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THE SYNTHESIS OF 7,7-DIFLUORONORBORNADIENE AND ITS QUADRICYCLANE ISOMER

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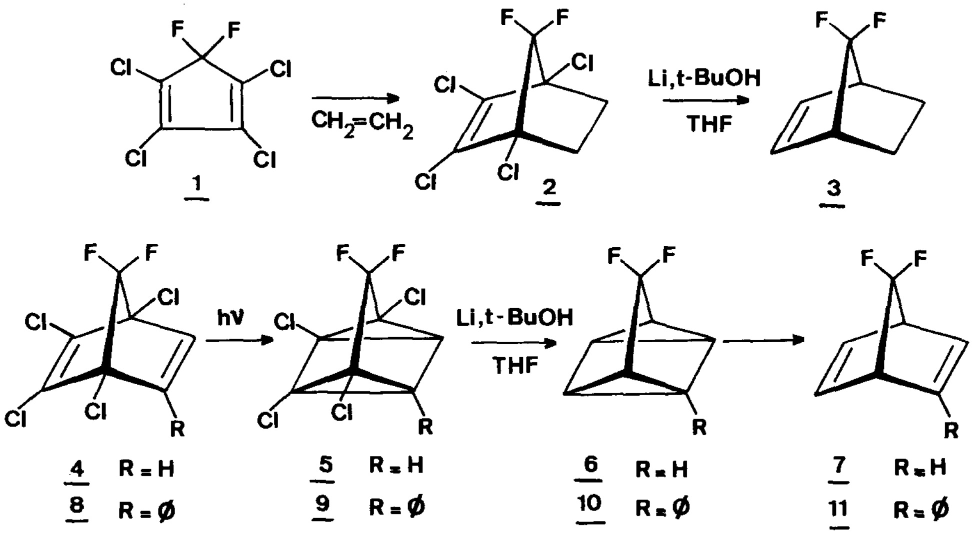
We recently reported that 7,7-difluoronorbornene (3) could be conveniently prepared by reductive dechlorination of the 4+2 adduct (2) obtained from tetrachlorodifluorocyclopentadiene (1) and ethylene[1]. In principle the same procedure should be applicable to the diene analogues of 2 for the synthesis of 7,7-difluoronorbornadiene (4). However, the dissolving metals method failed in that further reduction of the diene occurred[1]. We now wish to announce a simple way of circumventing this difficulty which has not only the advantage of affording 7,7-difluoroquadricyclane (5), but which at the same time provides useful insights on how substituents influence the 'thermally forbidden' quadricyclane-norbornadiene isomerization[2].

Irradiation of a cooled pentane solution of 1,2,3,4-tetrachloro-7,7-difluoronorborna-2,5-diene (4) for 15 hours at 15°C in a photochemical reactor (254 nm, 900 W) gave its quadricyclane isomer 5 as the sole product in quantitative yield[3]. Compound 5 is a colourless solid, m.p. 35.5-36.6° and is quite stable; however, heating at 130° causes complete reversion to 4. Subjection of 5 to the action of lithium dissolving in t-butanol and tetrahydrofuran at 60° for 7 hours effected smooth reductive dechlorination to give 7,7-difluoroquadricyclane (6) in 30% yield. Simple heating, albeit to 360°, was sufficient to bring about quantitative isomerization of 6 to 7,7-difluoronorbornadiene (7). Further heating of 7 to 400° left the molecule unscathed.

Attempts to apply this synthetic route to derivatives of 4 gave rise to unexpected, but surmountable difficulties. Similar irradiation of 1,2,3,4-tetrachloro-5-phenyl-7,7-difluoronorborna-2,5-diene (8) for 16 hours at -40° resulted in a 100% conversion to the quadricyclane (9). However, the quadricyclane skeleton in 9 proved to be remarkably fragile. Reversion of 9 to 8 was perceptibly fast at 25°, its half-life being about 4½ hours. Nevertheless, by working at 0-5°, reductive dechlorination could be effected with dissolving lithium. Extraction of the reaction mixture with ether at 0° gave a mixture of the expected 2-phenyl-7,7-difluoroquadricyclane (10) together with much of its norbornadiene isomer 11. Warming the solution to room temperature caused rapid and complete conversion to 11.



Apart from securing the ready synthesis of the 7,7-difluoronorbornadiene and quadricyclane, molecules of considerable potential for probing chemical reactivity, the stabilities of the C-7 skeletons are sufficiently unusual to merit comment. No thermal rearrangement of 7 to cycloheptatriene occurs despite the feasibility of 1,3 sigmatropic shift or rupture to a diradical[4]; neither does cheletropic extrusion of the potentially stable difluorocarbene take place[5]. Although the fission of quadricyclane to norbornadiene is a disallowed thermal process, it occurs in the parent hydrocarbon at moderate temperatures (140-220°)[6] and almost spontaneously (<25°) when oxygen or sulphur is substituted at C-7[7]. On the other hand, substitution by fluorine at C-7 dramatically reinforces the disallowedness in conferring the greatest stability on the quadricyclane skeleton known so far. This finding unambiguously reveals that the fluoromethyl grouping stabilizes small rings[8], in particular the cyclopropane ring, by strengthening the carbon-carbon bond which is opposite the point of attachment of the grouping[9]. Moreover, it is most probable that the greatest stabilizing effect will obtain when the carbon-fluorine bond is parallel with the plane of the cyclopropane ring. Definitive calculations and structural applications of this novel electronic effect will be reported elsewhere[10].

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