

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

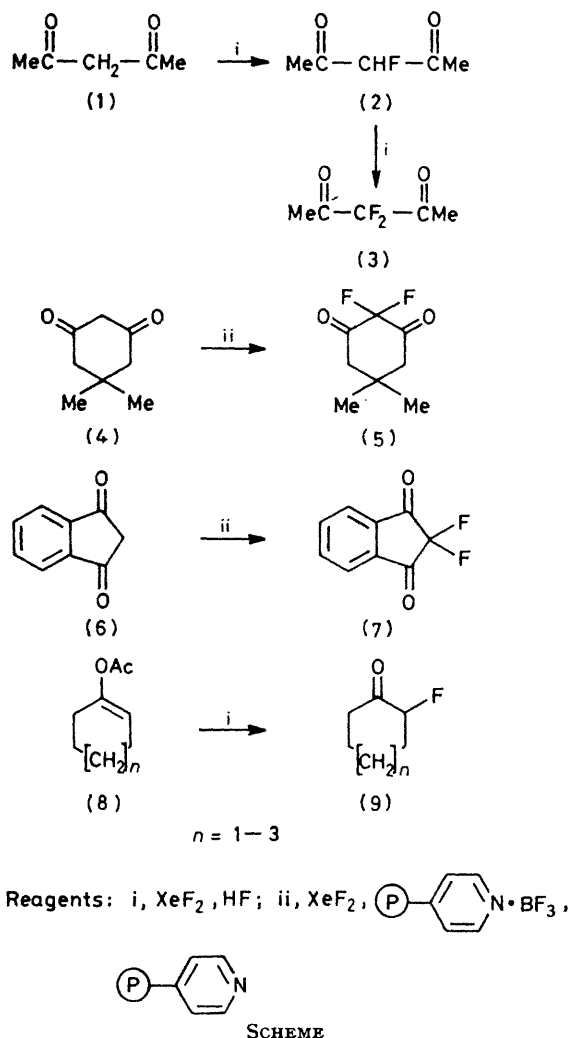
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Summary Fluorination of 1,3-diketones with xenon difluoride in the presence of the insoluble cross-linked polystyrene-4-vinylpyridine complex with boron trifluoride and insoluble cross-linked polystyrene-4-vinylpyridine resins resulted in the formation 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, $C_{18}XeF_6$, 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 stoichiometric 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



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 ,⁸ and recently with $\text{CF}_3\text{CF}_2\text{OF}$ 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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