Organic Chemistry

Interaction of fluoroalkyl-containing β-diketones with amines

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The composition of products of the interaction of asymmetric fluoroalkyl-containing β-diketones with amines was studied. Mixtures of regioisomeric β-aminovinylketones and products of cleavage and secondary condensation are formed, depending on the temperature, the solvent, the nature of the fluorinated and nonfluorinated substituents in the β-diketone, and the basicity of the amine. The major product is a β-aminovinylketone in which the NH_2 group is removed from the fluoroalkyl substituent. No β-aminovinylimines, products of condensation involving two electrophilic centers, were observed.

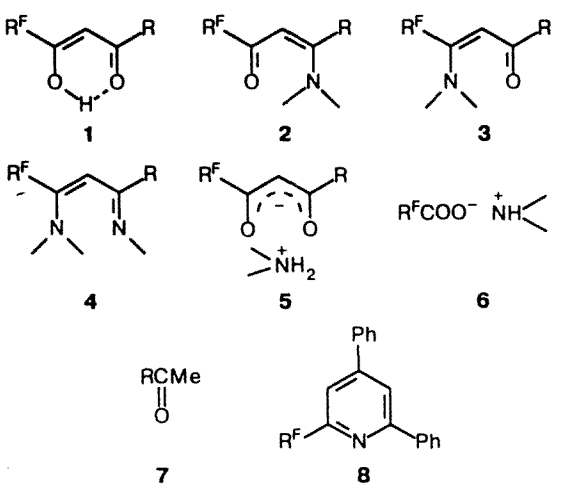
Key words: fluoroalkyl-containing β-diketones, amines, condensation; regioisomeric β-aminovinylketones; β-aminovinylimines.

Condensation of β-diketones with ammonia and amines is the basic method for the synthesis of β-aminovinylketones (AVK), which are valuable synthons and reagents for GLC determination of minor amounts of metals.[1,2]

In the reactions of asymmetric β-diketones, the nonequivalence of the electrophilic centers C(1) and C(3) makes possible the formation of either one or both regioisomeric AVK, β-aminovinylimine (AVI), or a mixture of all these products. The differences in the reactivities of the electrophilic centers C(1) and C(2) should be the most pronounced in asymmetric polyfluorinated β-diketones **1**, because the inductive effects of substituents R^F and R are different.

The literature data are restricted to the interaction of some fluoroalkyl-containing β-diketones with ammonia, methylamine, dimethylamine, aniline, ethylenediamine, diethylenetriamine, and triethylenetetramine. The formation of both regioisomeric AVK **2** and **3**,[3–8] and salts **5**[9] has been reported.

In this work we have studied the composition and structure of the products formed as a result of the interaction of a wider variety of fluoroalkyl-containing β-diketones **1** with amines (Table 1) and compared the results obtained with the literature data.



In nonpolar solvents (*n*-hexane, benzene, toluene) at 20 °C, diketones **1** almost immediately react with highly basic amines to form stable salts **5**. Condensation occurs either when mixtures of β-diketones and amines are refluxed in solvents that make it possible to remove the liberated water (benzene, toluene) or when these mix-

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Table 1. Products of the interaction of fluorinated β-diketones **1** with amines

