Reactions of regioisomeric fluoroalkyl-containing β-aminovinyl ketones with hydrazines

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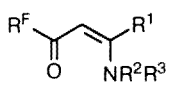
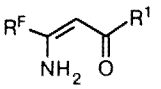
Fluoroalkyl β-alkyl-β-aminovinyl ketones react with hydrazine hydrate to give the respective pyrazoles, and with phenylhydrazine they form a mixture of pyrazoles and 5-hydroxy-Δ^2-pyrazolines. Alkyl(aryl) β-fluoroalkyl-β-aminovinylketones do not react with the hydrazines mentioned above. With 2,4-dinitrophenylhydrazine, both types of fluoroalkyl-containing β-aminovinyl ketones give only hydrazones of the corresponding methyl alkyl(aryl) ketones.

Key words: regioisomeric fluoroalkyl β-aminovinyl ketones; pyrazoles; 5-hydroxy-Δ^2-pyrazolines.

We have shown previously[1] that regioisomeric fluoroalkyl β-aminovinyl ketones (AVK) (**1** and **2**) give functionalized Δ^2-isoxazolines in the reaction with hydroxylamine. In this work, the reactions of **1** and **2** with hydrazines were studied. Regioisomeric (fluoroalkyl)pyrazoles and, by analogy with literature data,[1–5] substituted Δ^2-pyrazolines would be expected as the result of these interactions.



1a–d



2a–d

1a: $R^F = CF_3$, R^1 = Me, R^2 = H, R^3 = Ph

1b: $R^F = C_3F_7$, R^1 = Bu^t, $R^2 = R^3$ = H

1c: $R^F = H(CF_2)_2$, R^1 = Et, $R^2 = R^3$ = H

1d: $R^F = H(CF_2)_2$, R^1 = Me, R^2 = H, R^3 = Ph

2a: $R^F = CF_3$, R^1 = Ph

2b: $R^F = HCF_2$, R^1 = Ph

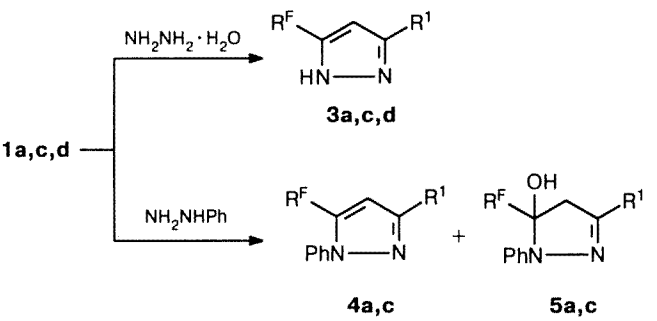
2c: $R^F = C_3F_7$, R^1 = Bu^t

2d: $R^F = H(CF_2)_2$, R^1 = Me

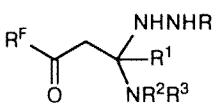
Compounds **1** form the corresponding pyrazoles **3** upon reflux with the equimolar amount of hydrazine hydrate in MeOH or EtOH, irrespective of the type of R^F and R^1, and with phenylhydrazine they give complex mixtures of products, from which *N*-phenylpyrazoles (**4**) and 5-hydroxy-Δ^2-pyrazolines (**5**) were isolated (Scheme 1).

However, AVK **2** do not react under similar conditions with hydrazine hydrate and phenylhydrazine.

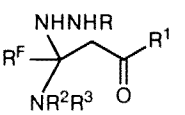
Scheme 1



The differences in the reactivity of AVK **1** and **2** with respect to hydrazines can be explaned in the following manner. In the first stage of the reaction, hydrazines give reversibly addition products on the enamine electrophilic center: **A1** and **A2**. However due to the direct influence of R^F the nucleophilicity of the NHR group in adduct **A2** is reduced and is insufficient for ring closure.



A1



A2

When regioisomeric AVK **1** and **2** react with 2,4-dinitrophenylhydrazine (DNPH), the traditional reagent for the carbonyl group, they give only the corresponding hydrazones of methyl alkyl(aryl) ketones (**6**) (Scheme 2).

