Room-temperature Fluorination of Alkenes with Caesium Fluoroxysulphate

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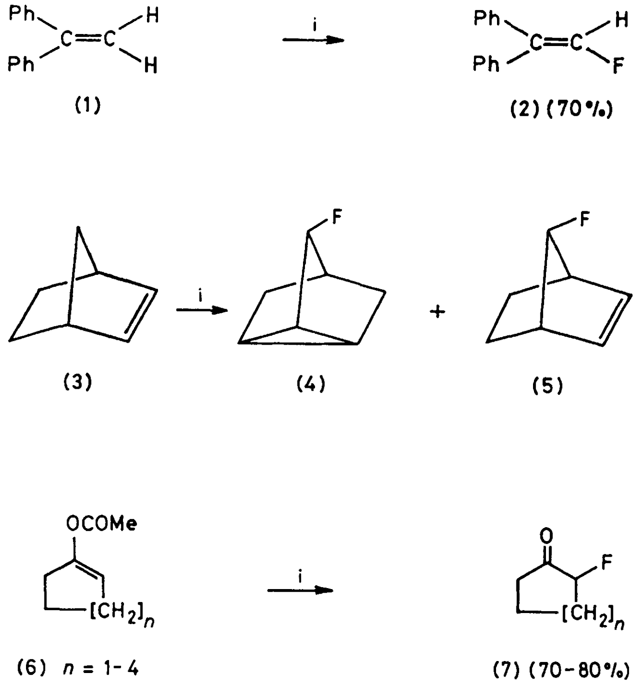
Summary Room-temperature fluorination of 1,1-diphenylethene with caesium fluoroxysulphate resulted in the formation of 2-fluoro-1,1-diphenylethene; norborn-2-ene gave only 7-fluoronortricyclene and 7-*syn*-fluoronorborn-2-ene, while reactions with various cyclic enol acetates gave α-fluorocycloalkanones in high yield.

THE choice of reagent for room-temperature fluorination of olefins is limited.[1] The reactivity of various fluorinating reagents has been tested on 1,1-diphenylethene and markedly different results have been observed. Room-temperature fluorination with xenon difluoride gave vicinal difluorides,[2] while in the reactions with substituted aryliodine(III) difluorides[3] or polymer-supported aryliodine(III) difluorides[4] rearranged geminal difluorides were isolated. Low-temperature reaction with fluorine resulted in three products[5] and in the reaction with fluoroxytrifluoromethane five products were formed.[6]

Recently we have found that caesium fluoroxysulphate is a mild, easily handled fluorinating reagent for the fluorination of alkoxy-substituted benzene and naphthalene derivatives.[7] We now report the reactivity of caesium fluoroxysulphate[8] with various substituted alkenes. In a typical experiment, carried out in a polyethylene vessel, to a stirred suspension of CsSO$_4$F (1·2 mmol) in methylene dichloride (3 ml), a solution of the olefin (1 mmol) in methylene dichloride (1 ml) was added and the mixture was stirred at room temperature from 2 to 24 h. Then methylene dichloride (10 ml) was added, the insoluble product was filtered off, and the filtrate was washed with water and dried (Na$_2$SO$_4$). The solvent was evaporated off *in vacuo*, the mixture was analysed by ^{19}F n.m.r. spectroscopy, and the products were isolated by gas chromatography. The 24-hour reaction with 1,1-diphenylethene (**1**; Scheme) gave 2-fluoro-1,1-diphenylethene (**2**) in 70% yield as the sole product. Reaction with 10 mmol of (**1**) gave (**2**) in 61%



SCHEME. i, CsSO$_4$F, CH$_2$Cl$_2$, 25 °C.

yield. We have also found that reaction in acetonitrile (a convenient solvent for the fluorination of aromatic molecules[7]) gave a complex reaction mixture. Reaction with 2-phenylprop-1-ene resulted, after g.l.c. separation, in 30% of 3-fluoro- and 32% of 3,3-difluoro-2-phenylprop-1-ene.

The different reactivity of $CsSO_4F$ from other fluorinating agents stimulated us to study its reaction with norborn-2-ene, usually used as a model for the study of reaction pathways. The 6-hour reaction of norborn-2-ene (**3**) in methylene dichloride solution gave only two products in the relative ratio 1 : 1·08 [(**4**) : (**5**)] which were isolated by preparative g.l.c. to give (**4**) (22%) and (**5**) (31%). On the basis of spectroscopic data, which were identical with those of authentic samples,[9] we established that 7-fluoronortricyclene (**4**) and 7-*syn*-fluoronorborn-2-ene (**5**) were formed. The reactivity of caesium fluoroxysulphate again markedly differs from that of the other reagents.[9]

The room-temperature fluorination of the cyclic enol acetates (**6**) gave α-fluorocycloalkanones (**7**) in high yields (70—88%). The structures of the products were established by comparison of their spectroscopic data with those of authenthic samples.[10]

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