- 7. H. Lau and J. Martin, J. Am. Chem. Soc., <u>100</u>, 7077 (1978).
- 8. J. Chiang, J. Luloff, and E. Schipper, J. Org. Chem., 34, 2397 (1969).
- J. Kasperek and G. Kasperek, J. Org. Chem., <u>43</u>, 3393 (1978).
 H. Kharasch, J. Chao, and H. Brown, J. Am. Chem. Soc., <u>62</u>, 2393 (1940).
- 11. A. Weissberger (editor), The Chemistry of Heterocyclic Compounds, Vol. 21/1, Interscience, New York (1966).
- 12. A. Nudelman, Int. J. Sulfur Chem., <u>6</u>, 1 (1971).
- 13. W. Price and S. Smiles, J. Chem. Soc., 2858 (1928).

SALT FORMATION BY REACTION OF FLUORINE-CONTAINING **B-DIKETONES WITH AMINES**

K. I. Pashkevich and V. I. Filyakova

UDC 542.951.7:543.442.3:547.233+547.551

On heating unsymmetrical polyfluorinated β -diketones with NH₃ and with amines condensation occurs on one of the carbonyl groups with the formation of β -aminovinylketones [1, 2]. In [3, 4] in the condensation of β -diketones with N-nucleophiles the recorded condensation intermediates derived from PMR were the geminal hydroxyamines (II), (III).

Fluoroalkyl substituents stabilize geminal adducts of carbonyl compounds with nucleophiles [5]. For that reason we undertook the task of isolating adducts of polyfluorinated B-diketones (Ia-g) with ammonia and with amines. However, it appears that β -diketones (Ia-g) with NH3, methylamine, and dimethylamine at 10-20°C do not form adducts (II) or (III) but salts (IV) (see Table 1). We verified this by chemical methods and by PMR spectra

> $R_{\mathbf{F}} = HCF_{2}^{\circ}(\mathbf{a}); C_{2}F_{5}(\mathbf{b}); H(CF_{2})_{2}(\mathbf{c}-\mathbf{e}, \mathbf{g}); H(CF_{2})_{4}(\mathbf{f}); R^{1} = Me(\mathbf{a}-\mathbf{c}, \mathbf{f}); Bu(\mathbf{d});$ t - Bu (e); $H(CF_2)_2$ (g).

The condition for the formation of stable salts (IV) is an adequate difference between the acid-base properties of the β -diketone and the amine. Thus acetylacetone (pK_a = 9.05 ± 0.04 [6]) does not form a stable ammonium salt. The same thing was observed in the reaction between aniline and unsymmetrical polyfluorinated β -diketones (Ia-f) (pK_a = 6.61-4.70 [6]), although for the symmetrical β -diketone (Ig) (pKa = 2.43 ± 0.073 [6]) we obtained a stable salt (IVk).

The reactions of compounds (IVa-k) with copper (II) acetate at \sim 20°C yield the Cu(II) β -diketone salts. With dry HCl the corresponding β -diketones and amine hydrochlorides are formed in quantitative yields



Institute of Chemistry, Ural Science Center, Academy of Sciences of the USSR, Sverdlovsk. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 3, pp. 623-627, March, 1984. Original article submitted February 3, 1983.

$\bigoplus_{NH_2R^2R^3}$	R spectrum, δ , ppm (solvent)	=CH			CeFGFs Col.+CD.COCD.)	1.0	$\left \begin{array}{c} CCI_{4}+CD_{3}COCD_{3} \\ \vdots \\ F_{2}CF_{2} \\ 14.50 \\ 14$				CCI ₄ +CD ₃ COCD ₃) Not			
	Md		- <u></u>		6,05 (100%	5,90() 			5,48(<u>`</u>		
	IR spectru ^v C # 0, cm -1		1640	1630	1630	1630	1630	1630	1650	1660	1640	1630	1655	
	Molecular formula		C ₅ H ₉ F ₂ NO ₂	C ₆ H ₈ F ₅ NO ₂	C ₆ H ₉ F ₄ NO ₂	C9H15F4NO2	C9H15F4NO2	C ₈ H ₉ F ₈ NO ₂	C ₇ H ₁₁ F ₄ NO ₂	C ₁₀ H ₁₇ F ₄ NO ₂	$C_{10}H_{17}F_4NO_2$	C ₁₁ H ₁₉ F ₄ NO ₂	C ₁₃ H ₁₁ F ₈ NO ₂	
	Found /calculated, %	z	9,40	9,15 6,60	6,33 7,6	6,0 3	5,81	5,71 4,65	4,62	1	1	-	3,90 3,83	_
		Н	6.04	3,80 3,80	3,64 4,08	3,98 6,31	6,16 6,10	6,16 2,90	2,99 5,14	5,10 6,67	6,60 6,68	6,60 7,02	7.01 2.79 3.03	: R ³ = H
		0	39,12	33,01 33,01	32,59	35,69	47(08 43,99	44,08 31,60	31,69 38,91	38,71 46,55	46,33 46,09	46,33 48,10	(8.35 (2.35 42,75	he rest
	Yield,%		94	64	96	95	95	96	93	95	94	93	06	, for t
	, K		Н	II	Ш	Н	Н	Н	Me	Me	Me	Me	hh	(³ = Me
		Ē.	Me	Me	Me	Bu	t-Bu	Me	Me	Bu	ng-1	t-Bu	$H(CF_2)_2$	(IVj) F
	· · · ·	년 31 1	HCF2	$C_{2}F_{5}$	$H(CF_2)_2$	$H(CF_2)_2$	$H(CF_2)_2$	H (CF ₂) 4	II (\mathbf{CF}_2) 2	II (\mathbf{CF}_2) 2	$H(\mathbf{CF}_2)_2$	$H(CF_2)_2$	$H(CF_2)_2$	compound
	Com- pound		(IVZ)	(q VI)	(IV c)	(PAI)	(IVe)	(JAI)	(IVg)	(IV ħ)	(IVI)	(IVj)	(IVk)	*For