β-Diketone	R^F	R	Amine	Solvent (synthetic procedure)[a]	Yields of products (%)					
					1[b]	**2**	**3**	**6**	**7**	**8**
1a	CF_3	Me	NH_3	C_6H_6 (*A*)	—	57	—	5	[c]	—
			$MeNH_2$	C_6H_6 (*A*)	—	46	—	7	[c]	—
			$PhNH_2$	C_6H_6 (*B*)	—	63	—	—	—	—
			$PhNH_2$	MeOH (*C*)	—	80	—	—	—	—
			α-Naphthylamine	MeOH (*C*)	—	80	—	—	—	—
1b	CF_3	Ph	NH_3	C_6H_6 (*A*)	8	12	60	13.7	6	—
			$MeNH_2$	C_6H_6 (*A*)	—	41	11.7	—	14	4
			$PhNH_2$	MeOH (*C*)	—	90	—	—	—	—
			Morpholine	MePh (*B*)	—	76	—	—	—	—
			Piperidine	MePh (*B*)	—	76	—	—	—	—
			α-Naphthylamine	MeOH (*C*)	—	—	61	—	—	—
			$PhNH_2$	MePh (*B*)	15	76	4	—	15	—
1c	CF_3	C_6H_4Cl	$PhNH_2$	MePh (*B*)	—	50	34	—	[c]	—
			$PhNH_2$	MeOH (*C*)	—	70	—	—	10	—
1d	CF_3	$C_6H_4NO_2$	NH_3	MePh (*A*)	—	—	—	75	70	—
			$MeNH_2$	MePh (*A*)	—	—	—	70	68	—
			$PhNH_2$	MePh (*B*)	17	72	8	—	[c]	—
			$PhNH_2$	MeOH (*C*)	—	78	—	—	—	—
1f	CF_3	C_6H_4Br	$PhNH_2$	MePh (*B*)	—	88	—	—	[c]	—
1g	CF_3	C_6H_4Me	$PhNH_2$	MePh (*B*)	—	67	7.5	—	[c]	—
			$PhNH_2$	MeOH (*C*)	—	90	—	—	—	—
1h	CF_3	C_6H_4OMe	$PhNH_2$	MePh (*B*)	—	68	17	—	—	—
1i	CF_3	C_6H_4Cl	α-Naphthylamine	MeOH (*C*)	—	—	37	—	10	—
1j	CF_3	C_6H_4Br	α-Naphthylamine	MeOH (*C*)	—	—	20	—	—	—
1k	$H(CF_2)_2$	Me	NH_3	C_6H_6 (*A*)	10	51	—	5.5	[c]	—
			$MeNH_2$	C_6H_6 (*A*)	25	46	—	—	[c]	—
			$PhNH_2$	MePh (*B*)	—	64	—	—	—	—
			$PhNH_2$	MeOH (*C*)	—	72	—	—	—	—
			α-Naphthylamine	MeOH (*C*)	—	55	—	—	—	—
			Morpholine	MeOH (*C*)	—	56	—	—	—	—
1l	$H(CF_2)_2$	Bu^n	NH_3	C_6H_6 (*A*)	—	60	—	—	[c]	—
			$PhNH_2$	MePh (*B*)	—	54	—	—	[c]	—
			$MeNH_2$	C_6H_6 (*A*)	21	54	—	—	[c]	—
1m	$H(CF_2)_2$	Bu^t	$MeNH_2$	C_6H_6 (*A*)	44	16	—	10	[c]	—
			NH_3	C_6H_6 (*A*)	—	15	—	—	[c]	—
			$PhNH_2$	MePh (*B*)	76	15	—	—	[c]	—
1n	$H(CF_2)_2$	Ph	NH_3	C_6H_6 (*A*)	20	35	8.5	—	10	3
			$MeNH_2$	MePh (*A*)	15	31.4	21	—	10	4
			$PhNH_2$	C_6H_6 (*B*)	30	43	—	—	12	—
1o	$H(CF_2)_4$	Me	NH_3	C_6H_6 (*A*)	—	64	—	—	—	—
1p	$H(CF_2)_4$	Ph	NH_3	MePh (*A*)	20	60	—	—	10	—
			$MeNH_2$	C_6H_6 (*A*)	—	57	—	—	—	—
			$PhNH_2$	MePh (*B*)	15	45	—	—	8	—

[a] See Experimental. [b] In many cases unreacted β-diketone **1** was isolated from the reaction mixture. Yields of products are given without regard to conversion. [c] The presence of the corresponding methylketone in the reaction mixture was determined by GLC by comparison with authentic samples. No quantitative estimations were carried out.

tures are kept for a prolonged period of time at 20 °C in polar protic solvents (methanol, ethanol). We should emphasize that alcohols can be used as solvents only for the reactions of diketones **1** with weakly basic amines. Under these conditions highly basic amines cause solvolysis of β-diketones, and only an aprotic solvent can be used for the reactions with them.

Unlike their nonfluorinated analogs, which are capable of forming condensation products at both the electrophilic centers (AVK **2** or **3** and ABI **4**),[1] polyfluorinated

β-diketones **1** react with ammonia and amines to form condensation products involving only one electrophilic center, fluorinated AVK. Neither using a large excess of amine, increasing the duration of the reaction or the amine concentration, increasing the temperature or pressure, or adding boron trifluoride etherate in catalytic and equimolar amounts lead to the product of condensation involving both electrophilic centers, AVI **4**.

