Russian Journal of General Chemistry, Vol. 72, No. 6, 2002, pp. 899–900. Translated from Zhurnal Obshchei Khimii, Vol. 72, No. 6, 2002, pp. 962–963.
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Gas-Chromatographic Study of Hydrazine Reaction with Metal β-Diketonates

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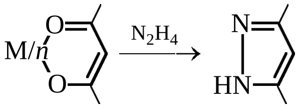
Received September 22, 2000

Abstract — When treated with hydrazine, metal β-diketonates undergo decomposition to form the corresponding pyrazoles, irrespective of the kinetic stability of the chelates. With substituted metal chelates, the main reaction products are pyrazoles bearing in position *4* the γ-substituent of the compex. Other products are formed when the substituent has centers sensitive to nucleophilic substitution and/or elimination. The reaction can be used for structural assessment of the starting β-diketonate.

Pyrazoles are most commonly prepared by reaction of β-diketones with hydrazine [1]. In the last few years a great many metal chelates have been prepared, whose ligands have never been isolated and sometimes are impossible to isolate [2]. This prompted us to study the possibility of preparing pyrazoles directly from metal chelates and, in particular, from γ-substituted metal complexes. The reactions were accomplished by heating the complexes with excess hydrazine in alcohol. The reaction completion was established by TLC by the disappearance of the spot of the starting chelate (with chromium and cobalt complexes) or by the discoloration of the reaction mixture. The reaction products were analyzed by GC–MS.

The reactions with unsubstituted complexes were studied using as examples chromium(III), cobalt(III), aluminum(III), iron(III), and copper(II) acetylacetonates. The reactions all gave 3,5-dimethylpyrazole as a single reaction product.

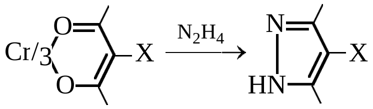


I–V **VI**

M = Cr (**I**), Co (**II**), Fe (**III**), Al (**IV**), *n* = 3; M = Cu (**V**), *n* = 2.

The reactions are complete within a few minutes and are equally fast both with the kinetically labile copper complex and the stable chromium complex. Chromium(III) formylacetonate reacts in a similar way to give 3-methylpyrazole.

The reactions between substituted metal complexes and hydrazine were studied using as examples substituted chromium(III) acetylacetonates **VII**–**XIII**. Irrespective of the nature of substituent X, the major reaction product was 3,5-dimethylpyrazole bearing substituent X in position *4*.



VII–XIII **XIV–XX**

X = Cl (**VII, XIV**), Br (**VIII, XV**), NO_2 (**IX, XVI**), SPh (**X, XVII**), SCH_2CH_2Cl (**XI, XVIII**), $SP(O)(OEt)_2$ (**XII, XIX**), phthalimido (**XIII, XX**).

Subsitutient at the central carbon atom of the chelate ring exerts appreciable rate effect on the decomposition of the complexes. The reactions with chloro-, bromo-, nitro-, thiophenyl, and thiochloroethyl-substituted chelates are as fast as with the unsubstituted complex and are complete within a few minutes. Complex **XII** decomposes within 10 h, while compound **XIII** does not decompose completely even after 30-h refluxing.

The chromatograms of the decomposition products of halo-substituted chromium(III) acetylacetonates contain a large peak of 4-chloro(bromo)-2,5-dimethylpyrazole and a minor peak of 2,5-dimethylpyrazole, implying elimination of the substituent under the action of hydrazine. The peak of pyrazole **VI** comprises no more than 20%, by the total ion current, of the peak of pyrazole **XIV** or **XV**.

The chromatogram of the decomposition products of the phtalimido-substituted complex contains, along with the peak of pyrazole **XX**, a large peak assigned, by the mass spectrum and the retention time, to Cr(acacH)$_3$. In the thin-layer chromatogram of the reaction mixture this compound was not found. Therefore, it was assumed that the latter product is formed by pyrolysis of undecomposed complex **XIII** in the injector of the gas chromatograph.

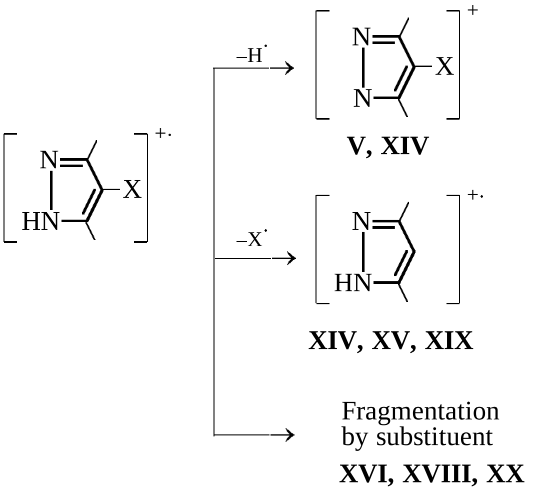
Among minor decomposition products of Cr[acacSP(O)(OEt)$_2$]$_3$ we identified PirzS–Spirz (Pirz is 2,5-dimethylpyrazole) and PirzSEt. The total intensity of these two peaks was 10% of the intensity of the peak of PirzSP(O)(OEt)$_2$.

The most intricate decomposition pattern is characteristic of Cr(acacSCH$_2$CH$_2$Cl)$_3$. The chromatogram contains two peaks of equal intensity, assigned to PirzSCH$_2$CH$_2$Cl and PirzSCH$_2$CH$_2$OCH$_2$CH$_3$. In addition, two less intense peak are present, whose mass spectra correspond to PirzS–SPirz and PirzSH. The peak of PirzSCH$_2$CH$_2$Cl comprises 33–35% of the total ion current. Probably, such an intricate reaction pattern is explained by occurrence of substitution and elimination reactions involving the chlorine atom.

Attempted reaction of hydrazine with metal chelates in DMF or DMSO failed. The complexes undergo decomposition even upon prolonged heating. Replacement of ethanol by methanol has no effect of the reaction pattern. These finding suggest that solvent is directly involved in reaction. Probably, alcohol reversibly expels ligands from the coordination sphere, thus making them available for reaction with hydrazine. Such reactions have been described for iron and chromium complexes [3].

The mass spectra of the pyrazoles obtained all contain molecular ion peaks (100–80% of the base peak). The principal fragmentation pathways are shown below.

The reaction we described here can be used for structural assessment of metal chelates, since the low volatility of these compounds, lability under chromatographic conditions, and paramagnetic nature makes them difficult to study by traditional mathods.



X = SH (**XIV, XV, XIX**), S (**XVI, XVIII, XX**).

EXPERIMENTAL

Chelate, 20–30 mg, and 200 mg of hydrazine were heated under reflux in 2 ml of alcohol until the complex decomposed. The reaction mixture was diluted with 20 ml of water, and the reaction product was extracted with 1 ml of chloroform. The organic extract was analyzed on a gas chromatograph with a mass-selective detector under the following conditions: HP-5890 (series II)/5972 GC–MS system (Hewlett–Packard), injection volume 1 μl, split 1:20, carrier gas helium (0.7 ml/min), scan range *m*/*z* 50–410, injector temperature 280°C, detector temperature 280°C, temperature program 50 to 280°C at 20 deg/min, and ionizing energy 70 eV.

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