The formation of hydrazones **6** can be explained by hydrolysis of AVK **1** and **2** under reaction conditions (compare with known data[6]). The capture of the result-

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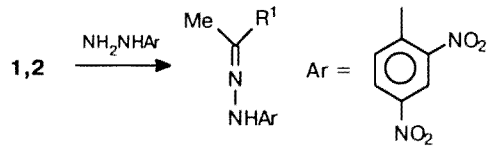
1066-5285/96/4512-2868 $15.00

Scheme 2



6

ing methyl alkyl(aryl) ketones as hydrazones **6** leads to the shift of the equilibrium toward the latter. Similar transformations likely take place in the reaction of AVK **1** and **2** with hydrazine hydrate and phenylhydrazine. It is this fact that can account for moderate yields of pyrazoles **3** and **4** and incomplete recovery of AVK **1** and **2** from the reaction mixture. However, only when DNPH was used is one of the products of the cleavage readily isolated as hydrazone.

Experimental

Regioisomeric AVK **1** and **2** were obtained according to the known procedures[7,8].

IR spectra were recorded on Specord 75-IR instrument as dispersions in Vaseline oil, ^{1}H NMR spectra were recorded on a Tesla BS-567A spectrometer ($CDCl_3$, Me_4Si is the internal standard). TLC was performed on Silufol UV-254 plates using $CHCl_3$ as the eluent. For visualization of substances, aqueous solutions of cupric acetate and $KMnO_4$ were used. Reaction mixtures were chromatographed on columns with Silica gel L 40/100 in $CHCl_3$.

The data of elemental analysis for all compounds obtained agreed with the structures presented.

Reactions of AVK 1 and 2 with hydrazine hydrate. Catalytic amounts of $BF_3 \cdot Et_2O$ were added to a solution of equimolar amounts of AVK and hydrazine hydrate in MeOH or EtOH, and the mixture was refluxed (10—31 h), and the course of the reaction was monitored by TLC. After completion of the reaction, the solvent was evaporated, and the residue was recrystallized from *n*-hexane.

From 0.5 g (2.3 mmol) of AVK **1a** and 0.11 g (2.3 mmol) of hydrazine hydrate, 0.17 g (52%) of 3-methyl-5-trifluoromethylpyrazole **3a** was obtained, m.p. 87—88 °C. IR, ν/cm^{-1}: 1590 (C=N). ^{1}H NMR, δ: 2.28 (s, 3 H, Me); 6.27 (s, 1 H, =CH—); 12.20 (br.s,* 1 H, NH).

From 0.5 g (3 mmol) of AVK **1c** and 0.15 g (3 mmol) of hydrazine hydrate, 0.33 g of 5-ethyl-3-(1,1,2,2-tetrafluoroethyl)pyrazole **3c** was obtained, m.p. 94—95 °C. IR, ν/cm^{-1}: 1590 (C=N). ^{1}H NMR, δ: 1.22 (t, 3 H, $\underline{Me}CH_2$, J = 7.51 Hz); 2.64 (q, 2 H, $MeC\underline{H}_2$, J = 7.51 Hz); 5.96 (tt, 1 H, $\underline{H}CF_2CF_2$, ^2J = 53.76 Hz, ^3J = 3.75 Hz); 6.29 (s, 1 H, =CH—); 11.38 (br.s,* 1 H, NH).

From 0.8 g (3 mmol) of AVK **1d** and 0.15 g (3 mmol) of hydrazine hydrate, 0.22 g (42%) of 3-methyl-5-(1,1,2,2-tetrafluoroethyl)pyrazole **3d** was obtained, m.p. 105—106 °C. IR, ν/cm^{-1}: 1590 (C=N). ^{1}H NMR, δ: 2.28 (s, 3 H, Me); 5.96 (tt, 1 H, $\underline{H}CF_2CF_2$, ^2J = 53.76 Hz, ^3J = 3.52 Hz); 6.27 (s, 1 H, =CH—); 12.20 (br.s,* 1 H, NH).

From the reactions of AVK **2a**, **2b**, and **2d** with hydrazine hydrate, only the original AVK were recovered (60—65% of the amount taken for the reaction), which were identified with the authentic samples of AVK by TLC and melting points.