The nature of substituents R^F and R in the starting β-diketone has a crucial effect on the result of condensation. If R = Alk, AVK **2** are obtained, in which the amino group is removed from the fluoroalkyl substituent, irrespective of the bulk of R (Me, Bu^n, or Bu^t), the length of the fluoroalkyl substituent ($CF_3...C_6F_{13}$ or $HCF_2...H(CF_2)_4$), and the nature of the amine. The reaction is accompanied by the cleavage of β-diketone at the C(1)—C(2) bond to yield salts of polyfluorinated carboxylic acids **6** and methylketones **7**. When R = Bu^t, as a result of steric hindrances, the yield of AVK **2** sharply decreases, the reaction time increases, and the fraction of cleavage products increases; however, no condensation involving the electrophilic center C(1) occurs to form AVK **3**.

When R = p-XC_6H_4 condensation of asymmetric fluorinated β-diketones with ammonia, methylamine, and aniline results in a mixture of regioisomeric AVK **2** and **3**. In the case when R^F = CF_3 or HCF_2, isomer **3** predominates (80—90%), even if amines with bulk substituents are used (α-naphthylamine, *N*-aminocarbazole). However, the fraction of isomer **3** sharply decreases in the mixture when the length of R^F increases. No correlation between the acceptor ability of substituent X and the ratio of AVK isomers **2** and **3** is observed. In addition to AVK **2** and **3**, cleavage products **6** and **7** are formed during the reaction. Among the compounds of this series, β-diketone **1d** (X = NO_2), which does not form AVK when it reacts with ammonia and dimethylamine and gives only cleavage products **6** and **7** when heated in nonpolar aprotic solvents is noteworthy. At the same time the reaction of β-diketone **1d** with weakly basic aniline leads to AVK **2** in a high yield.

Additionally, in some cases we succeeded in isolating 2,4-diphenyl-6-fluoroalkylpyridines **8**, which are the products of the secondary condensation of AVK **3** with one of the products of acidic cleavage, acetophenone, from the reaction mixture. We confirmed this by an alternative synthesis. Under these conditions AVK **2** does not react with acetophenone.

The nature of the solvent, the temperature and the catalyst affect the composition of the condensation products of aryl-containing β-diketones **1** (R = p-XC_6H_4) with amines more dramatically than in the case when R = Alk. In aprotic solvents (benzene and toluene) condensation of β-diketones **1** to yield AVK occurs only in the presence of a catalyst (sulfuric acid or boron trifluoride etherate), and the use of a high-boiling solvent favors AVK formation. However, the same factors also favor the appearance of products **6**—**8**. In protic solvents (methanol, ethanol), the reaction with weakly basic amines often occurs even at room temperature (sometimes boiling is required). In this case products **6**—**8** are almost absent from the reaction mixture, and one of the isomeric forms, AVK **2** or **3**, is formed preferably.

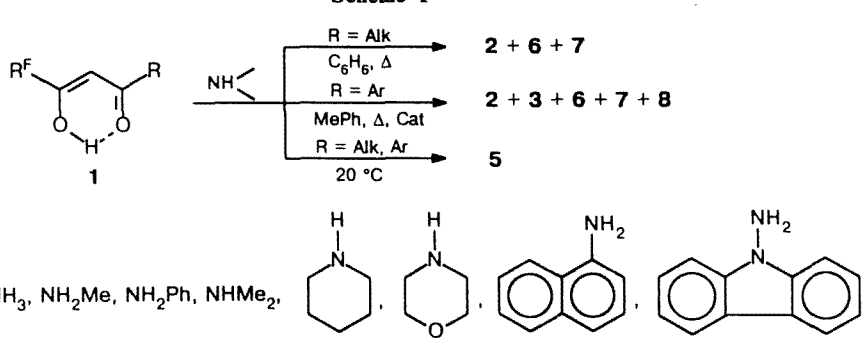
Our attempts to synthesize AVK by condensation of all mentioned β-diketones **1** with highly basic amines containing bulky substituents (*tert*-butylamine, diethylamine, pyrrolidine, and dicyclohexylamine), failed. Depending on the temperature and solvent either salts **5** (in saturated and aromatic hydrocarbons at 20 °C) or products of acid cleavage (in polar protic solvents at 20 °C or in aromatic hydrocarbons after boiling) were isolated.

