca. 40 c/s broad) (both chemical shifts are in ppm downfield from TMS as external reference). The ^{19}F spectrum was very complex and was not completely analysed. The following features were noted: tertiary fluorine peaks at 109·5, 130·5 and 131 (all in ppm upfield from

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[6] T. Rimmington, R. Stephens and J. C. Tatlow, unpublished; D. R. Sayers, R. Stephens and J. C. Tatlow, *J. Chem. Soc.* 3035 (1964).

[7] J. Burdon and D. H. Whiffen, *Spectrochem. Acta* **12**, 139 (1958).

trifluoroacetic acid as internal reference); and two AB patterns, the first having δ_A at 28 and δ_B at 32·5 ppm with J_{AB} = 252 c/s, and the second, δ_A at 51·5 and δ_B at 63·5 ppm, with J_{AB} = 180 c/s.

Dehydrofluorination of 3H/4H-*hexafluorocyclopentene.* The olefin[8] (3·0 g) was bubbled through molten KOH hydroxide as in the previous experiment, but at 150°. The product (2·1 g) was separated by GCL into 1H-*pentafluorocyclopentadiene* (0·25 g) [Major mass peaks at 156 ($C_5F_5H^+$), 137 ($C_5F_4H^+$) and 106 ($C_4F_3H^+$)], unreacted 3H/4H-hexafluorocyclopentene (0·35 g), and the major dimer of 2H-pentafluorocyclopentadiene (0·45 g) (identified by IR). 1H-pentafluorocyclopentadiene had ν_{max} at 1770 and 1670 cm^{-1}.

This reaction was repeated on 12·6 g of the olefin and the products (6·6 g) were kept in a sealed tube at 50° for 16 hr to ensure complete dimerization of the polyfluorinated cyclopentadienes. Separation by GLC (6′ × ¼″ diam column; packed with silicone gum on Celite; temp 80°; N_2 flow-rate 5 l./hr) of a sample (3·2 g) of the products gave a complex mixture (2·0 g) and the major dimer (see later) of 1H-pentafluorocyclopentadiene (0·4 g) (IR). The complex mixture was further separated by GLC (same column and approximately the same conditions as in the previous experiment) into 1H-pentafluorocyclopentadiene (trace), unreacted 3H/4H-hexafluorocyclopentene (0·2 g), three unknown compounds, the major one of which had the same retention time as the minor dimer of the 1H-diene (see later) (ca. 0·2 g altogether), and the major dimer of 2H-pentafluorocyclopentadiene (0·8 g), all the known compounds being identified by IR.

Dimerisation of 1H-*pentafluorocyclopentadiene.* The diene (0·4 g) was kept at 10–15° in a sealed tube for one month. A quantitative yield of a colourless crystalline solid, m.p. 70–75°, b.p. 155° was obtained; it was (GLC) a mixture of two dimers (ca. 5:2) of 1H-pentafluorocyclopentadiene. (Found: C, 38·3; H, 0·5. Top mass spectrum peak, 312. Calc. for $C_{10}H_2F_{10}$: C, 38·5; H, 0·6% mol. wt 312); it had ν_{max} at 1760 and 1690 cm^{-1}. The ^1H spectrum of the mixed dimers in CCl_4 showed two broad peaks of equal intensity at 5·8 (—CH═) and 3·5 ppm (⪢CH—). The ^{19}F spectrum was complex and clearly was that of a mixture of two components, one of which comprised about 70% of the mixture. The major component showed tertiary fluorines at 94, 117 and 136 ppm, and two AB patterns [δ_A = 14·5, δ_B = 30 (ppm), J_{AB} = 270 c/s, and δ_A = 36·5, δ_B = 53 (ppm), J_{AB} = 185 c/s].

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