TEMPLATE REACTIONS OF FLUORINE-CONTAINING 1,3-DIKETONES WITH ETHYLENEDIAMINE

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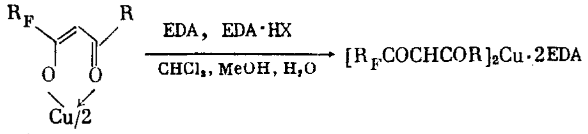
Depending on the nature of the dicarbonyl fragment, the reaction of fluorinated copper(II) bis(1,3-diketonates) with ethylenediamine and its monoprotonated salts under mild conditions gives N,N'-ethylenebis(aminovinyl ketones) and/or 1,4-diazepines. In excess ethylenediamine, copper(II) and nickel(II) N,N'-ethylenebis(aminovinyl ketonates) undergo cyclization to 1,4-diazepines.

Template reactions of acetylacetone and trifluoroacetylacetone (TFAA) with triethylenetetramine give not only 1,3-diketone chelates, but also a 13-membered macrocyclic complex [1]. However, with ethylenediamine (EDA) on Cu^{2+} and Ni^{2+} matrices, unfluorinated 1,3-diketones form chelates of N,N'-ethylenebis(aminovinyl ketones) [1], and TFAA and hexafluoroacetylacetone (HFAA) form only nickel(II) bis(1,3-diketonates) [2]. Higher-degree conversions of metal chelates of fluorine-containing 1,3-diketones and their derivatives with EDA are not known.

In the present paper, we studied the reaction of metal chelates of fluorinated 1,3-diketones (Ia-d) and N,N'-ethylenebis(aminovinyl ketones) (Va), (Vb), and (VIa) with EDA.

It was shown that with excess EDA or monoprotonated salts of EDA in $CHCl_3$, MeOH, and water, compounds (Ia-d) form adducts similar to that described in [3].



(Ia— d) (IIa—d)

$X = Cl, ClO_4$.

$R = Me, R_F = CF_3$ (I a), (IIa), $H(CF_2)_2$ (Ib), (IIb);

$R = Ph, R_F = H(CF_2)_2$ (Ic), (IIc); $R = R_F = CF_3$ (Id), (IId).

The IR spectrum of (IIc), recovered in pure form, indicates that the chelate structure in the adduct ($\nu(C{=}O) = 1620\ cm^{-1}$) is retained [4].

Unlike solutions in MeOH and water, solutions of (IIa-d) in $CHCl_3$ are unstable: during standing (~20°C) or heating, the adducts decompose with the formation of $[Cu(EDA)_2]^{2+}$ and probably ligands, which react with excess EDA under the reaction conditions in various ways (see scheme at top of following page).

The numbers in parentheses correspond to the yields of the products in the presence of EDA salts.

The formation of cyclic compounds (IVa) and (IVd) under such mild conditions was unexpected both in the case of TFAA (there were no data on such cyclization of TFAA with EDA) and in the case of HFAA: a 1,4-diazepine was obtained from HFAA only by sublimation of the stable 2HFAA·EDA salt under vacuum (80-100°C), and heating of this salt in benzene did not result in significant changes of it [3].

However, under these conditions, (Ib) formed only N,N'-ethylenebis(aminovinyl ketone) (IIIb), similarly to the corresponding 1,3-diketone with EDA [5]. Similarly to the reaction

