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The Preparation and Some Properties of 3-Substituted 2,4-Pentanedionato Metal(II, III) Complexes

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In the substitution reactions of phenol, benzenethiol, and their sodium salts on the chelate ring of 3-bromo-2,4-pentanedionato metal complexes (metal=iron(III), aluminium(III), and beryllium(II)), benzenethiol was found to be substituted for bromine, while phenol was not substituted under the same conditions. In the case of sodium salts, both sodium phenoxide and benzenethiolate gave substituted products. The UV and PMR data of tris(3-substituted 2,4-pentanedionato)aluminium(III) complexes gave some information on the substituted groups.

The electrophilic substitution on the chelate ring of acetylacetonato complexes is known to be brought about by various reagents, such as bromine,[1,2] iodine,[1] *N*-halosuccinimides,[1,5] and nitro derivatives,[3,4] while only a few reports have appeared on the further conversion of the substituted chelates.[6,7] It was found by Yoshida *et al.* that the bromine atom on the chelate ring of 3-bromo-2,4-pentanedionatocobalt(III), -chromium(III), or -aluminium(III) is replaced by benzenethiol or its derivatives.[7] On the other hand, we ourselves have previously reported that the bromine atom on the chelate ring of 3-bromo-2,4-pentanedionatoiron(III) is replaced by succinimide or phthalimide in the presence of sodium methoxide.[8] In this paper another nucleophilic substitution reaction will be presented for the bromine atom on the chelate ring of iron(III), aluminium(III), cobalt(III), or beryllium(II) complex by phenol, benzenethiol, or their sodium salts.

Experimental

The 3-position carbons of 2,4-pentanedionato metal(II, III) complexes were halogenated according to the procedure of Collman *et al.*[1]

The Syntheses of 3-Phenoxy-2,4-pentanedionato Metal(II, III) Complexes. *From Phenol*: A 20-ml dichloromethane solution of phenol (0.02 mol) was added to a solution of 3-bromo-2,4-pentanedionatoiron(III), -aluminium(III), -cobalt(III), -chromium(III), -beryllium(II), or their chloro compounds (0.005 mol) in 50 ml of dichloromethane, after which the mixture was left standing for 5—6 days at room temperature. However, phenol was found not to react with these complexes, and the starting material was recovered in each case.

From Sodium Phenoxide: A mixture of sodium phenoxide (0.02 mol) and tris(3-bromo-2,4-pentanedionato)iron(III) (0.005 mol) in 50 ml of dichloromethane was left to stand, with stirring, for three days at room temperature, after which the precipitates formed were filtered off. The filtrate was washed twice with aqueous sodium hydrogencarbonate and then with water. After the solution had been dried with anhydrous sodium sulfate, the dichloromethane was evaporated under a reduced pressure. The resulting solid was recrystallized from ethanol, yielding the red powder of tris(3-phenoxy-2,4-pentanedionato)iron(III) (abbreviated as Fe(acacOph)$_3$). Yield, 36% (based on Fe(acacBr)$_3$). Found: C, 62.79; H, 5.16%. Calcd for $C_{33}H_{33}O_9Fe$: C, 62.97; H, 5.28%. The other substituted products were also prepared according to the same procedure; their analytical results were as follows: Al(acacOph)$_3$. Yield, 31% (based on Al(acacBr)$_3$). Found: C, 66.18; H, 5.38%. Calcd for $C_{33}H_{33}O_9Al$: C, 66.00; H, 5.54%. Be(acacOph)$_2$. Yield, 22% (based on Be(acacBr)$_2$). Found: C, 67.62; H, 5.18%. Calcd for $C_{22}H_{22}O_6Be$: C, 67.52; H, 5.67%. Also from 3-chloro-2,4-pentanedionato metal(II, III) complexes, the same substituted products were obtained, but the yields were less than those from the bromo compounds. In the case of the chromium(III) complex, sodium phenoxide was not substituted by the same method or by reflux for three days; neither its bromo and chloro complexes gave a substituted product. As to the cobalt(III), both the bromo and chloro complexes were immediately decomposed by the same reaction.