Reactions of AVK 1 and 2 with phenylhydrazine. Equimolar amounts of AVK and phenylhydrazine were refluxed in MeOH or EtOH with TLC monitoring. In all cases, complex mixtures of products were obtained, which were separated by column chromatography.

From 0.9 g (3.9 mmol) of AVK **1a** and 0.42 g (3.9 mmol) of phenylhydrazine, 0.15 g (17%) of 3-methyl-1-phenyl-5-trifluoromethylpyrazole **4a** as a brown oil and 0.25 g (26%) of 5-hydroxy-3-methyl-1-phenyl-5-trifluoromethyl-Δ^2-pyrazoline **5a** were obtained. **4a**. IR, ν/cm^{-1}: 1590 (C=N). ^{1}H NMR, δ: 2.31 (s, 3 H, Me); 6.56 (s, 1 H, =CH—); 7.32—7.49 (m, 5 H, Ph). **5a**. M.p. 134—135 °C. IR, ν/cm^{-1}: 1590 (C=N); 3070—3500 (O—H). ^{1}H NMR, δ: 2.01 (s, 3 H, Me); 2.71, 3.41 (2 H, CH_2, AB-spectrum, $^2J_{AB}$ = 17.6 Hz); 3.19 (s, 1 H, OH); 7.16—7.54 (m, 5 H, Ph).

From 0.5 g (2.5 mmol) of AVK **1c** and 0.27 g (2.5 mmol) of phenylhydrazine, 0.35 g of white crystals with m.p. 87—88 °C was obtained. According to TLC, it was a mixture of two compounds, whose separation was unsuccessful. In the ^{1}H NMR spectrum, two sets of signals were observed, which were assigned by comparison with the spectra of the starting AVK **1c**, pyrazoles **3a,c,d**, and 5-hydroxy-Δ^2-pyrazoline **5a**:

a. Signals of pyrazole **4c**, δ: 1.30 (t, 3 H, $\underline{Me}CH_2$, J =7.51 Hz); 2.72 (q, 2 H, $C\underline{H}_2Me$, ^3J = 7.51 Hz); 5.76 (tt, 1 H, $\underline{H}CF_2CF_2$, ^2J = 43.52 Hz; ^3J = 3.52 Hz); 6.58 (s, 1 H, =CH—); 7.32—7.76 (m, 5 H, Ph).

b. Signals of 3-ethyl-5-hydroxy-1-phenyl-5-(1,1,2,2-tetrafluoroethyl)-Δ^2-pyrazoline **(5c)**, δ: 1.21 (t, 3 H, $\underline{Me}CH_2$, J = 7.28 Hz); 2.72 (q, 2 H, $C\underline{H}_2Me$, ^3J = 7.28 Hz); 3.19 (s, 1 H, OH); 2.99, 3.38 (2 H, CH_2, AB-spectrum, $^2J_{AB}$ = 18.8 Hz); 5.11 (tt, 1 H, $\underline{H}CF_2CF_2$, ^2J = 52.82 Hz, ^3J = 5.86 Hz); 7.32—7.76 (m, 5 H, Ph).

The ratio **4c** : **5c** (1 : 2) was determined from the ratio of the integral intensity of the signals.

From 0.5 g (2.5 mmol) of AVK **2b** and 0.27 g (2.5 mmol) of phenylhydrazine, 0.3 g (60%) of the starting AVK **2b** was recovered, m.p. 54 °C; the melting point of a mixture with the original AVK did not show depression. The IR-spectra of both samples were identical.

Reactions of AVK 1 and 2 with 2,4-dinitrophenylhydrazine. To a mixture of equimolar amounts of AVK and DNPH, 20 mL of EtOH and catalytic amounts of $BF_3 \cdot Et_2O$ were added, and the mixture was refluxed. The course of the reaction was monitored by TLC. After cooling the mixture, the precipitate was filtered off and recrystallized from EtOH.

From 0.9 g (3 mmol) of AVK **2c** and 0.6 g (3 mmol) of DNPH, 0.55 g (66%) of yellow crystals with m.p. 122 °C was obtained; the melting point of a mixture with pinacoline 2,4-dinitrophenylhydrazones did not show depression.

