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A CONVENIENT SYNTHESIS OF ACETYLENIC KETONES FROM β-DIKETONES USING α,α-DIFLUOROALKYLAMINES AND FREEZE-DRIED POTASSIUM FLUORIDE

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α,α-Difluoroalkylamines, such as 1-diethylamino-2-chloro-1,1,2-trifluoroethane (**1**) and 1-diethylamino-1,1,2,3,3,3-hexafluoropropane (**2**), were found to be useful dehydrating agents for the synthesis of acetylenic ketones from β-diketones in the presence of freeze-dried potassium fluoride in acetonitrile.

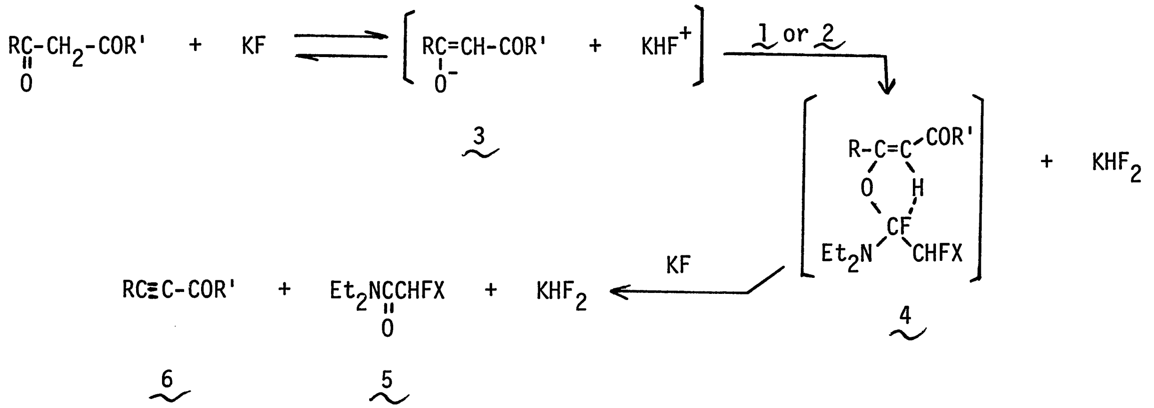
Adducts of fluoroolefins and dialkylamines, e.g., 1-diethylamino-2-chloro-1,1,2-trifluoroethane (**1**)[1] from chlorotrifluoroethene or 1-diethylamino-1,1,2,3,3,3-hexafluoropropane (**2**)[2] from hexafluoropropene, are known to be remarkable compounds as fluorinating reagents for alcohols,[1,2] and useful intermediates for fluorinated heterocycles,[3] however, no other utility of these adducts in organic synthesis has been studied.

$$CF_2{=}CFX \quad + \quad Et_2NH \xrightarrow{CH_2Cl_2\ (\text{or } Et_2O)} Et_2NCF_2CHFX$$

1 (X=Cl) ; **2** (X=CF_3)

On the other hand, an importance of carbonyl olefination reactions has been recognized in organic synthesis, and facile synthetic methods are highly desirable in recent years.[4]

This work describes a facile one-pot synthetic method of acetylenic ketones, which are versatile intermediates in organic synthesis,[5] by dehydration of β-diketones using **1** or **2** and freeze-dried potassium fluoride.[6]



The reaction pathway is apparently as shown above. The first step should be the nucleophilic attack of an enolate ion (**3**) generated from β-diketone and freeze-dried potassium fluoride assisted by the H-F bond formation, on **1** (or **2**), leading to a cyclic intermediate (**4**). The intermediate (**4**) would split up to a stable amide (**5**) and hydrogen fluoride, leaving an acetylenic ketone (**6**).

In this system, driving force to provide the acetylenic ketone may be explained by considering the formation of an ion pair of the type $K^+[F{-}{-}H_2O]^-$ for making the hydrogen-bond.[7,8]

Solid-supported fluoride, KF-Al_2O_3,[9] was also efficient in the above reaction, however, calcine-dried potassium fluoride gave only a trace of acetylenic ketones under the same conditions.

When other base-catalysts, e.g., NaH, NaOH, some lithium reagents, were used in the above reaction, the reaction mixture was tarry and no identified products were isolated.

Based on these results, we believe that the presently reported procedure provides a resonably available and selective one-pot synthetic method for acetylenic ketones from β-diketones.

TABLE I. Preparation of Acetylenic Ketones

β-Diketone	Acetylenic Ketone[a]	Yield (%)[b] using		Bp
		1	2	(°C/mmHg)
$PhCOCH_2COCH_3$	$PhC{\equiv}CCOCH_3$	69	72	124-126/13 (120/14)[e]
$PhCOCH_2COCF_3$	$PhC{\equiv}CCOCF_3$	75	68	86-88/16[c]
$p\text{-}ClC_6H_4COCH_2COCF_3$	$p\text{-}ClC_6H_4C{\equiv}CCOCF_3$	54	55	97-98/5[c]
$PhCOCH_2COC_2F_5$	$PhC{\equiv}CCOC_2F_5$	76	72	92-94/14[c]
$CH_3COCH_2COCH_3$	$CH_3C{\equiv}CCOCH_3$	44	53	82-84/75 (38/14)[e]
$CH_3COCH_2CO_2Et$	$CH_3C{\equiv}CCO_2Et$	48	57	87-89/31 (163)[d]
$PhCOCH_2CO_2Et$	$PhC{\equiv}CCO_2Et$	65	58	126-128/7 (144/13)[d]

a) Structures were confirmed by means of IR and NMR spectral data. b) Yield based on β-diketones.
c) New compound : The microanalysis was satisfactory agreement to the calculated value.
d) "Handbook of Chemistry & Physics," 55th ed., CRC Press, (1974/75). e) M.Fontain, J.Chauvelier, and P.Barchewitz, Bull.Soc.Chem.Fr., 2145 (1962).

In a typical example, a heterogeneous mixture of 2 (2.35 g, 15 mmol), benzoyl trifluoroacetone (2.16 g, 10 mmol), and freeze-dried potassium fluoride (1.77 g)[6] in acetonitrile (20 ml) was stirred for 24h at room temperature. After filtering the solid material, the filtrate was poured into water, and then oily material was extracted with diethyl ether. After removing the solvent, the residue was subjected to distillation affording trifluoroacetylacetylene in 68% (1.35 g) yield, bp 86-88 °C/16 mmHg. IR : 2110 cm^{-1} (C≡C). ^{1}H NMR (CCl_4) : δ 7.40 (Ar-H). ^{19}F NMR (from ext. CF_3CO_2H) : -1.5.

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