

• CHAPTER-IV •

CHAPTER IVELECTROPHILIC SUBSTITUTION REACTIONS OFMETAL COMPLEXES - PART II

(Acetoxylation Reactions)

1. Introduction :

The reactions of dinitrogen tetroxide (N_2O_4) with metal complexes containing salicylaldehyde, 2-hydroxyacetophenone, 2'-hydroxy chalcone, and the imines of salicylaldehyde, indicated the important role played by the coordinated metal ion in these reactions. Depending on the nature of the metal ion the yield of 3-nitro derivative was enhanced, and 3,5-dinitro derivative was directly obtained. These reactions prompted us to use the other milder nitrating agents. In literature¹⁻⁵ nitroacetic acid, CH_3COONO_2 , generated by the reaction of cupric nitrate $Cu(NO_3)_2 \cdot 2H_2O$ with acetic anhydride $(CH_3CO)_2O$, has been used to nitrate the acid labile complexes, such as $M(ptdn)_n$, $M(sal)_2$, $M(N-Rhapim)_2$ and $M[N,N'en(salim)_2]$. Our preliminary results of the reaction of nitroacetic acid with salicylaldehydato complexes indicated that no nitro derivative was obtained. Instead the acetoxy derivative of salicylaldehyde was obtained. Similarly it was interesting to observe for

the first time during our experiments that the reaction of acetic anhydride with salicylaldehydato complexes yielded the acetoxy derivative. It would be therefore profitable to analyse these acetoxylation reactions.

We have studied in detail the acetoxylation reactions of the complexes ML_2 [M = nickel (II), copper (II)], L being salicylaldehyde, 2-hydroxyacetophenone, 2'-hydroxy chalcone, and the imines of salicylaldehyde.

2. Experimental :

(a) Materials :

(i)	bis(salicylaldehydato)nickel (II)	<u>A</u>
(ii)	bis(salicylaldehydato)copper (II)	<u>C</u>
(iii)	bis(2-hydroxyacetophenonato)nickel (II)	<u>E</u>
(iv)	bis(2-hydroxyacetophenonato)copper (II)	<u>F</u>
(v)	bis(2'-hydroxychalconato)nickel (II)	<u>G</u>
(vi)	bis(2'-hydroxychalconato)copper (II)	<u>H</u>
(vii)	bis(N,n-butylsalicylaldiminato)nickel (II)	<u>I</u>
(viii)	bis(N,n-butylsalicylaldiminato)copper (II)	<u>J</u>

These complexes were synthesised by procedure similar to that given in the literature⁵⁻⁹. The solvents used in the present work were purified by literature method¹⁰.

Acetoxylation with acetic anhydride $(\text{CH}_3\text{CO})_2\text{O}$, in chloroform :

1. Acetoxylation of A

A mixture of A (0.3 g, 0.001 M) and $(\text{CH}_3\text{CO})_2\text{O}$ (10 ml) in chloroform (20 ml) was stirred at 25° for 24 h. The reaction mixture was reduced to a small volume in vacuo. The residue was extracted with chloroform. The chloroform extract was loaded on a silica gel (100-200 mesh) packed column using petroleum ether ($60-80^\circ$).

The fraction eluted with petroleum ether + benzene (1:1 v/v) afforded a colourless crystalline compound a (0.1 g, 30 %). The insoluble green residue in chloroform was B (0.04 g, 10 %).

Product a. colourless crystalline, m.p. 138.5° , found: C, 60.4; H, 4.2; $\text{C}_9\text{H}_8\text{O}_4$ requires C, 60.0; H, 4.4 %.

IR ν_{max} : 3150 (bm), 2960 (m), 2870 (m), 1740 (s), 1170(s), 1690(s), 1670 (m), 1650 (m), 1600 (w), 1580 (m), 1488 (w), 1450 (m), 1400(w), 1375 (m), 1370 (m), 1305 (w), 1280 (s), 1245 (m), 1210 (s), 1205 (s), 1190 (bs), 1160 (m), 1180 (w), 1157 (m), 1115 (s), 1095 (s), 1060 (w), 1045 (w), 1010 (s), 915 (vs), 875 (m), 850 (m), 835 (m), 810 (m), 790 (s), 765 (vs), 720 (m), 665 (m), 630 (m), 585 (m), 543 (m), 535 (w), 497 (w) cm^{-1} .

Product B, green crystalline, m.p. 250 °C (decomposes);
found, C, 27.7; H, 3.5; Ni, 32.8; $\text{NiC}_4\text{H}_6\text{O}_4$, anhydrous
requires C, 27.2; H, 3.4; Ni, 33.2 %.

IR ν_{max} : 1720 (m), 1710 (m), 1615 (s), 1590 (m), 1550 (s),
1530 (s), 1460 (s), 1410 (s), 1350 (s), 1160 (w), 1090 (m),
1070 (m), 1040 (s), 720 (w), 690 (s), 625 (s), 550 (m) cm^{-1} .

