CONCURRENT AMINATION OF CARBONYL GROUPS IN UNSYMMETRICAL β-DIKETONES BEARING POLYFLUOROALKYLARYL GROUPS

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UDC 542.958.3:547.572.3'161

The condensation of unsymmetrical β-diketones which have alkyl and fluoroalkyl substituents with amines takes place at the carbonyl linked to the unfluorinated substituent with the formation of only one of the isomers of the β-aminovinyl ketones (β-AVK) [1, 2]. It has turned out that unsymmetrical fluorine-bearing β-diketones with phenyl substituents (Ia-c) form a mixture of isomers of β-aminovinyl ketones (II), (III) and (IV), (V) on condensation with ammonia and methylamine, respectively.

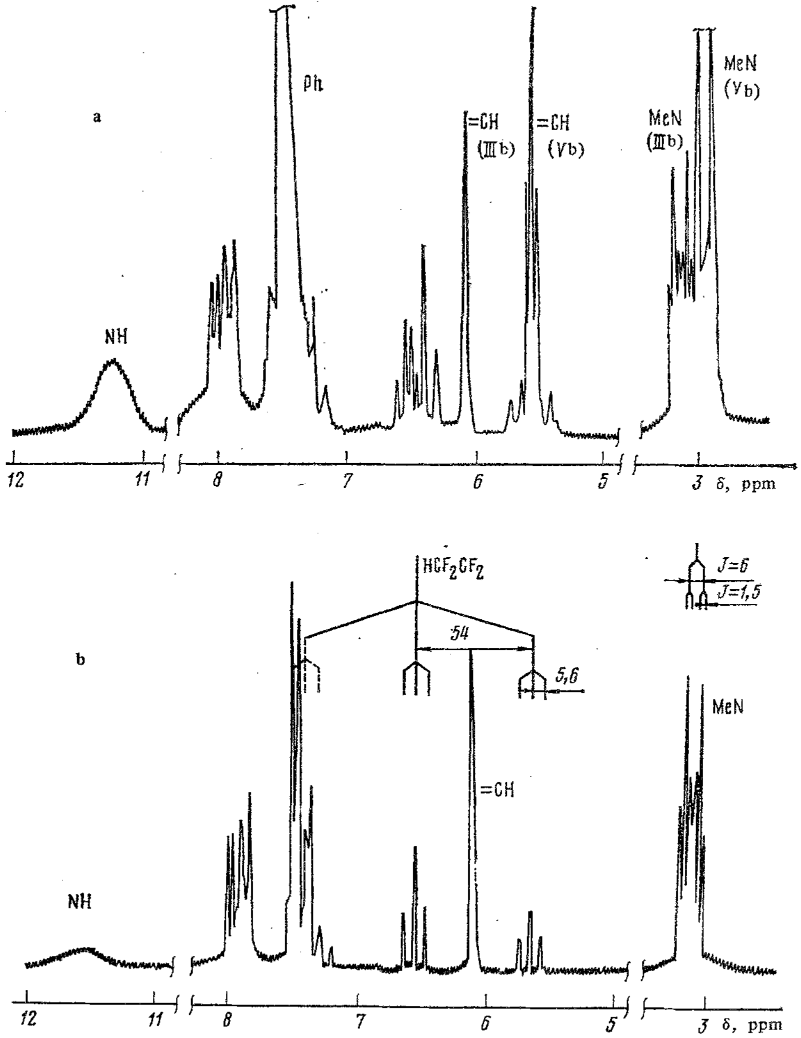

Fig. 1. PMR spectrum of the mixture of products (Vb) and (IIIb) (a) and 1-phenyl-3-methylamino-4,4,5,5-tetrafluoro-2-penten-1-one (comparison standard) (IIIb) (b) (J, Hz).

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Institute of Chemistry, Urals Science Center of the Academy of Sciences of the USSR, Sverdlovsk. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 10, pp. 2346-2349, October, 1981. Original article submitted December 23, 1980.

0568-5230/81/3010- 1931 $07.50

TABLE 1. Isomeric β-Aminovinyl ketones

Compound	mp or bp, °C (p, mm Hg)	Found/calculated %				Empirical formula	PMR spectrum, δ, ppm[a]						Isomer content in mixture, %
		C	H	F	N		$H(CF_2)_n$[b]	CH	NH . . . O	NH	$\underset{1}{H}-\overset{\vert}{N}-\underset{2}{Me}$[c]	Me_2N	
(IIa)	84–85	55,49 55,81	4,03 3,74	26,62 26,48	6,80 6,51	$C_{10}H_8F_3ON$	—	6,26 6,30[d]	7–8 (2H) 7–8 (2H)[d]		—	—	90
(IIb)	51--51,5	53,34 53,44	3,45 3,67	30,76 30,74	5,48 5,65	$C_{11}H_9F_4ON$	5,94 t. t	6,18 6,20[d]	7–8 (2H) 7–8 (2H)[d]		—	—	80
(IVb)	57–57,5	53,42 53,44	3,40 3,67	30,79 30,74	5,40 5,65		6,1 t. t	5,9	10,5 (1H)	6,6 (1H)	—	—	20
(IVc)	93–94 (1)	44,65 44,97	2,80 2,61	44,08 43,77	—	$C_{13}H_9F_8ON$	6,28 t. t	5,88	10,65 (1H)	6,5 (1H)	—	—	90
(IIIa)	41–41,5	57,80 57,64	4,33 4,39	24,55 24,86	6,10 6,11	$C_{11}H_{10}F_3ON$	—	6,25	10,9	—	3,14 d. q	—	70
(Va)	67–68	57,80 57,64	4,30 4,39	24,60 24,86	6,20 6,11		—	5,47	11,2	—	3,05 d	—	30
(IIIb)[e]	127–129 (1)	55,09 55,17	4,06 4,24	28,60 29,09	—	$C_{12}H_{11}F_4ON$	6,5 t. t	6,15	11,2	—	3,1 d.t	—	40
(Vb)[e]							6,35 t. t	5,55	11,3	—	2,95 d	—	60
(Vc)	131–132 (3)	46,79 46,54	3,16 3,06	—	4,05 3,87	$C_{14}H_{11}F_8ON$	6,4 t. t	5,52	11,4	—	3,05 d	—	90
(VIa)	91–92	59,52 59,25	4,78 4,97	—	5,88 5,75	$C_{12}H_{12}F_3ON$	—	5,8	—	—	—	3,1 s	—
(VIb)	61–62	44,88 45,07	5,27 5,20	—	6,45 6,57	$C_{13}H_{13}F_4ON$	6,04 t. t	5,52	—	—	—	2,95 s	—
(VIIb)	182 (2)	63,20 63,15	4,16 4,05	23,30 23,50	4,30 4,33	$C_{17}H_{13}F_4ON$	6,06 t. t	5,68	12,60	—	—	—	—
(VIIc)	70–71	53,49 53,91	2,99 3,09	—	3,28 3,31	$C_{19}H_{13}F_8ON$	6,25 t. t	5,66	12,50	—	—	—	—