Diphenylamine, which is weakly basic and sterically hindered, did not react with any of the studied β-diketones **1**.

Table 1 indicates that although the condensation of asymmetric β-diketones **1** with NH_3 and amines proceeds ambiguously, the major products of the reaction are AVK **2** in which the NH_2 group is removed from the fluoroalkyl substituent.

Thus, the interaction of fluoroalkyl-containing β-diketones with NH_3 and amines can be represented by general Scheme 1.

Scheme 1



NH< = NH_3, NH_2Me, NH_2Ph, $NHMe_2$,

R^F = CF_3, ..., C_6F_{13}, $H(CF_2)_n$; n = 1, 2, 4

R = Me, Bu^t, p-XC_6H_4; X = H, Me, OMe, Cl, NO_2, Br

Cat = BF_3, Et_2O, H_2SO_4

Table 2. Physicochemical characteristics of β-aminovinylketones **2** and **3**

AVK	Compound	M.p. /°C	Found / Calculated (%)						Molecular formula	IR, ν/cm^{-1},	^1H NMR (δ)		
			C	H	Br	Cl	F	N		C=O	=CH—	NH	other signals
2a	4-(*N*-Naphthylamino)-1,1,1-trifluoro-3-pentene-2-one	39	64.56 64.51	4.32 4.33	— —	— —	19.90 20.41	5.31 5.02	$C_{15}H_{12}F_3NO$	1600	5.64	12.77	1.96 (s, 3 H, Me); 7.21—7.94 (m, 7 H, naphthyl)
2b	4-(*N*-Morpholino)-4-phenyl-1,1,1-trifluoro-3-butene-2-one	146.7	58.81 58.95	5.09 4.95	— —	— —	— —	5.07 4.91	$C_{14}H_{14}F_3NO_2$		5.51	—	3.44 (m, 4 H, $N(CH_2)_2$); 7.26—7.99 (m, 5 H, Ph)
2c	4-(*N*-Piperidino)-4-phenyl-1,1,1-trifluoro-3-butene-2-one	137.8	63.42 63.60	5.81 5.69	— —	— —	— —	5.12 4.94	$C_{15}H_{16}F_3NO$	1640	5.47	—	1.70 (m, 6 H, $(CH_2)_3$); 3.49 (m, 4 H, $N(CH_2)_2$); 7.30—8.10 (m, 5 H, Ph)
3a	3-(*N*-Naphthylamino)-1-phenyl-4,4,4-trifluoro-2-butene-1-one	125	69.92 70.08	4.28 4.13	— —	— —	16.71 16.69	4.22 4.19	$C_{20}H_{14}F_3NO$	1620	6.56	12.60	7.21—7.95 (m, 12 H, naphthyl + Ph)
2d	4-(*N*-Phenylamino)-1,1,1-trifluoro-4-(*p*-chlorophenyl)-3-butene-2-one	66—67	58.99 58.99	3.41 3.39	— —	10.69 10.89	17.51 17.49	4.18 4.30	$C_{16}H_{11}ClF_3NO$	1610	5.76	12.70	7.20—8.70 (m, 9 H, Ar)
3b	3-(*N*-Phenylamino)-4,4,4-trifluoro-1-(*p*-chlorophenyl)-2-butene-1-one	—	58.99 58.97	3.41 3.60	— —	10.69 10.74	17.51 17.73	4.18 4.18	$C_{16}H_{11}ClF_3NO$	1640	6.53	—	7.20—8.70 (m, 10 H, NH + Ar)
2e	4-(*p*-Nitrophenyl)-1,1,1-trifluoro-4-(*N*-phenylamino)-3-butene-2-one	145	56.93 57.12	3.32 3.30	— —	— —	17.04 16.69	8.26 8.33	$C_{16}H_{11}F_3N_2O_3$	1610	5.80	12.55	7.26—7.99 (m, 9 H, Ar)
3c	1-(*p*-Nitrophenyl)-4,4,4-trifluoro-3-(*N*-phenylamino)-2-butene-1-one	—	56.93 57.02	3.32 3.33	— —	— —	17.04 17.00	8.26 8.28	$C_{16}H_{11}F_3N_2O_3$	1700	6.21	—	7.26—7.99 (m, 10 H, NH + Ar)
2f	4-(*p*-Bromophenyl)-1,1,1-trifluoro-4-(*N*-phenylamino)-3-butene-2-one	73	51.79 51.89	2.86 2.98	— —	— —	15.15 15.41	4.05 3.98	$C_{16}H_{11}BrF_3NO$	1610	5.76	12.60	6.90—8.00 (m, 9 H, Ar)
2g	4-(*p*-Methylphenyl)-1,1,1-trifluoro-4-(*N*-phenylamino)-3-butene-2-one	67	66.54 66.86	4.41 4.63	— —	— —	18.71 18.68	4.79 4.59	$C_{17}H_{14}F_3NO$	1615	5.76	12.70	2.40 (s, 3 H, Me); 7.25—7.48 (m, 9 H, Ar)