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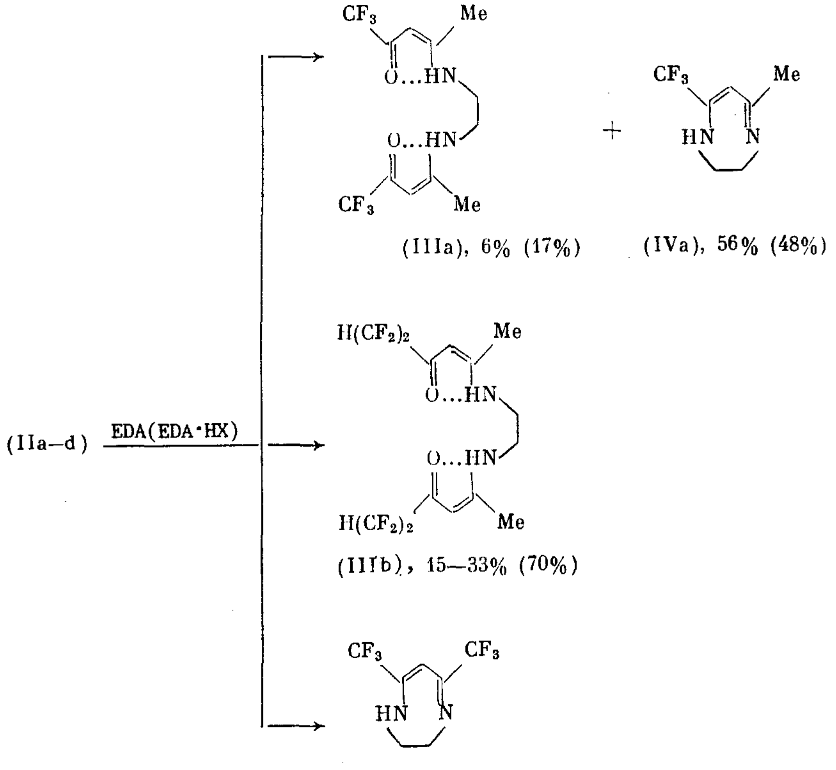


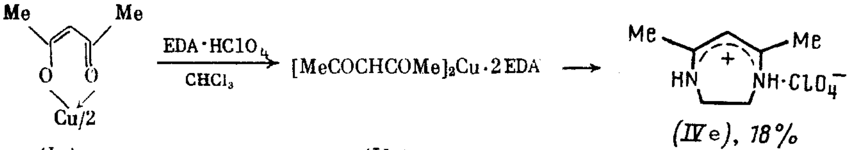
(IIIa), 6% (17%)   (IVa), 56% (48%)

(IIIb), 15–33% (70%)

(IVd), 30% (41%)

of 1,3-diketones with bulky substituents with EDA [6], the reaction of (Ic) did not give a condensation product, but was accompanied by acid cleavage of the diketone fragment, as indicated by the formation of acetophenone. Kinetically, the template effect in these cases is probably leveled off by increasing steric factors.

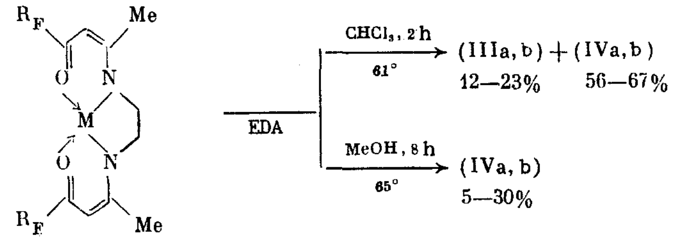
Unlike fluorine-containing copper 1,3-diketonates, acetylacetonate (Ie) formed with excess EDA a difficulty separable mixture of products; when EDA·HClO$_4$ was used, 2,3-dihydro-5,7-bismethyl-1,4-diazepine was recovered as its monohydroperchlorate (IVe)



(Ie)   (IIe)   (IVe), 18%

Heating of (IIa-e) in MeOH or water with EDA did not give significant conversions of chelates.

It was shown that the reactions of copper chelates of N,N'-ethylenebis(aminovinyl ketones) (Va) and (Vb) with excess EDA in CHCl$_3$ give not only [Cu(EDA)$_2$]$^{2+}$, but also N,N'-ethylenebis(aminovinyl ketones) (IIIa) and (IIIb) and 1,4-diazepines (IVa) and (IVb). From the reaction of (Va), (Vb), and (VIa) with EDA in MeOH, we recovered 1,4-diazepines (IVa) and (IVb) and the starting metal chelates (Va), (Vb), and (VIa).



(Va,b) (VIa)

M = Cu, $R_F = CF_3$ (IIIa), (IVa), (Va), H $(CF_2)_2$ (IIIb), (IVb), (Vb); M = Ni, $R_F = CF_3$ (IVa), (VIa).

The MeOH probably retarded the rate of decomposition of (Va), (Vb), and (VIa) as in the case with (Ia-e), possibly because of strong solvation by the solvent and also because of the reversibility of the reaction in the presence of $[Cu(EDA)_2]^{2+}$ (in $CHCl_3$, the insoluble copper chelate of EDA was withdrawn from the reaction sphere).

