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AN ELECTRON SPIN RESONANCE STUDY OF LONG-LIVED FLUOROALKYL RADICALS GENERATED BY PHOTOLYSIS OF HINDERED PERFLUOROALKENES

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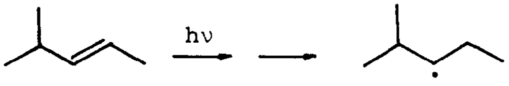
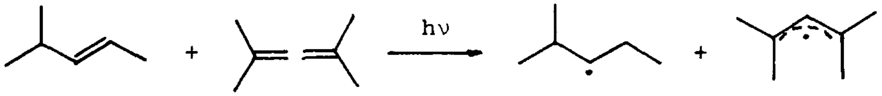
UV photolysis at room temperature of certain hindered perfluoroalkenes surprisingly gives rise to long lived perfluoroalkyl radicals resulting by a fluorine atom addition to the alkene. Perfluoro-2-methyl-3-pentene (I), readily available from hexafluoropropene, is particularly active and gives intense ESR spectra of radical II [67.0G(αF), 14.10G(βF), 29.85G(2βF), 2.63G(9γF), 25°C]. This unprecedented intermolecular F atom transfer implies the formation of a geminate fluoroallylic radical which is not observed under our experimental conditions. Photolysis of mixtures I and another hindered perfluoroalkene yields mixtures of radicals which result by F atom addition to both alkenes. With perfluorotetramethylallene, for example, the novel F-allylic radical III was observed which can also be prepared by alternative techniques [18.3G(1F), 10.7G(12F), 0°C]. If the photolysis is carried out in the presence of simple hydrocarbons and alcohols, H atoms are abstracted and the resulting carbon-centered radicals add to the perfluoroalkene giving rise to a numerous family of new persistent radicals IV (R = CH_3, C_2H_5, c-C_3H_5, C_3H_7, C_4H_9, c-C_6H_{11}, C_6H_5, CH_2OH etc., R = CH_3: 64.5G(αF), 12.55G(βF), 34.87G(βF), 2.80G(9γF), 25°C). The reactivity of methane, ethane, cyclopropane and benzene,



I F· II



III

IV

which are relatively unreactive towards free radical attack, is particularly noteworthy. The identity of these radicals was confirmed by their independent generation using established sources of R· radicals. The ready addition of reactive radicals to I and the persistence of the radical adducts **IV** suggest that I may find applications as a radical-detecting 'spin trap'. The structural and dynamic information that can be obtained from the ESR parameters and the mechanisms of these novel photoreactions will be elaborated.