TABLE 1. Salts of Unsymmetrical Polyfluorinated β -Diketones with Amines

On boiling with benzene or toluene the salts (IV) form mixtures of the corresponding β -diketones (I) and β -aminovinylketones (V)*



Long standing of the salts (IV) at ~ 20 °C yields the corresponding β -aminovinylketones. It is important that under these conditions a mixture of equivalent amounts of various salts, for example (IVb) and (IVg) yields only two of the four possible β -aminovinulketones (V), i.e., (Va) and (Vb).



It is interesting to note that the salts (IV) can play the role of aminating agents for β -diketones inasmuch as reaction of equivalent amounts of different salts (IV) with β -diketones yields β -aminovinylketones (V) having the alkyl substituent of lesser volume.



EXPERIMENTAL

IR spectra were taken on a UR-20 spectrometer in a mineral oil mull, PMR spectra on a Perkin-Elmer R-12B (60 MHz, with a TMS internal standard).

The β -diketones and their copper chelates obtained by reaction with the salts were identified by their IR spectra and TLC by comparison with known substances synthesized as in [7]. Amine hydrochlorides were identified by IR spectra. Known samples of NH₄Cl,, NH₃MeCl^{\odot}, and NH₃PhCl were used as standards.

Salts (IVa-j) were synthesized by the following general method. After dissolving the appropriate β -diketone in abs. ether, ammonia, methylamine or dimethylamine was passed through until the exothermic reaction ceased. The solution was diluted with cold isohexane until a precipitate formed which was filtered and reprecipitated from ether solution by isohexane. Yields of the characteristic salts (IVa-j) are shown in Table 1.

<u>N-Phenylammonium(1,1,2,2,6,6,7,7-octafluorohepta-3,5-dionate) (IVk).</u> Compound (Ig), 1,1,2,2,6,6,7,7-octafluorohepta-3,5-dione, 1 g (3.6 mmoles), was mixed with 0.35 g (3.6 mmoles) of aniline. The white crystals formed were reprecipitated from ether solution by isohexane. Salt (IVk), 1.2 g (90%) was obtained.

 $\frac{\text{Decomposition of Ammonium}(1,1,2,2,-\text{tetrafluorohexa-}3,5-\text{dionate}) (IVc) \text{ on Heating.}}{(34 \text{ mmoles}) \text{ of ammonium}(1,1,2,2-\text{tetrafluorohexa-}3,5-\text{dionate}) (IVc) \text{ was added } 30 \text{ ml of}}$

*On heating dimethylammonium(1,1,2,2-tetrafluoro-6,6-dimethylhepta)3,5-dionate (IVj) formation of the corresponding β -aminovinylketone was not observed. dry benzene and refluxed in a Dean-Stark apparatus until cessation of separation of water. The benzene was distilled off, the residue reprecipitated from ether by isohexane. There was obtained 3.2 g (50%) of 1,1,2,2-tetrafluoro-5-aminohex-4-en-3-one, mp 61.5-62.5°C (see [1]). The filtrates were consolidated, the solvent distilled off, and the residue distilled. There was obtained 1.9 g(30%) of 1,1,2,2-tetrafluorohexa-3,5-dione (Ic), bp 139-140°C (see [7]).

The decomposition of salts (IVa-i) was carried out in an analogous manner. The characteristics of the β -aminovinylketones and β -diketones obtained agreed with the data of [1] and [7].

