Fluoride-catalysed Michael Addition of Simple Nitro-olefins to β-Diketones

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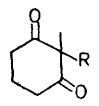
Summary Potassium fluoride-catalysed Michael addition of nitroethylene and 2-nitropropene to β-diketones is described.

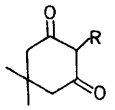
BASE-SENSITIVE lower members of nitro-olefins have been rarely used in Michael addition with carbonyl compounds as acceptors.[1] We have found that KF catalyses the Michael addition of 1,3-dicarbonyl compounds and simple nitro-olefins, giving in addition to the expected adducts, their transformation products in some cases.

2-Methylcyclohexane-1,3-dione (Ia) and nitroethylene (2 mol equiv.) gave the adduct (Ib) (62%) on heating with KF (1·2 mol. equiv.) in xylene at 100 °C for 2 h, whereas other bases such as NaH failed to catalyse the reaction.



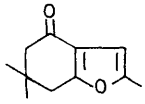
(I)

a; R = H
b; R = $[CH_2]_2$ NO_2
c; R = $CH_2CH(NO_2)Me$
d; R = CH_2COMe



(II)

a; R = H
b; R = $CH_2CH(NO_2)Me$



(III)

Reaction of (Ia) with 2-nitropropene under similar conditions gave a mixture of the nitroketone (Ic) and the triketone (Id). Longer reaction time (25 h) resulted in an almost quantitative yield (92%) of (Id) at the expense of (Ic).

1,3-Diketones which have no C(2)-alkyl substituent gave 2-methyl-4-acylfurans on treatment with 2-nitropropene. Thus, dimedone (IIa) gave the ketofuran (III) (52%) after 9·5 h. The nitroketone (IIb) was not isolated.

When treated with KF or KHF_2 in refluxing xylene, the nitroketone (Ic) was quantitatively converted into the triketone (Id), whereas 2-nitro-octane or the nitroketone (Ib) was recovered unchanged indicating that keto and secondary nitro groups are required for this transformation.

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[1] For a recent review, see H. H. Baer and L. Urbas, in 'The Chemistry of the Nitro and Nitroso Groups,' Part 2, ed. H. Feuer, pp. 136—145, Interscience, New York, 1970.