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The Nucleophilic Substitution of Dicarboxylic Imides on the Chelate Ring of Tris(3-bromo-2,4-pentanedionato)iron(III)

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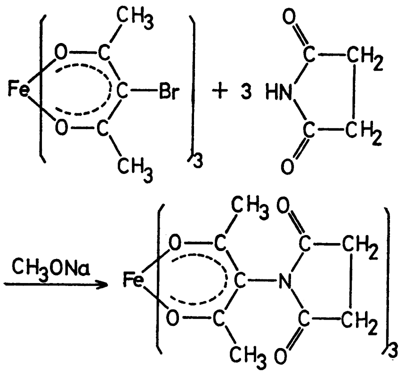
Synopsis. Succinimide and phthalimide were found to be capable of acting as a nucleophilic substituent on the chelate ring of tris(3-bromo-2,4-pentanedionato)iron(III) complex. No analogous reaction has been found between this complex and the other dicarboxylic imides, nor between other metal complexes and dicarboxylic imides including these two imides.

The electrophilic substitution on the chelate ring of acetylacetonato complexes is brought about by various reagents such as bromine,[1,2] iodine,[1] *N*-halosuccinimides,[1,5] nitro derivatives,[3,4] acyl derivatives[4] and chloride of iodine[1] or sulfur[6] *etc.*, while only a few reports have appeared on the further conversion of the substituted chelates.[6,7] The nucleophilic substitution reaction reported by Yoshida *et al.*[7] deserves the special attention. They found that the bromine atom on the chelate ring of 3-bromo-2,4-pentanedionato metal complexes is replaced by thiophenol or its para-substituted derivatives. During the course of our investigation on the mechanism of a similar reaction using mercaptanes, alcohols and alkoxides as substituents, we encountered in most cases the decomposition of chelate or the reduction of central metal and occasionally the formation of alkoxy bridged binuclear complexes.[8] In the present studies, we came across an unexpected result in which some dicarboxylic imides were substituted for bromine of tris(3-bromo-2,4-pentanedionato)iron(III).

3-Carbon of tris(2,4-pentanedionato)iron(III) was brominated by means of *N*-bromosuccinimide. Then the brominated compound, after isolation, was to be examined as to the substitution reaction of sodium methoxide. This reagent was accidentally added to the solution of complex without removal of succinimide, which is one of the byproducts of bromination. After being left to stand for three days, deposited white precipitates were separated by filtration, and the filtrate was evaporated in a vaccum. Orange plates thus obtained were recrystallized from dichlormethane–methanol solution. The results of elemental analysis, molecular weight and infrared spectrum indicate that this compound is tris(3-succinimido-2,4-pentanedionato)iron(III), the bromine atom at the 3-position of every chelate being replaced by succinimide, instead of the methoxide group. The departure of bromine was recognized by the fact that the white precipitates were soluble in water and silver bromide was formed by the addition of aqueous solution of silver nitrate. The analytical value and molecular weight were as follows. Found: C, 49.53; H, 4.66; N, 6.38%; mol wt, 631; mp 143—146 °C decomposed. Calcd for $FeC_{27}H_{30}N_3O_{12}$: C, 50.33; H, 4.69; N, 6.52%; mol wt, 644.4.



For the sake of confirmation, the brominated compound was isolated and examined. 1.97 g (0.003 mol) of tris(3-bromo-2,4-pentanedionato)iron(III) and 0.99 g (0.01 mol) of succinimide were dissolved in 180 ml of dichlormethane to which was added 0.54 g (0.01 mol) of sodium methoxide dissolved in 25 ml of methanol. After being left to stand for three days, an orange substance was obtained by the same procedure as above. This was also identified as tris(3-succinimido-2,4-pentanedionato)iron(III), A.

In a similar way, phthalimide reacted with tris(3-bromo-2,4-pentanedionato)iron(III), producing orange red crystals of hexagonal prism, which was confirmed to be tris(3-phthalimido-2,4-pentanedionato)iron(III), B. Found: C, 58.63; H, 3.91; N, 5.15%; mol wt, 750; mp 235—240 °C decomposed. Calcd for $FeC_{39}H_{30}N_3O_{12}$: C, 59.41; H, 3.84; N, 5.33%; mol wt, 788.5.

In the infrared spectra, product A and B show a peak at 1705 and 1725 cm^{-1}, respectively, both of them being attributed to the stretching vibration of carbonyl group vicinal to the imide nitrogen. The stretching vibration of the chelated carbonyl groups appears at 1545 cm^{-1} for the original brominated material. The peak shifts to 1580 cm^{-1} for product A and 1582 cm^{-1} for product B. In the region 1100—710 cm^{-1}, product B has peaks assigned to the benzene ring (Table 1).

Table 1. Characteristic absorption peaks of the original complex and the products in the infrared spectra, cm^{-1}

	$\nu(C=O)_1$	$\nu(C=O)_2$	ν (benzene ring)
$Fe(Br\text{-}acac)_3$		1545	
Product A	1705	1580	
Product B	1725	1582	1100 1090 880 800 720 710

$\nu(C=O)_1$: Carbonyl vicinal to the imide group.
$\nu(C=O)_2$: Chelated carbonyl.

The absorption peaks in the visible and ultraviolet region are given in Table 2 for the original material and products A and B. The metal reduction and

TABLE 2. ABSORPTION MAXIMA OF THE ORIGINAL COMPLEX AND THE PRODUCT SIN THE ELECTRONIC SPECTRA, nm (log ε)

	π—π*			t_{2g}—π*	π—e_g[9]
Fe(Br–acac)$_3$	240^{sh} (4.15)	292 (4.34)		375 (3.46)	470 (3.57)
Product A	244 (4.43)	268 (4.45)		347 (3.56)	432 (3.67)
Product B	244 (4.65)	270^{sh} (4.48)	303^{sh} (4.15)	347 (3.59)	433 (3.68)

oxidation bands and the band due to the intraligand transition of each one appear at an adequate position with reasonable extinction for the 1,3-diketone complexes. The shoulder at 303 nm of product B might originate from phthalimide residue, whose intense absorption at around 250 nm seems to hide the π—π* transition band of product B.

These substitution reactions proceed also with the addition of potassium hydroxide instead of sodium methoxide. No change is observed in the absence of hydroxides or methoxides, in contrast to the substitution of thiophenol which is considerably inhibited by the addition of such a proton acceptor as pyridine or piperidine as well as in the basic solvent such as acetone, methanol, ether or dimethyl sulfoxide.[7] The disparity arises from the fact that the reaction depends on whether intermediate adducts exist in the case of thiophenol substitution or the coulombic attraction is dominant enough to promote the reaction.

The present reaction with succinimide or phthalimide seems to be characteristic of iron(III) complex. Aluminum(III), chromium(III), cobalt(III) and copper(II) complexes of the same ligand show no change with various dicarboxylic imides including these two imides. No other substituent has been found as regards the reaction involving this iron(III) complex.

The reaction seems to be a kind of Gabriel reaction. Bacon and Karim reported on the extension of copper-catalyzed reaction,[10] in which the substitution of phthalimide for halogen of aryl halide is catalyzed by copper(I) iodide. Application of this catalyst to the present reaction resulted in failure, suggesting a different mechanism.

Experimental

The electronic spectra and the infrared spectra were measured on a Hitachi 124 type Spectrophotometer and Hitachi 215 type Spectrophotometer, respectively. The elemental analyses were carried out by means of a Yanagimoto MT 2 CHN corder. A Hitachi 115 Vapour Pressure Osmometer was used for the determination of molecular weights. Reagents of guaranteed grade were used without further purification.

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