<u>Reaction of Ammonium(1,1,2,2-tetrafluorohexa-3,5-dionate)(IVc) with Copper(II) Ace-</u> <u>tate.</u> To a solution of 1 g (5 mmoles) of ammonium(1,1,2,2-tetrafluorohexa-3,5-dionate (IVc) in ethanol was added 0.8 g (5 mmoles) of copper (II) acetate. The mixture was allowed to stand for several days at $\sim 20^{\circ}$ C. The excess copper (II) acetate was filtered off. Water was added to the filtrate until a precipitate came out, which was filtered and dried. There was obtained 0.98 g (95%) of copper(II) bis(1,1,2,2-tetrafluorohexa-3,5-dionate), mp133°C (see [7]).

Salts (IVa-k) react in an analogous manner with copper(II) acetate.

Reaction of Ammonium(1,1,2,2-tetrafluorohexa-3,5-dionate) (IVc) with Gaseous HCl. Dry HCl was passed through a solution of 1 g (5 mmoles) of ammonium(1,1,2,2-tetrafluorohexa-3,5dionate) (IVc) in abs. ether until the exothermic reaction ceased. The NH₄Cl precipitate formed was filtered off. To the filtrate was added 0.9 g (5 mmoles) of copper(II) acetate. It was refluxed 1 h, the ether distilled off, the residue reprecipitated from methanol solution by means of water. There was obtained 1 g (98%) of copper(II)bis(1,1,2,2-tetrafluorohexa-3,5-dionate), mp 133° (see [7]). The NH₄Cl was washed with dimethylformamide and reprecipitated by acetone from an aqueous solution. Obtained was 0.26g (99%) of NH₄Cl.

Reaction of N-Phenylammonium(1,1,2,2,6,6,7,7-octafluorohepta-3,5-dionate) (IVk) with Gaseous HCl. Dry HCl was passed through a solution of 1 g (2.7 mmoles) of salt (IVk) in abs. ether until the exothermic reaction ceased. The precipitate of aniline hydrochloride which came down was filtered off, washed with ether, and excess solvent removed in a vacuum. White crystals with a mp 197-198°C were obtained, 0.32 g (91%), (see [8]). To the filtrate was added 0.36 g (2 mmoles) of copper(II) acetate, it was refluxed about 1 h, the ether distilled off, the remaining solvent removed from the residue in a vacuum. There was obtained 0.6 g (73%) of the chelate with a mp of 117-118°C identified by comparison with a known sample of copper(II) bis(1,1,2,2,6,6,7,7-octafluorophepta-3,5-dionate).

Decomposition of Ammonium(1,1,2,2-tetrafluorohexa-3,5-dionate)(IVc) at 20°C. Placed in a weighing bottle were 1.5 g (7.4 mmoles) of ammonium(1,1,2,2-tetrafluorohexa-3,5-dionate) which was kept at 20°C until the salt was completely decomposed (monitored by TLC). The dark brown oil formed was extracted several times with boiling isohexane. The extracts were combined and then cooled. The crystals which came out were filtered. There was obtained 1.25 g (92%) of 1,2,2,2-tetrafluoro-5-aminohex-4-en-3-one, mp 61.5-62.5°C (see [1]).

Decomposition of Ammonium(1,1,1,2,2-pentafluorohexa-3,5-dionate) (IVb) at 20°C. In an analogous manner from 1 g (4.5 mmoles) ammonium(1,1,1,2,2-pentafluorohexa-3,5-dionate) (IVb) was obtained 0.85 g (92%) 1,1,1,2,2-pentafluoro-5-aminohex-4-en-3-one, mp85-86°C (see [9]).

Decomposition of Ammonium(1,1,2,2,3,3,4,4-octafluoroocta-5,7-dionate)(IVf) at 20°C. In an analogous manner from 1 g (3.3 mmoles) of ammonium(1,1,2,2,3,3,4,4-octafluoroocta-5,7dionate) (IVf) was obtained 0.85 g (91%) of 1,1,2,2,3,3,4,4-octafluoro-7-aminooct-6-en-5-one, mp 72-73°C (see [1]).