From 0.25 g (1 mmol) of AVK **1a** and 0.05 g (1 mmol) of DNPH, 0.18 g (75%) of yellow crystals with m.p. 125 °C was obtained; the melting point of a mixture with an authentic sample of acetone 2,4-dinitrophenylhydrazones did not show depression.

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References

1. O. A. Kuznetsova, V. I. Filyakova, and K. I. Pashkevich, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 1306 [*Russ. Chem. Bull.*, 1996, **45**, 1245 (Engl. Transl.)].
2. K. I. Pashkevich, V. I. Saloutin, and I. Ya. Postovskii, *Uspekhi Khimii*, 1981, **50**, 325 [*Russ. Chem. Rev.*, 1981, **50** (Engl. Transl.)].

* Signal disappears upon addition of CD_3COOD.

3. J.-L. Peqlion, R.-E. Pastor, and A.-R. Cambon, *Bull. Soc. Chim. Fr.*, 1980, II-309.
4. K. N. Zelenin, *Org. Prep. Proced. Int.*, 1995, **27**, 519.
5. K. N. Zelenin, V. V. Alekseyev, A. R. Tygysheva, and S. I. Jakimovitch, *Tetrahedron*, 1995, **51**, 11251.
6. L. N. Bazhenova, V. I. Filyakova, V. E. Kirichenko, and K. I. Pashkevich, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1991, 664 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1991, **40**, 581 (Engl. Transl.)].
7. K. I. Pashkevich, V. I. Filyakova, Yu. N. Sheinker, O. S. Anisimova, and I. Ya. Postovskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1979, 2087 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1979, **38** (Engl. Transl.)].
8. K. I. Pashkevich and A. Ya. Ajzikovich, *Dokl. Akad. Nauk SSSR*, 1979, **244**, 618 [*Dokl. Chem.*, 1979, **244** (Engl. Transl.)].

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Polyferroorganosiloxanes as catalysts of oxidation processes

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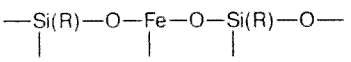
Polyferroorganosiloxanes were studied as catalysts for homogeneous oxidation of alkanes by hydrogen peroxide under mild conditions. In the oxidation of cyclohexane the catalysts are characterized by high efficiency (conversion of hydrogen peroxide is 25%) and stability (up to 80 cycles per g-at. Fe). The main product of the oxidation in the presence of 2,4,6-tri-*tert*-butylphenol is cyclohexanol (up to 35% per H_2O_2).

Key words: polyferroorganosiloxanes, catalysts, oxidation of hydrocarbons, activation of hydrogen peroxide.

The known iron-containing catalysts of homogeneous oxidation of organic compounds by hydrogen peroxide, which are mono- or polynuclear complexes of iron ions, exist in homogeneous catalytic media as individual ions of di- and triatomic clusters.[1—4] Iron-containing catalysts of a new type, in which Fe atoms exist in the covalently linked form in the siloxane chain, were studied in this work. The main structural fragment of polyferrophenylsiloxanes (PFPS) is the following:



(R is phenyl).

The procedures of synthesis developed make it possible to control the content of Fe in PFPS. When the content of Fe increases, Fe—O—Fe metalloxane fragments appear in the polymer structure. The synthesis and structure of PFPS have been described previously.[5]

We found that PFPS are capable of catalyzing the alkane oxidation by hydrogen peroxide in the presence of $HClO_4$. The oxidation of cyclohexane results in the formation of alkylhydroperoxide and cyclohexanol, the oxidation of methane gives methanol, and styrene oxidizes to benzaldehyde and small amount of styrene oxide (Table 1).

The reaction is highly efficient: conversion of hydrogen peroxide calculated from the yield of the products of oxidation is equal to 25% (in the case of common Fe-catalysts, the efficiency of oxidation of cyclohexane by hydrogen peroxide is not greater than 8—10%). Another specific feature of PFPS is the stability of the catalyst under the reaction conditions: the number of working cycles (calculated per g-at. Fe) until the inactivation of the catalyst is equal to 70—80.

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