Octafluorocyclohepta-1,3,5-triene and Hexafluorotropone

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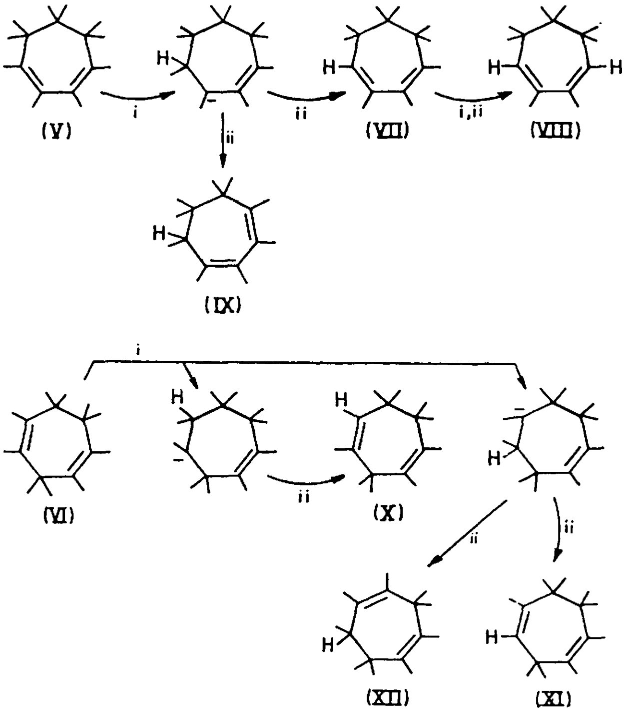
Summary The title compounds have been made for the first time, from dodecafluorocycloheptanes *via* appropriate fluorocycloheptadienes.

Fluorinations of benzene and of cyclopentane or cyclopentadiene with cobalt trifluoride gave ranges of polyfluorocyclo-hexanes[1] and -pentanes,[2] respectively. Dehydrofluorinations of suitable members of each series then afforded products with maximum unsaturation; respectively polyfluoro-benzenes[1] and -cyclopentadienes.[3] We now report analogous compounds in the cycloheptane series.

Comparable fluorinations of cycloheptane and of cyclohepta-1,3,5-triene had already been reported.[4] Though there was some rearrangement to give polyfluoromethylcyclohexanes, the major products were polyfluorocycloheptanes, including isomeric dodecafluorocycloheptanes (boiling range 105—114°). Techniques used were analogous to those described earlier.[1,2] Any undecafluorocycloheptanes present were in a highly complex mixture (b.r. $>114°$; $<25\%$ of the crude) not yet characterised. Therefore, the precursors chosen for the present work were a 1*H*,3*H*- (I), b.p. 106°, and a 1*H*,4*H*-dodecafluoride (II), b.p. 108°, (the major individual components) which, together with their stereoisomers (III), b.p. 113°, and (IV), b.p. 114°, comprised 20% of the mixture.

Treatment of (I)—(IV), separately or in admixture, with conc. aqueous KOH gave[4] decafluorocyclohepta-1,3- (V) (b.p. 88°) and -1,4-diene (VI) (b.p. 85·5°) which were readily separable. Introduction of further unsaturation into (V) and (VI) was done *via* an extension of our earlier work[5] on reactions of fluorocycloalkenes with $LiAlH_4$, which resulted in stepwise replacement of fluorine by hydrogen, involving an addition–elimination pathway. For the present purposes, the milder $NaBH_4$[6] was used; the results are shown in the Scheme. Products (IX) and (XII) with allylic hydrogen, arising[5] from an overall double bond shift, were required not the major ones (VII), (X), and (XI) resulting from simple replacement of vinylic fluorine by hydrogen.



Scheme. All bonds are to fluorine unless otherwise specified. Reactions i, $NaBH_4$; ii Loss of F^-.

Each of the desired dienes (IX) and (XII) was obtained, though in small yield, and was then dehydrofluorinated but the products were labile to aqueous alkali. The first successful reactions involved rapid passage through molten KOH to limit the contact time. A much better reagent was powdered KOH in benzene; this gave octafluorocyclohepta-1,3,5-triene (XIII), b.p. 110—111°, from (XII) in high yield. In fluorocarbon chemistry, $>CF_2$ groups are normally very stable, though if flanked each side by $-CF=CF-$, hydrolysis with conc. H_2SO_4 is possible (perfluorocyclohexa-1,4-diene afforded[7] tetrafluoro-*p*-benzoquinone). The cycloheptatriene (XIII) was extremely susceptible to hydrolysis and even in moist air or a wet solvent gave hexafluorotropone (XIV). This crystallised in flat plates, m.p. 102—103° and was monoclinic ($a = 13{\cdot}38$, $b = 9{\cdot}31$, $c = 5{\cdot}86$ Å; $\beta = 93°39'$). (XIV) was relatively stable; it did not give a hydrate (*cf.* most fluoro-ketones), and showed no obvious tendency to rearrange to a benzenoid structure (*cf.*[8] hexachloro- and hexabromo-tropone). In a nucleophilic substitution reaction, with NaOMe (1 mol. equiv.) (XIV) afforded a symmetrical tetrafluorodimethoxytropone (XV) as the major product. It seems, on the evidence thus far, that (XIV) shows some behaviour reminiscent of polyfluoro-aromatic compounds. Further *X*-ray crystallographic studies of hexafluorotropone are being undertaken by Dr. T. A. Hamor. Compounds (I)—(XV) are all new, and gave correct elemental analyses and have u.v., i.r., n.m.r. and mass spectra in accord with their structures.

(*Received*, *24th April* 1972; *Com.* 688.)

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