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Abstract

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Acyloxy Derivatives of Cobalt, Nickel, and Manganese

In recent years a large number of works have been published in the field of studying the properties of acyloxy derivatives of various metals. The methods used for obtaining acyloxy derivatives of metals with higher monobasic acids—saponification of fats with metal oxides or hydroxides, an exchange reaction of alkali soaps with metal salts, or the interaction of carboxylic acids with metal salts—usually lead to the preparation of mixtures of basic metal salts, sometimes of inconstant composition. Individual works indicate the possibility of obtaining neutral salts for some transition metals. Thus, for example, by the interaction of dry $CoCl_2$, a fatty monobasic acid, and ammonia in absolute alcohol, diacyloxy derivatives of cobalt with higher acids were obtained ([1]), and by the action of sodium alcoholate and a fatty acid on a dry cobalt salt, diacyloxy derivatives of cobalt with lower acids were obtained ([2]).

There is a report on the formation of tetraacyloxyzirconium ([3]) upon heating zirconium tetrachloride for many hours with higher acids in benzene until hydrogen chloride is completely removed. An analogous method is recommended for obtaining acyloxy derivatives of manganese ([4]) with both monobasic and dibasic acids. When anhydrous $MnCl_2$ is heated with an excess of acid to a temperature 10-15° above the melting point of the corresponding acid, diacyl-oxy derivatives of manganese are obtained. After removal of hydrogen chloride, the product, washed free of excess acid, gives a satisfactory analysis for manganese content. This method is applicable only to fusible acids. Probably, owing to the necessity of heating for many hours at high temperature, side products are formed in the case of high-melting acids; the manganese compounds described have the appearance of black powders.

Table 1

Experiment No.	Starting reagents: acetylacetonates	Starting reagents: fatty acids	Molar ratio of reagents	Medium	Yield, %	Composition of the compound obtained
1	Zirconium tetraacetylacetonate	Stearic	1 : 4	Benzene	~100	$(C_{18}H_{35}O_2)_4Zr$
2	Same	Palmitic	1 : 4	Benzene	~100	$(C_{16}H_{31}O_2)_4Zr$
3	» »	Lauric	1 : 4	Benzene	~100	$(C_{12}H_{23}O_2)_4Zr$
4	» »	ω-Chloroenanthic	1 : 4	Benzene	~100	$(C_{11}H_{20}O_2Cl)_4Zr$
5	» »	Enanthic		Enanthic acid	~100	$(C_7H_{13}O_2)_4Zr$
6	» »	Caproic		Caproic acid	~100	$(C_6H_{11}O_2)_4Zr$
7	» »	Valeric		Valeric acid	~100	$(C_5H_9O_2)_4Zr$
8	Cobalt triacetylacetonate	Stearic	1 : 3	Xylene	55	$(C_{18}H_{35}O_2)_2Co$
9	Cobalt diacetylacetonate	Stearic	1 : 2	Xylene	52	$(C_{18}H_{35}O_2)_2Co$
10	Manganese triacetylacetonate	Stearic	1 : 3	Xylene	90	$(C_{18}H_{35}O_2)_2Mn$
11	Same	Palmitic	1 : 3	Xylene	67	$(C_{16}H_{31}O_2)_2Mn$

Table 2

Experiment No.	Starting reagents: acetylacetonates	Starting reagents: acids	Molar ratio of reagents	Medium	Yield, %	Composition of the compound obtained (I)	Composition of the final product* (II)	Found, % C	Found, % H	Found, % N	Calculated, % C	Calculated, % H	Calculated, % N
1	Cobalt diacetylacetonate	Azelaic	1 : 1	Benzene	64	$Co(C_9H_{14}O_4)$	Same	43.83	6.38	5.94	44.09	5.71	
2	Manganese triacetylacetonate	Azelaic	1 : 2	Benzene	95	$[Mn(C_9H_{14}O_4)]_5C_6H_6$	Same	47.35	6.34	6.30	47.73	5.93	
3	Cobalt diacetylacetonate	Adipic	1 : 1	Tetrahydrofuran	79	$[Co(C_6H_8O_4)]_4 \cdot C_4H_8O$	Same	38.42	5.38	4.62	38.02	4.52	
4	Same	Fumaric	1 : 2	Tetrahydrofuran	78	$Co(C_4H_2O_4) \cdot C_4H_8O$	Same	39.14	3.92	4.09	39.19	4.08	
5	Manganese triacetylacetonate	Fumaric	1 : 3	Tetrahydrofuran	48	$[Mn(C_4H_2O_4)]_5 \cdot C_4H_8O$	Same	31.37	2.05	4.01	31.43	1.98	
6	Cobalt diacetylacetonate	Terephthalic	1 : 1	Pyridine	45	$Co(C_8H_4O_4) \cdot \frac{1}{4}C_5H_5N$	$Co(C_8H_4O_4) \cdot C_5H_5N$	63.11	4.23	4.34	63.49	4.24	4.23
7	Same	Cinnamic	1 : 2	Benzene	72	$Co(C_9H_7O_2)_2 \cdot 2C_5H_5N$	Same	65.27	4.95	5.33	65.77	4.96	5.51

