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Bromination of [(2-Salicylidene)alkanoato(2-)] metal(II) Complexes

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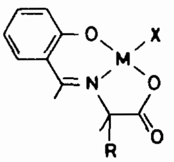
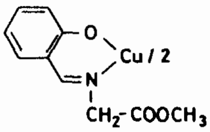
It is a well established fact that coordination enormously alters the reactivity of coordinated ligands (see for example refs. 1, 2), This can be particularly demonstrated on the amino acid Schiff base metal complexes which can undergo both nucleophilic and electrophilic reactions. This ability, which arises from the activation of an α-proton of the condensed amino acid, is a consequence of the formation of a reactive carbanion. We attempted to utilize this fact for the bromination of metal complexes I and II, prepared according to literature [3–5]:



I



II

I: *a*, M = Cu, R = H, X = H_2O; *b*, M = Cu, R = H, X = Pyridine; *c*, M = Zn, R = H, X = H_2O; *d*, M = Ni, R = H, X = H_2O; *e*, M = Cu, R = CH_3, X = H_2O; *f*, M = Cu, R = $CH(CH_3)_2$, X = H_2O; *g*, M = Cu, R = CH_2CONH_2, X = H_2O; *h*, M = Cu, R = CH_2CONH_2, X = Pyridine; *i*, M = Cu, R = $(CH_2)_2$-$CONH_2$, X = H_2O.

In principle, bromination can proceed either on the aromatic ring or on the amino acid chelate ring. However, results obtained show that bromination both by N-bromosuccinimide and dioxanedibromide, irrespective of the molar ratio metal complex: bromination agent and the character of the metal ion, leads to 3,5-dibromosalicylaldehyde. Similarly the character of the ligand coordinated to the fourth copper(II) site also has no influence on the orientation of incoming bromine. However, results further indicate (see Table I) that the solvent has some influence: 3,5-dibromosalicylaldehyde was formed only when bromination proceeded in methanol: water 1:1 solvent. On the other hand when bromination was made in $CHCl_3$, both 5-bromosalicylaldehyde and 3,5-dibromosalicylaldehyde were formed depending on the molar ratio metal complex: bromination agent. Bromination of I*a*–*i* in position 3 and 5 of an aromatic ring is the result of insufficient α-proton activation in the Schiff base metal complex.

TABLE I. Analysis of the Bromination Products.

Metal Complex		%C	%H	%N	%Br
I *a*·H_2O	calcd.	24.92	2.07	3.22	36.80
	found	25.00	1.85	3.11	35.57
b	calcd.	36.72	2.20	6.12	34.93
	found	36.08	1.97	6.19	33.99
c·H_2O	calcd.	25.91	1.67	3.35	38.21
	found	26.02	1.87	3.15	38.94
d·H_2O	calcd.	25.22	2.10	3.26	37.31
	found	24.95	2.26	3.14	36.98
e·H_2O[a]	calcd.	26.81	2.46	3.13	36.72
	found	26.63	2.53	3.24	37.00
e·$2H_2O$[b]	calcd.	31.01	3.62	3.62	20.65
	found	30.96	3.73	3.82	20.84
e·H_2O[c]	calcd.	26.81	2.46	3.13	36.72
	found	26.85	2.44	3.76	37.01
f	calcd.	31.55	2.63	3.06	34.95
	found	31.69	2.73	3.11	35.11
g	calcd.	27.88	2.13	5.92	33.75
	found	27.68	2.09	6.06	34.17
h	calcd.	32.50	2.56	7.11	27.05
	found	32.61	2.70	7.13	27.65
i	calcd.	27.50	2.31	5.35	30.52
	found	27.61	1.99	5.29	30.40

[a]molar ratio metal complex:bromination agent 1:2 (in $CHCl_3$). [b]ratio 1:1 (in $CHCl_3$). [c]ratio 1:1 in methanol water 1:1.

Bromination of glycine ester in II, after the decomposition of the bromination product (see Experimental), gave on the chromatogram three ninhydrin-positive spots with R_F = 0.3, 0.4 and 0.5. Compounds corresponding to R_F = 0.3 and 0.5 were identified using standards as a glycine and glycine ester. Since in II the electronic density at the α-carbon atom is markedly reduced [6], we suppose that bromination of the glycine ester (R_F = 0.4) occurred partially (detailed study will be published elsewhere).

Experimental

Bromination: To 20 mmol of the proper metal complex dissolved or suspended in 50% methanol (or $CHCl_3$) 20, 40 or 60 mmol of solid N-bromosuccinimide were added. The reaction mixture was then heated under stirring to 50 °C. On cooling to room temperature, the product of bromination was deposited.

In the case of bromination with dioxane-dibromide, the proper mmoles of bromine dissolved in 50 ml of dioxane, were added drop by drop to 20 mmol of metal complex dissolved in the above mentioned solvents. Stirring the reaction mixture at room temperature led to the crystallization of the brominated product.

The brominated product was dissolved in 1:1 HCl. After a short time needle-like crystals deposited. These were washed with water and dried. *Anal.* Calcd. for 5-bromosalicylaldehyde: 41.82%, C; 2.51%, H; 39.80%, Br. Found: 41.52%, C; 2.50%, H; 40.93%, Br. *Anal.* Calcd. for 3,5-dibromosalicylaldehyde: 30.11%, C; 1.44%, H; 57.26%, Br. Found: 30.20%, C; 1.40%, H; 56.58%, Br.

The isolated products were further characterised by infrared spectra (KBr-disk method, Perkin-Elmer apparatus) which were compared both with those of standards prepared and with spectra given in Sadtler's tables. The infrared spectrum of 5-bromosalicylaldehyde corresponds to that registered under No 5768, while the spectrum of 3,5-dibromosalicylaldehyde to that of No 34486.

The brominated complex of II was suspended in acidified 50% methanol and then decomposed by H_2S. The CuS was filtered off and the filtrate was, after neutralization, passed through a column of Dowex 50WX8 (H^+ form). After washing the column with water, elution with 1 *M* ammonia was made. The eluate was evaporated to dryness, dissolved in a minimum amount of 50% methanol and chromatographed on ready-made silica gel plates (Silufol-Kavalier, ČSSR) using 70% n-propanol as solvent. Detection was made with 0.1% ethanolic solution of ninhydrine.

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