Reaction of Ammonium(1,1,2,2-tetrafluoro-6,6-dimethylhepta-3,5-dionate) (IVe) and 1,1,2,2,3,3,4,4-Octafluoroocta-5,7-dione (If). To 2g (8 mmoles) of ammonium 1,1,2,2-tetrafluoro-6,6-dimethylhepta-3,5-dionate (IVe) was added 2.2 g (8 mmoles) of 1,1,2,2,3,3,4,4octafluoroocta-5,7-dione (If) which was maintained at 20°C with monitoring of the extent of the reaction by means of TLC. After chromatography on a silicate column (with chloroform as eluant) 1.6 g (88.5%) of 1,1,2,2,-tetrafluoro-6,6-dimethylhepta-3,5-dione (Ie) bp 172-147°C see [7]), and 1.9 g (84%) of 1,1,2,2,3,3,4,4-octafluoro-7-aminoocta-6-en-5-one (Vc), mp 72-73°C, (see [1]) were obtained. Reaction of Ammonium(1,1,2,2,3,3,4,4-octafluoroocta-5,7-dionate (IVf) and 1,1,2,2,-Tetrafluoro-6,6-dimethylhepta-3,5-dione (Ie). To 1.25 g (4 mmoles) of ammonium(1,1,2,2,3,3, 4,4-octafluoroocta-5,7-dionate (IVf) was added 0.92 g (4 mmoles) of 1,1,2,2,-tetrafluoro-6,6-dimethylhepta-3,5-dione (Ie) which was kept at 20°C until salt (IVf) disappeared as monitored by TLC. After chromatography on a silicate column (with chloroform as eluant) 0.085 g (92.5%) of 1,1,2,2-tetrafluoro-6,6-dimethylhepta-3,5-dione (Ie) and 1.1 g (95%) of 1,1,2,2,3,3,4,4-octafluoro-7-aminooct-6-en-5-one (Vc), mp 72.5-73.5 (see [1]) were obtained.

Reaction of Ammonium(1,1,2,2-tetrafluoro-6,6-dimethylhepta-3,5-dionate) (IVe) with Acetylacetone. In an analogous manner from 1 g (4 mmoles) of ammonium(1,1,2,2-tetrafluoro-6,6-dimethylhepta-3,5-dione) (IVe) and 0.4 g (4 mmoles) of acetylacetone there was obtained 0.86 g (95%) of 1,1,2,2-tetrafluoro-6,6-dimethylhepta-3,5-dione (Ie) and 0.35 g (87.5%) of 2-aminopent-2-en-4-one, mp 42-43°C (see [10]).

Decomposition of a Mixture of Ammonium(1,1,1,2,2-pentafluorohexa-3,5-dionate) (IVb) and N-Methylammonium(1,1,2,2-tetrafluorohexa-3,5-dionate)(IVg). Mixed carefully were 5 g (22.6 mmoles) of ammonium(1,1,2,2-pentafluorohexa-3,5-dionate) (IVb) and 4.9 g (22.6 mmoles) of N-methylammonium(1,1,2,2-tetrafluorohexa-3,5-dionate) (IVg), which were then transferred to a weighing bottle and maintained at 20°C, monitoring the extent of the reaction by means of TLC. After chromatography on a silicate column (with chloroform as eluant) 1.2 g (30%) of 1,1,2,2-tetrafluoro-5-(N-methylamino)-hex-4-en-3-one (Vb), mp 32-33°C (see [1]) and 1.5 g (33%) of 1,1,1,2,2-pentafluoro-5-aminohex-4-en-3-one (Va) were obtained. Found C 35.51; H 2.96; N 6.60. C_gH_gF_gON. Calculated: C 35.48; H 2.97; N 6.89%. PMR spectrum (CC14, δ, ppm): 2.12 s (Me), 5.42 (= CH), 7.2 (NH), 10.9 (NH...0). Also obtained was 6.5 g of a mixture of β-aminovinylketones (Va) and (Vb).

CONCLUSIONS

Polyfluorinated β -diketones form stable salts with ammonia and amines.

LITERATURE CITED

- 1. K. I. Pashkevich, V. I. Filyakova, Yu. M. Sheinker, O. S. Anisimova, I. Ya. Postovskii, and E. F. Kuleshova, Izv. Akad. Nauk SSSR, Ser. Khim., 2087 (1979).
- K. I. Pashkevich, V. I. Filyakova, and I. Ya. Postovskii, Izv. Akad. Nauk SSSR, Ser. Khim., 2346 (1981).
- 3. M. Cocivera and K. W. Woo, J. Am. Chem. Soc., 98, 7366 (1976).
- 4. S. I. Selivanov, R. A. Bogatkin, and B. A. Ershov, Zh. Org. Khim., <u>18</u>, 909 (1982).
- 5. W. A. Sheppard and C. M. Sharts, Organic Fluorine Compounds, W. A. Benjamin, New York (1969), p. 437.
- 6. K. I. Pashkevich, V. I. Saloutin, L. G. Egorova, and I. Ya. Postovskii, Zh. Obshch. Khim., 49, 212 (1979).
- 7. V. I. Saloutin, K. I. Pashkevich, and I. Ya. Postovskii, Zh. Vses. Khim. O-va, <u>21</u>, No. 2, 238 (1976).
- 8. I. T. Goronovskii, Yu.P. Nazarenko, and E. F. Nekryach, Short Handbook of Chemistry, [in Russian], Naukova Dumka, Kiev (1974), p. 414.
- 9. V. I. Filyakova, K. I. Pashkevich, and I. Ya. Postovskii, Izv. Akad. Nauk SSSR, Ser. Khim., 2651 (1981).
- 10. J. Weinstein and G. M. Wyman, J. Org. Chem., 23, 1618 (1958).