In the presented reactions of (Va), (Vb), and (VIa), the template role of the transition metal ions is obvious because the formation of 2,3-dihydro-1,4-diazepines is not characteristic of aminovinyl ketones having an amino group at carbon bonded to a hydrocarbon substituent rather than to a fluoroalkyl substituent [7].

EXPERIMENTAL

The IR spectra of the compounds were recorded on a Specord 75 IR spectrometer (white mineral oil). The PMR spectra were measured on a Tesla BS-567 A spectrometer (100 MHz, acetone-d_6, with respect to TMS). Column chromatography was carried out on silica gel L100/250, the eluent was MeOH, and thin-layer chromatography was carried out on Silufol UV-254 plates in MeOH.

Chelates of N,N'-ethylenebis(aminovinyl ketones) (Va), (Vb), and (VIa) were obtained according to [8] and [9].

Reaction of Bis(1,1,1-trifluoro-2,4-pentanedionato)copper (Ia) with Ethylenediamine. We stirred 1.85 g (5 mmoles) of (Ia) in 30 ml of $CHCl_3$ and 6 g (10 mmoles) of anhydrous EDA. The (violet) reaction mixture was boiled for 2 h. As a result of the reaction, two layers formed, i.e., a lower (chloroform) layer, which became colorless, and an upper (aqueous) layer, containing $[Cu(EDA)_2]^{2+}$ and EDA. The upper layer was washed with 20 ml of $CHCl_3$, the extracts were combined, and the solvent was removed. The residue was recrystallized from MeOH. We obtained 0.1 g (6%) of (IIIa) with mp 154-156°C (cf. [8]). IR spectrum (ν, cm^{-1}): 3350, 1580 (NH), 1620 (C=O), 1550 shoulder (C=C). After removal of MeOH and subsequent extraction of the residue with hot hexane, we obtained 1.2 g (56%) of (IVa), mp 116-117°C (cf. [7]). The physicochemical constants corresponded to those given in [7].

Similarly, from 1.85 g (5 mmoles) of (Ia), 6.5 g (25 mmoles) of $EDA \cdot 2HClO_4$, and 1.5 g (25 mmoles) of anhydrous EDA, we obtained 0.3 g (17%) of (IIIa) with mp 154-156°C and 0.8 g (48%) of (IVa) with mp 116-117°C.

Reaction of Bis(1,1,2,2-tetrafluoro-3,5-hexanedionato)copper (Ib) with Ethylenediamine. Method a. We boiled 5 g (11.5 mmoles) of (Ib) and 6.93 g (115 mmoles) of anhydrous EDA for 2 h in $CHCl_3$. The chloroform layer was separated, and after the solvent was removed, the resinous residue was extracted with hot CCl_4. We obtained 1.5 g (33%) of (IIIb) with mp 96-98°C (cf. [5]). The physicochemical constants corresponded to those given in [5].

Method b. The reaction was carried out for 24 h at 20°C. From 5 g (11.5 mmoles) of (Ib) and 6.93 g (115 mmoles) of EDA, we obtained similarly 0.68 g (15%) of (IIIb) with mp 96-98°C.

Method c. From 2.3 g (5 mmoles) of (Ib), 3.5 g (25 mmoles) of $EDA \cdot 2HClO_4$, and 1.5 g (25 mmoles) of anhydrous EDA after boiling in $CHCl_3$ for 2 h, we obtained 3.2 g (70%) of (IIIb) with mp 96-98°C.

Reaction of Bis(1,1,2,2,-tetrafluoro-5-phenyl-3,5-heptanedionato)copper (Ic) with Ethylenediamine. During stirring of 2.8 g (5 mmoles) of (Ic) with 3 g (50 mmoles) of anhydrous EDA in 30 ml of $CHCl_3$, we obtained (IIc) in the form of a pink precipitate. The precipitate was filtered, washed with 30 ml of water to remove $[Cu(EDA)_2]^{2+}$ and EDA, dried under vacuum, and washed with 20 ml of benzene. We obtained 1.8 g (53%) of (IIc) with decomposition temperature 148°C. IR spectrum (ν, cm^{-1}): 1580, 3240, 3110 (NH), 1620 (C=O). During heating for 2 h, the pink color disappeared, and the chloroform layer became colorless. After separation of the lower layer and removal of $CHCl_3$, from the residue after column chromatography we obtained 0.4 g (67%) of acetophenone, which was identified in comparison with a known sample according to IR spectra and thin-layer chromatography (R_f = 0.75).

