Room Temperature Fluorination of 1,3-Diketones and Enol Acetates with Xenon Difluoride

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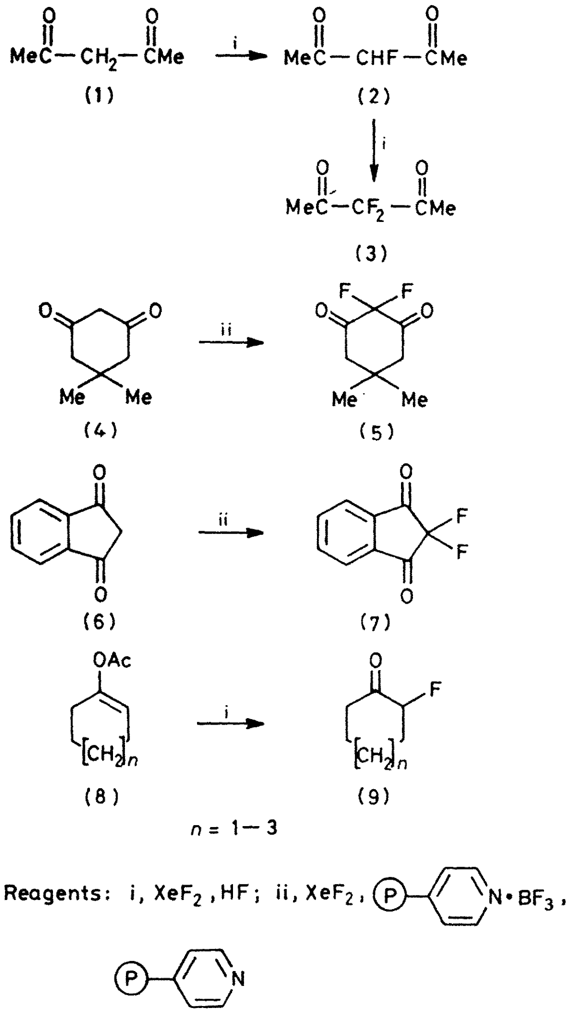
Summary Fluorination of 1,3-diketones with xenon difluoride in the presence of the insoluble cross-linked polystyrene–4-vinylpyridine complex with boron trifluoride and insoluble cross-linked polystyrene–4-vinylpyridine resins resulted in the formation of mono- and di-fluoro products, while reactions with enol acetates in the presence of hydrogen fluoride gave α-fluoroketones.

FLUORINATION of 1,3-diketones has received much less attention than reactions involving other halogens. However, some reactions with perchloryl fluoride in the presence of base resulted in the formation of mono-[1] or di-fluoro products,[2] but this reagent may lead to violent explosions.[3] Recently, the first example of the fluorination of β-diketones, resulting in monofluoro products, by the graphite–xenon hexafluoride intercalate, $C_{19}XeF_6$, was published.[4] The advantages of using xenon difluoride as a mild selective fluorinating agent are well known.[5] We now report that xenon difluoride readily reacts with acetylacetone (**1**) (Scheme) at 25 °C in methylene chloride with anhydrous hydrogen fluoride as catalyst. A stoicheiometric amount of xenon difluoride did not favour the formation of the monofluoro product (**2**), the difluoro product (**3**) being the only product. The use of 2 equiv. of xenon difluoride gave a 70% yield of (**3**), which was purified by preparative g.l.c. and identified by i.r., n.m.r., and mass spectroscopy.[2] A



SCHEME

ratio of substrate to XeF$_2$ of 2·3 : 1 and higher dilution conditions were needed for the monofluoro product (**2**) to be obtained.

The hydrogen fluoride-catalysed fluorination of 5,5-dimethylcyclohexane-1,3-dione (**4**) with 2 mol. equiv. of xenon difluoride gave a low yield of a complex mixture, together with an insoluble high-melting product. The use of the insoluble cross-linked polystyrene–4-vinylpyridine complex with boron trifluoride† and xenon difluoride improved the overall yield, but a complex mixture was still obtained. However, the following conditions gave only 2,2-difluoro-5,5-dimethylcyclohexane-1,3-dione (**5**). To a solution of the diketone (**4**) (1 mmol) in methylene chloride (20 ml) were added insoluble cross-linked polystyrene–4-vinylpyridine (50% pyridine rings; 600 mg), xenon difluoride (2 mmol), and insoluble cross-linked polystyrene-4-vinylpyridine–boron trifluoride complex (100 mg), the mixture was stirred at room temperature for 20 h, filtered, and evaporated under reduced pressure, and the product (**5**) purified by g.l.c. (85% yield). Indane-1,3-dione (**6**) reacted similarly to give the difluoro-product (**7**) in 80% yield.

Enol acetates have been successfully fluorinated with CF_3OF[6] and ClO_3F,[3] and recently with CF_3CF_2OF prepared *in situ*.[7] We now report that HF-catalysed fluorination of cyclic enol acetates (**8**) with xenon difluoride at room temperature gave the α-fluorocycloalkanones (**9**), the purity and yields of which depend strongly on moisture exclusion and on the amount of hydrogen fluoride. To produce compounds (**9**), only catalytic amounts of hydrogen fluoride were used, since larger proportions resulted in increased amounts of the cycloalkanones. With catalytic amounts of HF the fluoro-compounds (**9**) were formed in 60—85% yields, accompanied by 2—17% of the cycloalkanones, depending on the conditions and ring size (larger rings gave larger amounts of cycloalkanone).

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† Insoluble cross-linked polystyrene-4-vinylpyridine complex with boron trifluoride was prepared by passing boron trifluoride through a suspension of polystyrene-4-vinylpyridine containing 2% pyridine rings. The polymeric complex contains 1·04% of boron.

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