The Syntheses of 3-Phenylthio-2,4-pentanedionato Metal(II, III) Complexes. *From Benzenethiol*: A solution of benzenethiol (0.03 mol) in 20 ml of dichloromethane was slowly stirred, into a solution of tris(3-bromo-2,4-pentanedionato)iron(III) (0.005 mol) in 50 ml of dichloromethane. After standing for 2 h at room temperature, the solution was washed with aqueous sodium hydrogencarbonate and water, and then dried with anhydrous sodium sulfate. The dichloromethane was removed and the resulting tarry solid was recrystallized from ethanol–water. Yield, 18%(based on Fe(acacBr)$_3$). Found: C, 58.25; H, 5.29%. Calcd for $C_{33}H_{33}O_6S_3Fe$: C, 58.49; H, 4.91%. The other substituted products were also synthesized by the same procedure; the analytical results were as follows: Be(acacSph)$_2$. Yield, 55%(based on Be(acacBr)$_2$). Found: C, 61.98; H, 5.49%. Calcd for $C_{22}H_{22}O_4S_2Be$: C, 62.39; H, 5.24%. The substituted products were not obtained from 3-chloro-2,4-pentanedionatoiron(III) or -beryllium(II) under the same conditions.

From Sodium Benzenethiolate: The substituted products were obtained according to the procedure used for the preparations of 3-phenoxy-2,4-pentanedionato metal(II, III) complexes. The analytical results were as follows: Fe(acacSph)$_3$. Yield, 24%(based on Fe(acacBr)$_3$). Found: C, 57.94; H, 4.93%. Calcd for $C_{33}H_{33}O_6S_3Fe$: C, 58.49; H, 4.91%. Al(acacSph)$_3$. Yield, 43%(based on Al(acacBr)$_3$). Found: C, 61.01; H, 5.30%. Calcd for $C_{33}H_{33}O_6S_3Al$: C, 61.10; H, 5.13%. Be(acacSph)$_2$. Yield, 37%(based on Be(acacBr)$_2$). Found: C, 62.21; H, 5.42%. Calcd for $C_{22}H_{22}O_4S_2Be$: C, 62.39; H, 5.24%.

Measurements. The electronic spectra in solution and the infrared spectra using KBr pellets were measured on a Hitachi 124-type spectrophotometer and a Hitachi 215-type spectrophotometer respectively. The PMR spectra were recorded with a JEOL-MH 100 spectrophotometer at a frequency of 100 MHz. The chemical shifts were determined in ppm, using TMS as the internal standard. The elemental analyses were carried out by means of a Yanagimoto MT 2 CHN Corder.

TABLE 1. THE ELECTRONIC, INFRARED, AND PMR DATA OF THE TRIS(3-SUBSTITUTED 2,4-PENTANEDIONATO)ALUMINIUM(III) COMPLEXES

Complex	Electronic spectra λ max(nm) in CH_2Cl_2	Infrared spectra cm^{-1} (KBr pellets)		PMR spectra δ values (ppm) in CCl_4	
		C=C[a]	C–H[b]	Methyl group	Phenyl group
$Fe(acacOph)_3$	277, 387, 480	1485	820	—	—
$Al(acacOph)_3$	270^{sh}, 310	1490	825	2.06	6.80—7.20
$Be(acacOph)_2$	270^{sh}, 316	1492	824	2.04	6.80—7.19
$Fe(acacSph)_3$	253, 280^{sh}, 340^{sh}, 435	1489	805	—	—
$Be(acacSph)_2$	253, 292, 320^{sh}	1479	824	2.34	6.80—7.20

sh=shoulder; acacOph=3-phenoxy-2,4-pentanedione anion; acacSph=3-phenythio-2,4-pentanedione anion.
a) The band assigned to the skelton stretching of the phenyl group[2]. b) The C–H -out-of-plane bending of the phenyl group[2].

