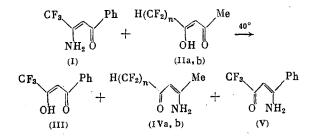
EXCHANGE REACTION BETWEEN FLUORINE-CONTAINING β -DIKETONES AND β -AMINOVINYLKETONES

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An unusual reaction of fluorine-containing β -aminovinylketones (AVK) (I) and β -diketones (II) has been discovered. This reaction involves the exchange of the NH₂ and OH group and leads to (III) and (IV). The formation of AVK (IV) is in accord with the data on the reaction of asymmetric fluorine-containing β -diketones with NH₃ and amines [1]. In addition to (III) and (IV), AVK, which is the product of the isomerization of AVK (I), was isolated [2].



n = 2 (a) and 4 (b).

A solution of 1 g (4.6 mmoles) (I) in 0.86 g (4.6 mmoles) (IIa) was maintained at constant 40°C for 120 h. The mixture was separated and subjected to elution on a column packed with silica gel L 100/250, eluting first with hexane and then with $CHCl_3$ to give (in order of elution): 0.48 g (48.3%) β -diketone (III), 0.1 g (11.6%), AVK (I), 0.2 g (23.2%) AVK (V), and 0.37 g (46%) AVK (IVa).

Analogously, 1.08 g (5 mmoles) (I) and 1.43 g (5 mmoles) (IIb) gave 0.43 g (40%) (III), 0.2 g (18.5%) AVK (I), 0.15 g (13.8%) AVK (V), and 0.53 g (38%) AVK (IVb).

The reaction products were characterized by comparison with authentic samples of (III)-(V) (depressed melting points of mixed samples were not noted), thin-layer chromatography, and IR spectroscopy.

β-Diketones (II) and (III) were obtained according to our previous procedure [3], while AVK (I) and (IV) were obtained according to a previous method [1, 4]. AVK (V) was obtained by the transamination of 1-phenyl-1-(N-phenylamino)-4,4,4-trifluoro-1-buten-4-one [5].

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