Reaction of Bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)copper (Id) with Ethylenediamine. Method a. A mixture of 2.4 g (5 mmoles) of (Id) in 30 ml of $CHCl_3$ and 3 g (50 mmoles) of anhydrous EDA was heated for 2 h. After separation of the lower layer, removal of $CHCl_3$, and recrystallization from hexane (two times), we obtained 0.7 g (30%) of (IVd) with mp 109-110°C. The physicochemical constants corresponded to those given in [3].

Method b. Similarly, from 2.4 g (5 mmoles) of (Id), 2.7 g (45 mmoles) of anhydrous EDA, and 1.3 g (5 mmoles) of EDA·$2HClO_4$, we obtained 0.95 g (41%) of (IVd) with mp 109-110°C.

Reaction of Bis(2,4-pentanedionato)copper (Ie) with Ethylenediamine. We heated a mixture of 1.3 g (5 mmoles) of (Ie), 2.7 g (45 mmoles) of anhydrous EDA, and 1.3 g (5 mmoles) of EDA·$2HClO_4$, separated the $CHCl_3$ layer, and removed the solvent. Column chromatography of the residue gave 0.4 g (18%) of (IVe) with mp 138-140°C (cf. [10]) and IR spectrum (ν, cm^{-1}): 1610, 1595 ($C{=}N^+$, $C{=}C$), 3100, 3320, 1530 (NH), 620, 1050 (ClO_4). PMR spectrum (δ, ppm): 5.12 s (CH, 1H), 3.77 m (CH_2, 4H), 2.29 s (Me, 6H), 8.86 br. s (NH, 2H).

Reaction of N,N'-Ethylenebis(1,1,1-trifluoro-4-amino-2-pentenonato)copper (Va) with Ethylenediamine. Method a. We boiled a mixture of 1.98 g (5 mmoles) of (Va) and 1.5 g (25 mmoles) of anhydrous EDA in 20 ml of $CHCl_3$ for 2 h. We separated the lower layer and washed the upper layer (mixture of $[Cu(EDA)_2]^{2+}$, EDA, and water) with $CHCl_3$ (2 × 10 ml). We combined the extracts, removed $CHCl_3$, and carried out recrystallization from MeOH. We obtained 0.2 g (12%) of (IIIa) with mp 154-156°C. The data of elemental analysis corresponded to the calculated values. After addition of water to the filtrate, we obtained 1.0 g (56%) of (IVa) with mp 115-117°C. The physicochemical constants corresponded to those given in [7].

Method b. We boiled a mixture of 1.98 g (5 mmoles) of (Va), 1.5 g (25 mmoles) of anhydrous EDA, and 20 ml of MeOH in an Ar atmosphere for 8 h. After cooling, we added 30 ml of water and filtered 1.2 g (60%) of the starting (Va) with sublimation temperature 220°C (cf. [8]). We identified it according to the mp of a sample mixed with a known sample and according to IR spectra. The filtrate was evaporated and washed with 10 ml of water. We obtained 0.27 g (15%) of (IVa) with mp 115-117°C. The physicochemical constants corresponded to those given in [7].

Reaction of N,N'-Ethylenebis(1,1,2,2-tetrafluoro-5-amino-3-hexenonato)copper (Vb) with Ethylenediamine. Method a. We boiled a mixture of 2.3 g (5 mmoles) of (Vb), 1.5 g (25 mmoles) of anhydrous EDA, and 20 ml of $CHCl_3$ for 2 h. After removal of $CHCl_3$, the residue was dissolved in the minimum amount of MeOH and precipitated with water. We obtained 0.46 g (23%) of (IIIb) with mp 96-98°C. The physicochemical constants corresponded to those given in [5]. The filtrate was evaporated to dryness. After column chromatography, we obtained 1.4 g (67%) of (IVb) (oil). IR spectrum (ν, cm^{-1}, in a thin layer): 3100, 3240, 1535 (NH), 1610, 1570 ($C{=}N$, $C{=}C$). PMR spectrum (δ, ppm): 5.08 s (CH, 1H), 3.88 m (CH_2, 2H), 3.38 m (CH_2, 2H), 2.06 s (Me, 3H), 6.59 t. t ($H(CF)_2$, 1H, J = 53.29; 5.86 Hz), 5.04 br. s (NH, 1H).