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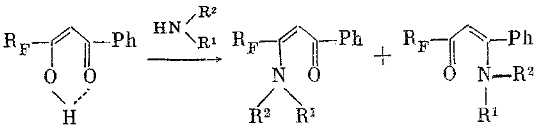
[a] Integral intensities of all signals in the PMR spectrum correspond to the structures given.

[b] $J_{HCF_2} = 54$, $J_{HCF_2CF_2} = 5.6$ Hz.

[c] For (Va), (Vb), and (Vc), $J_{12} = 6$ Hz; for (IIIa) and (IIIb), $J_{12} = 6$, $J_{Me...R_F} = 1.3–1.5$ Hz.

[d] Solvent was octafluorotoluene.

[e] The mixture of isomers (IIIb) and (Vb) could not be separated; the ratio was determined from the PMR spectrum (see Fig. 1). The analytical data and boiling point are given for the mixture.



(Ia—c) (IIa—b); (IIIa—b) (IVb—c); (Va—c); (VIa—b); (VIIb—c)

$R_F = CF_3$ (a), $H(CF_2)_2$ (b), $H(CF_2)_4$ (c); $R^1 = R^2 = H$ (II), (IV); $R^1 = H$, $R^2 = Me$ (III), (V); $R^1 = R^2 = Me$ (VI); $R^1 = H$, $R^2 = Ph$ (VII).

The PMR spectra of the lower-boiling compounds (IIa-b) contain a very broad two-proton signal for the NH_2 group at 7-8 ppm and the methine proton signal at 6.0-6.3 ppm characteristic of β-AVK which contain fluoroalkyl substituents in the α position to NH_2 [3]. The PMR spectra of the high-boiling polymers (IVb-c) show two broad one-proton signals: an NH_2 proton that participates in the intramolecular hydrogen bond (10.5-10.65 ppm) and an exocyclic NH proton at 6.5-6.6 ppm. The CH= signal position with 5.5-5.9 ppm was characteristic of β-AVK with an amino group at the C linked to the unfluorinated substituent [1]. Furthermore, the PMR spectra of compounds (IIIa-b) show a spin–spin interaction of the MeN protons with the F atoms of the fluoroalkyl substituents (Fig. 1) which is absent in the isomeric β-AVK (Va-c), also confirming the isomer classification. In the reaction between the phenyl-substituted β-diketones (Ia-c) and dimethylamine and aniline, we succeeded in separating only β-AVK (VI) and (VII), due apparently to steric hindrance.

The direction of the reaction with respect to both electrophilic centers of the unsymmetrical polyfluoroalkylaryl-containing β-diketones as a whole confirms the scheme given in [1].

EXPERIMENTAL

The PMR spectra were obtained on a Perkin–Elmer R-12B spectrometer (60 MHz, CCl_4, internal standard TMS).

The reaction of β-diketones (Ia-c) with the amines was performed as in [1]. To increase the β-aminovinyl ketone yield, we carried out a multiple "amine bubbling–azeotropic distillation" operation. The isomers were separated by redistillation [the boiling point of (II) and (III) is lower than that of (IV) and (V)] with subsequent recrystallization from n-hexane.

1-Phenyl-3-methylamino-4,4,5,5-tetrafluoro-2-penten-1-one (IIIb) (Comparison Standard). A solution of 5 g (20 mmoles) of 1-phenyl-3-amino-4,4,5,5-tetrafluoro-2-penten-1-one in 10 ml absolute ethanol was placed in an ampul, and then a 2.5- to 3-fold molar excess of methylamine was condensed by cooling with liquid nitrogen. The cooled ampul was evacuated, sealed, and allowed to stand 2-3 days at ~20°C. After the alcohol had been driven off, the residue was distilled under vacuum. We obtained 2.8 g (51%) of (IIIb). Composition found: C 55.35; H 4.21; N 5.38%. Calculated composition for $C_{12}H_{11}F_4ON$: C 55.17; H 4.24; N 5.36%. The properties of the compounds synthesized are given in Table 1.

CONCLUSIONS

Unlike the unsymmetrical fluorine-containing β-diketones with alkyl substituents, the polyfluorinated β-diketones with phenyl substituents from a mixture of regioisomers of the β-aminovinyl ketones on condensation with ammonia and methylamine.

LITERATURE CITED

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