Results and Discussion

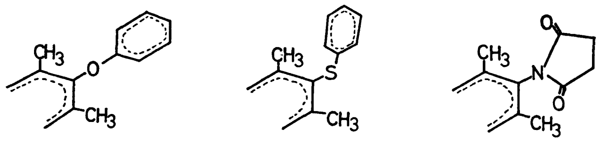
Electronic, Infrared, and PMR Spectra. From the data given in Table 1, we see that the 3-phenoxy derivatives of these metal complexes and phenylthio compounds show the band of the phenoxyl or phenylthio group at around 270 or 253 nm respectively. In the infrared spectra, these substituted compounds show the bands characteristic of a skeletal stretching and a CH-out-of-plane bending of the phenyl group at around 1490 and 820 cm^{-1} respectively.[7] In the PMR spectra, the methyl proton of acetylacetone shows a singlet signal in the range of 1.4—2.4 ppm, while the phenyl proton shows multiplet signals in the range of 6.8—7.4 ppm. The PMR spectrum of the iron(III) complex was not measured because of its paramagnetism.

The UV and PMR Spectral Data of the Tris(3-substituted 2,4-pentanedionato)aluminium(III) Complexes. From the UV data given in Table 2, we can see that the chloro, bromo, and phenoxy complexes show the absorption band due to a π-π^* transition of an acetylacetone ring at around 310 nm, while the acetylacetonato complex and its benzenethiol, succinimide, and phthalimide derivatives show the absorption bands at around 290 nm. It has been known that the absorption band of the π-π^* transition of benzene is shifted to longer wavelengths when the hydrogen of benzene is replaced by such a group as chlorine, bromine, or amine, which has lone-pair electrons taking part in the π system of benzene.[9] Therefore, the oxygen atom of the phenoxyl group in this compound has hybridized sp or sp^2 orbitals and the electrons of the nonhybridized p orbital must participate in the π system of the acetylacetone ring. The sulfur atom of the phenylthio group may have hybridized sp^3 orbitals and no electrons which take part in the π system of an acetylacetone ring; thus, the absorption band of the phenylthio compound shows no shift to longer wavelengths. The succinimido or phthalimido group of this compound is perpendicular to an acetylacetone ring because of the steric hindrance between the carbonyl group of these imides and the methyl group of the acetylacetone ring. Therefore, the absorption band arising from the π-π^* transition of the acetylacetone ring is not shifted. The PMR signals of the methyl protons of the chelated acetylacetone of the 2,4-pentanedionatoaluminium(III) complex, and its 3-bromo and 3-chloro compounds are shifted to lower magnetic fields in the order of their electronegativities. The PMR signal of the phenylthio compound is shifted to a lower magnetic field than that of the phenoxy compound. It can be said that this is caused by the ring-current effect of benzene. From the UV spectra and the fact that the PMR signal of the methyl group is a singlet in these compounds, the oxygen atom of the phenoxyl group can be said to have sp hybridized orbitals, while the sulfur atom of the phenylthio group has sp^3 hybridized orbitals. That is, the benzene ring of phenylthio group is situated nearer to the methyl group than that of the phenoxyl group. Thus, the methyl protons of phenoxy compounds are affected by the ring current of benzene more strongly than that of phenylthio compounds, and the PMR signal of the phenylthio compound is shifted to a lower magnetic field than that of the phenoxy compound. The PMR spectra of the 3-succinimido and 3-phthalimido compounds have also been compared. In spite of the strong electron attraction of a carbonyl group of these imides, the signal of the methyl protons of these compounds appears at nearly the same position as that of

TABLE 2. THE UV AND PMR SPECTRAL DATA OF THE TRIS(3-SUBSTITUTED 2,4-PENTANEDIONATO)-ALUMINIUM(III) COMPLEXES

$Al(acacX)_3$ X=	UV spectra λ max (nm) in CH_2Cl_2	PMR spectra[a] δ values (ppm) in CCl_4
Succinimido[b]	286	1.92
H	288	1.93
Phthalimido[b]	289	2.04
phS	292	2.36
Cl	308	2.29
Br	309	2.27
phO	310	2.03

a) Signals for the methyl group on the chelate ring.
b) The details of the syntheses of these complexes will be published.



The conformations of the substituted groups.

the 2,4-pentanedionato compound. This may arise from the magnetic anisotropy. The protons of methyl groups of the acetylacetone ring are situated over the π system of $\overline{O{-}\underset{|}{C}{-}N{-}\underset{|}{C}{-}O}$, because the plane of cyclic imides and the acetylacetone ring are perpendicular to each other. Thus, the anisotropic effects can shift the PMR signal to a higher magnetic field.

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