Table 2. (*continued*)

AVK	Compound	M.p. /°C	Found / Calculated (%)						Molecular formula	IR, ν/cm^{-1},	^{1}H NMR (δ)		
			C	H	Br	Cl	F	N		C=O	=CH—	NH	other signals
3d	1-(*p*-Methylphenyl)-4,4,4-trifluoro-3-(*N*-phenylamino)-2-butene-1-one	—	66.54 66.68	4.41 4.58	— —	— —	18.71 18.69	4.79 4.70	$C_{17}H_{14}F_3NO$	1630	6.55	—	2.42 (s, 3 H, Me); 7.25—7.48 (m, 10 H, NH + Ar)
2h	4-(*p*-Methoxyphenyl)-1,1,1-trifluoro-4-(*N*-phenylamino)-3-butene-2-one	54—55	63.59 63.53	4.60 4.59	— —	— —	17.40 17.75	4.16 4.36	$C_{17}H_{14}F_3NO_2$	1600	5.78	12.80	3.88 (s, 3 H, OMe); 7.46—7.97 (m, 9 H, Ar)
3e	4-(*p*-Methylphenyl)-4,4,4-trifluoro-3-(*N*-phenylamino)-2-butene-1-one	—	63.59 63.60	4.60 4.62	— —	— —	17.40 17.60	4.16 4.21	$C_{17}H_{14}F_3NO_2$	1600	6.93	—	3.89 (s, 3 H, OMe); 7.46—7.97 (m, 10 H, NH + Ar)
3f	3-(*N*-Naphthylamino)-4,4,4-trifluoro-1-(*p*-chlorophenyl)-2-butene-1-one	121	63.43 63.92	3.49 3.49	— —	— 9.38	16.17 16.17	3.76 3.72	$C_{20}H_{13}ClF_3NO$	1620	6.48	12.56	7.42—8.11 (m, 11 H, naphthyl + Ar)
3g	1-(*p*-Bromophenyl)-3-(*N*-naphthylamino)-4,4,4-trifluoro-2-butene-1-one	108	57.05 57.16	3.15 3.12	19.29 19.01	— —	13.85 13.56	3.28 3.33	$C_{20}H_{13}BrF_3NO$	1610	6.48	12.55	7.43—7.95 (m, 11 H, naphthyl + Ar)
2i	5-(*N*-Naphthylamino)-1,1,2,2-tetrafluoro-4-hexene-3-one	80	54.36 54.55	3.23 3.13	— —	— —	31.90 31.79	6.68 6.69	$C_{19}H_{13}F_7N_2O$	1590	5.76	12.88	1.99 (s, 3 H, Me); 6.21 (tt, 1 H, HCF_2CF_2, J_{H-CF_2} = 53.16 Hz, $J_{H-CF_2-CF_2}$ = 5.51 Hz); 7.34—7.97 (m, 7 H, naphthyl)
2j	6-(*N*-Carbazylamino)-1,1,1,2,2,3,3-heptafluoro-5-heptene-4-one	137	61.92 61.74	3.94 4.11	— —	— —	24.20 24.41	4.33 4.50	$C_{16}H_{13}F_4NO$	1625	5.75	12.22	1.92 (s, 3 H, Me); 7.20—8.13 (m, 8 H, carbazyl)

The *N*-nonsubstituted and *N*-monosubstituted AVK **2** and **3** obtained by us exist in the *cis*-enaminoketone form stabilized by intramolecular bonds (according to their ^{1}H NMR and IR spectra). Their spectral characteristics are the same as those reported earlier.[3,4,10] *N,N*-Disubstituted AVK (derivatives of dimethylamine, piperidine, and morpholine) also exist in the enaminoketone form. However, we did not study the isomerism of these compounds with respect to either the single bond or the double bond.