Experiment No.	Starting reagents: acetylacetonates	Starting reagents: acids	Molar ratio of reagents	Medium	Yield, %	Composition of the compound obtained (I)	Composition of the final product* (II)	Found, % C	Found, % H	Found, % N	Calculated, % C	Calculated, % H	Calculated, % N
8	Nickel diacetylacetonate	Cinnamic	1 : 2	Benzene	45	$Ni(C_9H_7O_2)_2$	Same	61.15	61.48	4.25	61.24	63.96	4.01
9	Manganese triacetylacetonate	Cinnamic	1 : 3	Benzene	84	$Mn(C_9H_7O_2)_2$		61.81	4.16				
10	Cobalt diacetylacetonate	Mandelic	1 : 2	Benzene	53	$Co(C_8H_7O_3)_2$	$Co(C_8H_7O_3)_2 \cdot 2C_5H_5N$	53.78	*30.90**	55.65***	53.20	30.87	4.52

* The final product was obtained after additional drying in a high vacuum or after reprecipitation followed by drying.
** Analysis of the crude product (I).
*** Analysis of the final product (II).

For the synthesis of acyloxy derivatives of molybdenum with aromatic and fatty monobasic acids, Wilkinson[5,6] used molybdenum hexacarbonyl as the starting material.

Three of the authors of this article described[7] a method for the synthesis of acyloxy derivatives of zirconium, manganese, and cobalt, based on an exchange reaction between metal acetylacetonates and monobasic fatty acids.

The results obtained in the cited work are given in Table 1.

In the present work, the possibility of applying the proposed method to the acetylacetonates of cobalt, nickel, and manganese was studied using dibasic fatty acids (saturated and unsaturated) as well as aromatic acids. Among the dibasic acids, azelaic, adipic, fumaric, and terephthalic acids were investigated.

Among the monobasic acids containing a benzene ring, cinnamic and mandelic acids were investigated.

The interaction of these acids was carried out with cobalt and nickel diacetylacetonates, as well as with manganese triacetylacetonate, in a nitrogen atmosphere under heating in vacuum to distill off volatile products.

The end of the reaction is indicated by a negative test for acetylacetonate groups in the substances formed. Usually the reaction lasts from 3 to 9 h. In most cases, purification of the compounds obtained was carried out by thorough washing with the same solvent in which the reaction had been conducted, and then with a light fraction of petroleum ether.

In some cases (see experiments No. 7, 9, 10 in Table 2), it proved possible to carry out additional purification by reprecipitating the substance with petroleum ether from a solution in pyridine or tetrahydrofuran. The results obtained are summarized in Table 2.

Exchange of the acetylacetonate groups of the compounds studied proceeds with sufficient ease both with monobasic and with dibasic acids. In the case of monobasic acids, compounds are formed that are soluble in tetrahydrofuran or pyridine. The reaction products with dibasic acids are distinguished by insolubility in ordinary organic solvents. These are infusible substances that very readily form strong complexes with pyridine, tetrahydrofuran, and benzene. The acyloxy derivatives of cobalt, nickel, and manganese obtained with dibasic acids apparently are polymers of the composition $(—Me—OOC—R—COO—)_x$.

The Debyegram obtained for cobalt azelate shows that the substance under investigation is a noncrystalline polymer. The insolubility, infusibility, and noncrystallinity of the polymer lead us to assume that the cobalt atoms in this substance are coordinatively bound to the carbonyl oxygens of neighboring molecules.

To obtain acyloxy derivatives of divalent manganese with dibasic acids, acetylacetonate of formally trivalent manganese was used, analogously to what was done for the reactions of manganese and cobalt triacetylacetonates with monobasic acids (see experiments No. 8, 10, 11 in Table 1).

The proposed method of exchange reaction between acetylacetonates of zirconium, manganese, nickel, and cobalt and carboxylic acids is a general one for obtaining acyloxy derivatives of transition metals.

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Note: Figure translations are in progress. See original paper for figures.