CONDENSATION OF POLYFLUORINATED ALDEHYDES WITH POLYFLUORINATED β-DIKETONES

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Aldehydes react with β-diketones (β-DK) in the presence of K_2CO_3 to form α,β-unsaturated ketones (α,β -UK) [1, 2].

We were the first to study the reaction of unsymmetrical (Ia-f) and symmetric fluorinated β-DK (Ig-i) in anhydrous ether in the presence of freshly roasted K_2CO_3 with aldehydes (IIa) and (IIb) to give only α,β-UK (IIIa)-(IIId) (Table 1) independently of the bulk of the substituents:

$$R_F'COCH_2COR + R_F''CHO \xrightarrow[\text{or } Et_3N]{K_2CO_3} R_F''CH{=}CHCOR$$

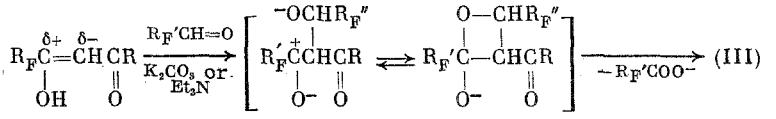
(Ia—i) (IIa—c) (IIIa—g)

R_F' = CF_3 (Ic, e, g); $H(CF_2)_2$ (Id, f, h); $H(CF_2)_4$ (Ii); C_6F_{13} (Ia, b);

R_F'' = $H(CF_2)_2$ (IIa), (IIIa, b); $H(CF_2)_4$ (IIc), (IIIg); $H(CF_2)_6$ (IIb), (IIIc—f);

R = Me(Ia, c, d), (IIIa, c); Ph (Ib, e, f), (IIIb, d); CF_3(Ig), (IIIe); $H(CF_2)_2$ (Ih), (IIIf); $H(CF_2)_4$ (Ii), (IIIg).

This may be explained by the regioselective addition of the aldehyde group oxygen at the enol carbon of the intermediate due to the predominant enolization of unsymmetrical fluorinated β-DK at the carbonyl group with the fluoroalkyl substituent [3]:



Similarly, only α,β-unsaturated esters are formed upon the condensation of aldehydes with β-ketoesters enolized at the β-carbon atom [1].

α,β-UK (IIIe)-(IIIg) cannot be obtained by condensation of symmetrical fluorinated β-DK (Ig)-(Ii) with fluorinated aldehydes (IIb) and (IIc) in the presence of K_2CO_3 since the potassium chelate of the symmetrical β-DK formed does not undergo this reaction. However, in the presence of catalytic amounts of Et_3N, these reactions give α,β-UK (IIIe)-(IIIg) in 20-55% yields (see Table 1). The compositions and structures of the products were supported

TABLE 1. Reaction of Polyfluorinated Aldehydes with β-DK

β-DK(I)	Aldehydes (II)	Product (III)	Yield, %
$C_6F_{13}COCH_2COMe$ (Ia)	$H(CF_2)_2CHO$ (IIa)	$H(CF_2)_2CH{=}CHCOMe$ (IIIa)	41
$C_6F_{13}COCH_2COPh$ (Ib)	»	$H(CF_2)_2CH{=}CHCOPh$ (IIIb)	65
CF_3COCH_2COMe (Ic)	$H(CF_2)_6CHO$ (IIb)	$H(CF_2)_6CH{=}CHCOMe$ (IIIc)	34
$H(CF_2)_2COCH_2COMe$ (Id)	»	»	68
CF_3COCH_2COPh (Ie)	»	$H(CF_2)_6CH{=}CHCOPh$ (IIId)	70
$H(CF_2)_2COCH_2COPh$ (If)	»	»	64
$CF_3COCH_2COCF_3$ (Ig)	»	$H(CF_2)_6CH{=}CHCOCF_3$ (IIIe)	51
$H(CF_2)_2COCH_2CO(CF_2)_2H$ (Ih)	$H(CF_2)_6CHO$ (IIb)	$H(CF_2)_6CH{=}CHCO(CF_2)_2H$ (IIIf)	20
$H(CF_2)_4COCH_2CO(CF_2)_4H$ (Ii)	$H(CF_2)_4CHO$ (IIc)	$H(CF_2)_4CH{=}CHCO(CF_2)_4H$ (IIIg)	55