Method b. A mixture of 2.3 g (5 mmoles) of (Vb) and 1.5 g (25 mmoles) of anhydrous EDA in 20 ml of MeOH was boiled in an Ar atmosphere for 8 h. After cooling, we added 30 ml of water and filtered 1.45 g (63%) of the starting (Vb) with mp 239-240°C. IR spectrum (ν, cm^{-1}): 1620 ($C{=}O$), 1525 ($C{=}C$). The filtrate was evaporated, and the resin was washed with water and dried under vacuum. After column chromatography, we obtained 0.12 g (5%) of (IVb) (oil), which was identified according to IR spectra in comparison with a known sample.

Reaction of N,N'-Ethylenebis(1,1,1-trifluoro-4-amino-2-pentenonato)nickel (VIa) with Ethylenediamine. We boiled a mixture of 1.94 g (5 mmoles) of (VIa) and 1.5 g (25 mmoles) of anhydrous EDA in 20 ml of MeOH in an Ar atmosphere for 8 h. We evaporated the MeOH to the minimum amount and precipitated with water 0.53 g (30%) of (IVa) with mp 116-117°C. The physicochemical constants corresponded to those given in [7]. The filtrate was evaporated to dryness, and after column chromatography of the residue, we obtained 0.68 g (35%) of the starting (VIa) with mp 270-271°C (cf. [9]).

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TROPYLATION AND PYRYLATION OF SALTS OF ALIPHATIC MONO-, DI-, AND TRINITRO COMPOUNDS

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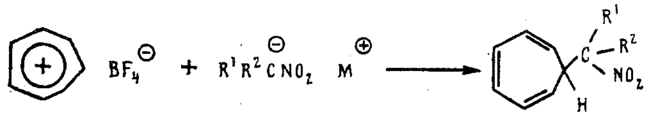
547.517-38

We have studied the reactions of salts of nitroalkanes with tropylium and 2,6-diphenylpyrylium salts leading to products of C-tropylation and C-pyrylation of the corresponding anions. The only exception is the salt of cyanodinitromethane, which is not tropylated. Splitting off of a HNO_2 molecule from the products of tropylation of nitroalkane anions to prepare nitroheptafulvenes was unsuccessful.

Reactions for the formation of new C—C bonds are the basis of synthetic organic chemistry. It is known that reactions of salts of nitroaliphatic compounds with activated aromatic and heteroaromatic compounds make it possible to prepare nitroalkylation products of aromatic substrates. In particular, reactions of pyridinium [1-4], quinolinium [5], acridinium [6], and some other azinium salts [7-9] with anions of various nitroalkanes have been well investigated. At the same time, such activated aromatic substrates as tropylium and pyrylium salts have practically not been studied in that respect. Known is the example of tropylation of 2-nitropropane [10], and also the reaction of 2,4,6-triphenylpyrylium salt with a salt of nitromethane, which yields 2,4,6-triphenylnitrobenzene through the ANRORC process [11].

We have studied the reaction of salts of dinitroaliphatic compounds, nitromethane, and trinitromethane with tropylium and 2,6-diphenylpyrylium salts with the purpose of examining the direction of tropylation and pyrylation in dependence of the structure of the anion.

It was found that water is the best medium to carry out the reaction. Mixing aqueous solutions of nitroalkane salts with aqueous solutions of tropylium fluoborate at ~20°C leads to momentary formation of a single reaction product that precipitates or separates out as an oil. The exception is nitromethane, of which the sodium salt on reaction with tropylium fluoborate in alcohol gives a mixture of two products (alcohol is taken instead of water because of the high basicity of the nitromethyl anion: $pK_a = 10.6$ [12]). The PMR, IR, and mass spectra, and also data of elemental analyses, show that all the compounds obtained, with the exception of (XI), are C-tropylation products of nitroalkane anions (Table 1):



(I) (II)-(VI)

$R^1 = H$, $R^2 = NO_2$ (II), $R^1 = R^2 = NO_2$ (III), $R^1 = NO_2$, $R^2 = COOEt$ (IV), $R^1 = NO_2$, $R^2 = 1/2(—CH_2—O—CH_2—O—CH_2—)$ (V), $R^1 = NO_2$, $R^2 = CH_3$ (VI).

During the study we found different behavior of anions of nitro- and dinitromethane, which can give mono- and ditropylated products: the anion of dinitromethane gives a single

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