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LONG-LIVED PERFLUOROALKYL FREE RADICALS: PREPARATION BY DIRECT FLUORINATION AND ALTERNATE ROUTES, PROPERTIES AND RATES AND MECHANISMS OF DISAPPEARANCE

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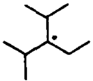
The discovery of a convenient synthesis of the remarkably stable F-2,4-dimethyl-3-ethyl-3-pentyl (1) and F-2,4-dimethyl-3-isopropyl-3-pentyl radicals (2) [JACS 1985, 718] has led us into a wider study of persistent perfluoroalkyl radicals as a new class of fluorinated intermediates. F-alkenes 3-8 DO give persistent radicals on direct reaction with elemental fluorine, whereas the F-alkenes 9-13 do NOT; these differences can be understood in terms of steric effects in the presumed radical intermediates. The sluggishness of the reaction of 1, 2 and 3 with elemental fluorine allows convenient direct measurement of rates; details will be presented. We have also found alternate thermal and photochemical routes to many other perfluoroalkyl radicals, e.g. 14-21, displaying a wide range of persistence and steric hindrance. Examples of our findings include the following: The F-ethyl groups of 21 are conformationally locked on the esr time-scale at 373 K, whereas those of 14 and 15 rotate freely at r.t.; surprisingly, the secondary radical 14 appears to be more persistent than its tertiary isomers 15 and 16.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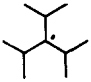
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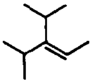
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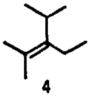
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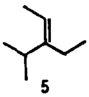
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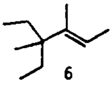
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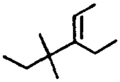
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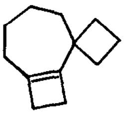
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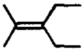
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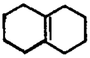
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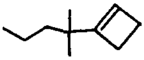
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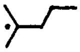
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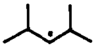
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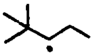
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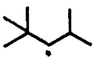
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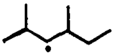
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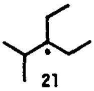
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