Preparation of Perfluoro-(1,2-dialkylcyclopentenes) and their Photochemical Isomerisation to Perfluoro(1-alkenyl-1-alkylcyclopropanes)

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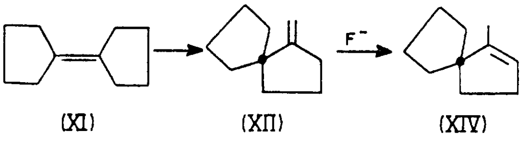
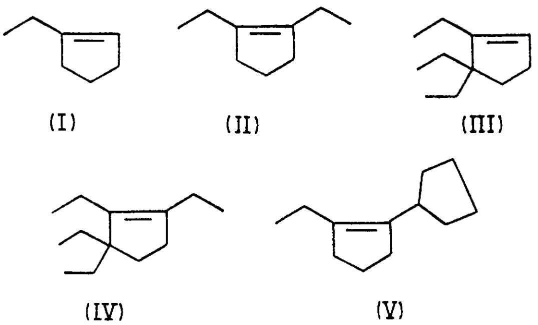
Summary Perfluoro-(1,2-dialkylcyclopentenes), conveniently prepared by the co-oligomerisation of a perfluoroalkene and perfluorocyclopentene, and photolysed in the liquid phase, undergo a 1,3-allylic shift to give the isomeric perfluoro-(1-alkenyl-1-alkylcyclopropanes) in high yield.

The fluoride ion-catalysed oligomerisation of perfluoroalkenes[1] and of perfluorocycloalkenes,[2] recently described, have been extended by the co-oligomerisation of tetrafluoroethylene and perfluorocyclopentene in the presence of caesium fluoride and with tetraglyme as solvent. The yields of the individual co-oligomers (I)—(V) so obtained can be optimised by suitable choice of reactant ratio. Hexafluoropropene similarly yields perfluoro-(1,2-di-isopropylcyclopentene).



(all compounds are perfluorinated)

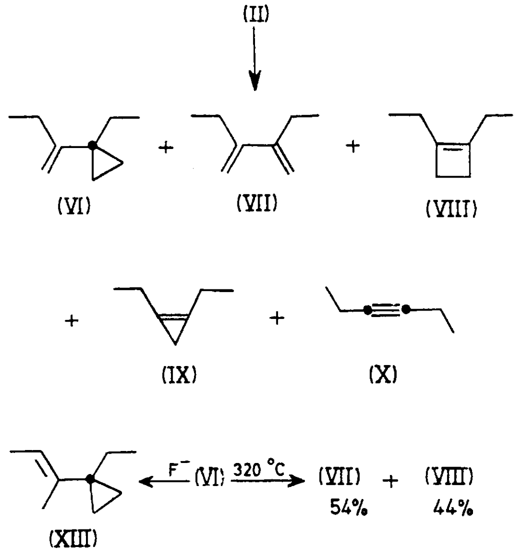
Photolyses of the perfluoro-(1,2-dialkylcyclopentenes) are related to those reported recently[3] for acyclic perfluoro-olefins, and lead to a 1,3-allylic shift with the unexpected formation in high yield of alkenylalkylcyclopropanes. Many examples are known of photolytic 1,3-allylic shifts in hydrocarbon chemistry, but in all except cyclopentene itself equilibrium strongly favours the cyclopentene rather than the vinylcyclopropane.[4] Thus photolysis of (II) (liquid phase, medium pressure lamp, no filter, silica tubes) gives the cyclopropane (VI) (55% yield), together with the diene (VII) (20% yield); minor products of the photolysis are the cyclobutene (VIII), the cyclopropene (IX), and the acetylene (X) (Scheme). The diene (VII) may arise through thermolysis of the cyclopropane (VI) at the relatively high ambient temperature (*ca.* 100 °C) during photolysis; separate pyrolysis of the cyclopropane (VI) gave the diene (VII) and the isomeric cyclobutene (VIII). The cyclopropane (VI) is not reconverted into the cyclopentene (II) by pyrolysis at a lower temperature (150—200 °C) as might have been anticipated on the basis of the reported thermal isomerisation of perfluorovinylcyclopropane to perfluorocyclopentene,[4,5] and of the many similar thermal isomerisations of hydrocarbon analogues.[6]



(all compounds are perfluorinated)

Scheme

Photolysis of perfluoro-(1,2-di-isopropylcyclopentene) affords the homologues of compounds (VI)—(X). Photolysis of (V), a homologue of (II) in which the two perfluoroalkyl groups are different, gives a mixture of both isomers expected from a 1,3-allylic shift. Perfluorocyclopentene dimer (XI) similarly gives the spirane (XII), and liquid phase photolysis of perfluorocyclohexene gives an 80% yield of perfluoromethylenecyclopentane with no volatile by-products. This last result contrasts with the complex mixture arising by gas-phase photolysis of perfluorocyclohexene in the presence of air, when only a 35% yield of perfluoromethylenecyclopentane is obtained.[7]



(all compounds are perfluorinated)

As anticipated, fluoride ion isomerisation of the terminal double bonds in compounds (VI) and (XII) gives the internal alkenes (XIII) and (XIV), respectively.

(*Received*, 30*th December* 1975; *Com.* 1434.)

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