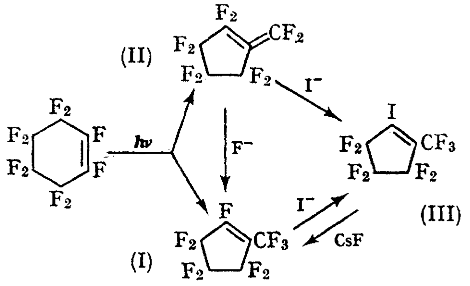
Photochemical Isomerisation of Decafluorocyclohexene

By G. CAMAGGI and F. GOZZO

(*Montecatini Edison S.p.A., Laboratorio Ricerche, Bollate, Milano, Italy*)

ALTHOUGH the photochemical behaviour of cycloalkenes has been the object of several investigations,[1] no such studies on perfluorocyclo-olefins have been published; we now report the photochemical isomerization of decafluorocyclohexene. Decafluorocyclohexene in the vapour phase, and preferably in the presence of small amounts of oxygen, was irradiated at 20° with light of 1849 Å for 72 hr. to give a mixture of perfluorocyclo-olefins (*ca.* 60% yield based on the starting material) and a high-boiling, perfluorinated liquid, which has not been yet characterized. The mixture was separated by gas–liquid chromatography into three main components, with peak areas in the approximate ratio of 1 : 3 : 6. They were, in order: the known[2] perfluoro-(1-methylcyclopentene) (I), starting material, and a new olefin (b.p. 54—55°), λ_{max} 1757 cm.$^{-1}$ ($C{=}CF_2$). The last named is an isomer of decafluorocyclohexene, as shown by mass-spectrometric measurements (top mass peak:

262). Its ^{19}F n.m.r. spectrum,[3] which shows three signals at 59·2, 111·1, and 136·0 p.p.m. (relative to internal CCl_3F) in the ratio of 1 : 2 : 2, is of the $A_2X_4M_4$ type system, consistent with the structure of perfluoro(methylenecyclopentane) (II). It underwent photochemical addition of chlorine and was oxidized by potassium permanganate in acetone to give octafluorocyclopentanone (*ca.* 40% yield) with correct infrared and mass spectra. When this olefin was treated at its reflux temperature with potassium fluoride solutions in either polar aprotic solvents, such as di-(2-methoxyethyl) ether, or even water, though in this case the reaction was rather slow, it isomerized to perfluoro-(1-methylcyclopentene) (I) with a correct infrared spectrum. The same isomerization was accomplished on heating perfluoro(methylenecyclopentane) with cæsium fluoride in a sealed tube at 100°; another exocyclic perfluoro-olefin, perfluoro-(1,2-dimethylenecyclobutane), is known to undergo a similar isomerization.[4] Both isomers (I) and (II), on treatment with cold, saturated solutions of sodium iodide in either acetone or acetonitrile, gave hexafluoro-1-iodo-2-trifluoromethylcyclopentene (III) (*ca.* 60% yield; b.p. 116—117°), λ_{max} 1642 cm.$^{-1}$ ($CI{=}C{\cdot}CF_3$); it showed a top mass peak at 370, with a consistent fragmentation pattern. Its ^{19}F n.m.r. spectrum[3] displays four signals at 62·5, 11·0, 108·9, and 131·0 p.p.m., relative to internal CCl_3F, in the ratio of 3 : 2 : 2 : 2 respectively. When the iodo-olefin (III) was heated with cæsium fluoride in a sealed tube at 100° it was converted back into (I).



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[3] L. Cavalli, unpublished work.

[4] R. E. Banks, M. G. Barlow, W. R. Deem, R. N. Haszeldine, and D. R. Taylor, *J. Chem. Soc.* (*C*), 1966, 981.