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TABLE 2. Characteristics of Fluorinated α,β-Unsaturated Ketones $R_F\overset{\beta}{C}H = \overset{\alpha}{C}HCOR$

Compound	R_F	R	bp, °C (p, mm Hg)	Found/calculated, %			Chemical formula	IR spectrum, ν, cm^{-1}*		PMR spectrum, δ, ppm †			
				C	H	F		C=O	C=C	H_α	H_β	R_F	R
(IIIa)	$H(CF_2)_2$	Me	79–80(30)	42,09 / 42,36	3,85 / 3,50	– / 44,67	$C_6H_6F_4O$	1705, 1690	1655	6,6 m	6,6 m	5,3–6,4t.t	2,4 s
(IIIb)	$H(CF_2)_2$	Ph	104(6)	56,52 / 56,91	3,36 / 3,47	32,1 / 32,73	$C_{11}H_8F_4O$	1680	1640	7,6 d.t	6,9 d.t	5,2–6,3t.t	7,4–8,0 m
(IIIc)	$H(CF_2)_6$	Me	80–82(8)	32,52 / 32,45	1,53 / 1,63	61,1 / 61,59	$C_{10}H_6F_{12}O$	1710, 1690	1640, 1650	6,8 m	6,8 m	6,7–6,8t.t	2,35 s
(IIId)	$H(CF_2)_6$	Ph	148(10)	41,42 / 41,63	2,08 / 1,87	52,6 / 52,75	$C_{15}H_8F_{12}O$	1685	1645	7,7 m	6,9 m	5,2–6,8tt.	7,2–8,0 m
(IIIe)	$H(CF_2)_6$	CF_3	62(5)	27,93 / 28,32	0,74 / 0,41	67,52 / 67,19	$C_{20}H_3F_{15}O$	1745	1650	7,16 m	7,16m	5,5–6,6t.t	–
(IIIf)	$H(CF_2)_6$	$H(CF_2)_2$	90(10)	28,60 / 28,97	1,30 / 0,88	69,6 / 66,64	$C_{11}H_4F_{16}O$	1730	1650	7,1 m	7,1 m	5,4–6,6t.t.	
(IIIg)	$H(CF_2)_4$	$H(CF_2)_4$	80(5)	28,86 / 28,97	1,18 / 0,88	66,8 / 66,64	$C_{11}H_4F_{16}O$	1735	1650	7,1 m	7,1 m	5,5–6,6t.t	

*$\nu_{CH,trans}$ = 975-980 cm^{-1}.
†$^3J_{HH}$ = 15, $^4J_{HF}$ = 2, $^3J_{HF}$ = 12, $^2J_{HF}$ = 52 Hz.

by elemental analysis and IR and PMR spectroscopy (Table 2). In their spectral properties, (IIIa)-(IIIf) were identical to trans-α,β-UK obtained previously by the aldol condensation of fluorinated aldehydes (IIa)-(IIc) with the corresponding methyl ketones [4].

EXPERIMENTAL

The PMR spectra were taken on a Tesla BS-567A spectrometer at 100 MHz in $CDCl_3$ relative to TMS. The IR spectra were taken neat on a Specord IR-75 spectrophotometer. The fluorinated aldehydes were obtained according to Pierce and Kane [5] and the β-DK were obtained according to our previous work [6].

Synthesis of a polyfluorinated α,β-unsaturated ketones. A sample of roasted K_2CO_3* was added to a solution of 10 mmoles fluorinated aldehyde (II) and 10 mmoles β-diketone (I) in 75 ml dry ether and stirred for 1-2 h. The reaction was monitored by thin-layer chromatography. The precipitate was filtered off. The solution was washed with water and dried over $MgSO_4$. Ether was evaporated and the residue was distilled in vacuum. The yields and physical constants of the products are given in Table 2.

CONCLUSIONS

1. Fluorinated aldehydes react regiospecifically with unsymmetrical fluorinated β-diketones with the formation of β-polyfluoroalkyl-α,β-unsaturated ketones.

2. α,β-Unsaturated ketones with two fluorinated substituents were obtained for the first time by the condensation of symmetrical fluorinated β-diketones with polyfluorinated aldehydes.

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*A catalytic amount of Et_3N was added in the case of symmetrical β-DK (Ig)-(Ii).