Experimental

^{1}H NMR spectra were recorded on a BS-567A (100 Hz) spectrometer in $CDCl_3$ with $SiMe_4$ used as the internal standard. IR spectra were recorded on a Specord 75 IR spectrophotometer in a 20 μm layer (for liquids) and in pastes with Vaseline oil (for solids). The GLC analysis was carried out on an LKhM-72 chromatograph (katharometer as detector, helium as carrier gas, a 1.0 m steel column, 5% Silicon SE-30 on Chromaton-N-AW-HMDS). TLC was carried out on Silufol UV-254 plates with $CHCl_3$ and CCl_4 as eluents, and visualization was conducted with aqueous solutions of copper acetate and $KMnO_4$. Mixtures were chromatographed on columns packed with L 100/250 silica gel using $CHCl_3$ as the eluent. The synthesized compounds were identified by their ^{1}H NMR and IR spectra and TLC or by comparison of them with authentic samples. Fluorinated β-diketones **1** were obtained by the well known procedure.[11] Conditions of the formation and properties of salts **5** were reported earlier.[9]

Characteristics of AVK **2** and **3** synthesized by us are given in Table 2.

Interaction of fluorinated β-diketones with amines. *A (for gaseous amines).* An amine was bubbled *via* a solution of fluorinated β-diketone in dry ether until the exothermic reaction was complete. The reaction flask was fitted with a Dean—Stark distillation head, benzene (toluene, xylene) was added (30 mL) to the reaction mixture, and the water liberated in the course of the reaction was distilled off azeotropically. The composition of the reaction mixture was monitored by TLC and GLC. The low-boiling components of the mixture were distilled off on a water bath, and the residue was cooled.

1. If the residue was crystallized, it was dissolved in ether. The undissolved crystals of salt **6** were filtered off and reprecipitated with ether from an ethanol solution. The resulting mother liquor was diluted with *n*-hexane cooled to −20 °C. The AVK precipitate that formed was filtered off, dissolved in ether, and precipitated with *n*-hexane.

2. If the residue was not crystallized, it was distilled *in vacuo* or chromatographed on a column; the composition of each fraction was monitored by TLC and GLC. The compositions of the reaction products are given in Table 1.

B (for high-basicity liquid and solid amines). A mixture of β-diketone **1** (0.05 mol), an amine (0.06 mol), benzene (toluene, or xylene) (50 mL), and 2—3 drops of boron trifluoride etherate or sulfuric acid was placed in a round-bottom flask fitted with a Dean—Stark distillation head and refluxed until liberation of water ended. Monitoring of the reaction mixture and isolation of the obtained products were carried out similarly to procedure A. The compositions of the reaction products are given in Table 1.

C (for low-basicity liquid and solid amines). Equimolar amounts of β-diketone **1** and an amine were dissolved in methanol and allowed to stand at room temperature until the starting compounds disappeared (TLC monitoring). The solvent was distilled off, and the residue was dissolved in ether and reprecipitated with *n*-hexane. The compositions of reaction products are given in Table 1.

2,4-Diphenyl-6-(trifluoromethyl)pyridine (alternative synthesis). A mixture of 2-amino-4-phenyl-1,1,1-trifluoromethyl-2-buten-4-one (1.5 g, 0.007 mol) and acetophenone (0.84 g, 0.007 mol) were refluxed until the aminovinylketone in the reaction mixture disappeared (TLC-monitoring). Chromatography on a column packed with silica gel (chloroform as the eluent) followed by recrystallization from *n*-hexane gave 2,4-diphenyl-6-(trifluoromethyl)pyridine (0.5 g, 24%), m.p. 850 °C. Found (%): C, 71.77; H, 4.10; N, 4.73; F, 19.20. $C_{18}H_{12}F_3N$. Calculated (%): C, 72.23; H, 4.04; N, 4.68; F, 19.04.

^{1}H NMR (CCl_4), δ: 7.3—8.4 (m, H arom.).

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