2. Acetoxylation of C with $(\text{CH}_3\text{CO})_2\text{O}$ in chloroform

The acetoxylation reaction of C (0.305 g, 0.001 M) was
carried out using a procedure similar to that used for the
acetoxylation reaction of A using $(\text{CH}_3\text{CO})_2\text{O}$.

The isolated product was loaded on a silica gel packed
column using petroleum ether (60-80 °). The fraction eluted
with petroleum ether + benzene (1:1 v/v) afforded a colourless
crystalline compound which was characterised as a (0.1 g, 30 %)
from the analytical data. The fraction eluted with chloroform
afforded a green crystalline compound D (0.168 g, 40 %).

Product D, green crystalline, m.p. 320 ° (colour changes at 90 °),
found, C, 51.6; H, 3.5; Cu, 15.4; $\text{CuC}_{18}\text{H}_{14}\text{O}_8$ requires
C, 51.2; H, 3.3; Cu, 15.0 %.

IR ν_{max} : 3050 (s), 2983 (s), 2960 (s), 2933 (s), 2870 (m),
1760 (bs), 1670 (bs), 1622 (s), 1610 (s), 1580 (w), 1490 (w),
1437 (m), 1350 (bm), 1280 (s), 1245 (bs), 1160 (s), 1120 (s),
1107 (m), 1090 (s), 1057 (s), 1030 (m), 1010 (s), 977 (m),
970 (m), 915 (s), 905 (s), 890 (s), 835 (s), 810 (bm),

795 (s), 760 (s), 750 (s), 725 (m), 705 (m), 690 (vs),
667 (s) cm^{-1} .

3. Acetoxylation of E with $(\text{CH}_3\text{CO})_2\text{O}$ in chloroform

The acetoxylation reaction of E (0.328 g, 0.001 M) was carried out using a procedure similar to that used for the acetoxylation of A using $(\text{CH}_3\text{CO})_2\text{O}$

The isolated product was loaded on a silica gel packed column using petroleum ether (60-80 $^\circ$). The fraction eluted with petroleum ether - benzene (1:1 v/v) afforded a pale pink crystalline compound b (0.09 g, 25 %). The insoluble residue in chloroform (0.174 g, 50 %), could not be characterised.

Product b, pale pink crystalline compound, m.p. 118-119 $^\circ$, found, C, 62.1; H, 5.4; $\text{C}_{10}\text{H}_{10}\text{O}_4$ requires C, 61.8; H, 5.1 %. IR ν_{max} : 3250 (bs), 3230 (bs), 1760 (s), 1670 (s), 1627 (s), 1583 (w), 1522 (bm), 1494 (m), 1383 (s), 1333 (m), 1293 (s), 1215 (s), 1192 (s), 1160 (w), 1130 (m), 1093 (s), 1035 (bm), 1015 (bs), 993 (m), 950 (m), 920 (s), 895 (m), 875 (s), 835 (m), 770 (s) cm^{-1} .

4. Acetoxylation of F with $(\text{CH}_3\text{CO})_2\text{O}$ in chloroform

The acetoxylation reaction of F (0.335 g, 0.001 M) was carried out using a procedure similar to that used for the acetoxylation reaction of A using $(\text{CH}_3\text{CO})_2\text{O}$.

The isolated product was loaded on a silica gel packed column using petroleum ether (60-80°). The fraction eluted with petroleum ether + benzene (1:1 v/v) afforded a pale pink crystalline compound which was identified as b (0.09 g, 25 %) from the analytical data. The insoluble residue in chloroform (0.174 g, 50 %) could not be characterised.

5. Acetoxylation of G with $(\text{CH}_3\text{CO})_2\text{O}$ in chloroform

A mixture of G (0.504 g, 0.001 M) and $(\text{CH}_3\text{CO})_2\text{O}$ (10 ml) in chloroform (20 ml) was stirred at 25° for 40 h, and was reduced in volume in vacuo. The residue was extracted with chloroform. The chloroform extract was reduced to a small volume in vacuo. The isolated product was loaded on silica gel packed column using petroleum ether (40-60°).

The fraction eluted with petroleum ether + benzene (1:1 v/v) afforded a yellow crystalline compound c (0.113 g, 20 %). The residue insoluble in chloroform could not be characterised.

Product c, yellow crystalline, m.p. 73.5°, Found, C, 72.3; H, 5.1; $\text{C}_{17}\text{H}_{14}\text{O}_4$ requires C, 72.3; H, 5.0 %.

IR ν_{max} : 1775 (s), 1725 (m), 1632 (s), 1614 (m), 1575 (bm), 1542 (w), 1514 (m), 1492 (s), 1448 (s), 1425 (m), 1342 (m), 1303 (s), 1275 (s), 1260 (s), 1235 (m), 1210 (bs), 1195 (s),

1175 (s), 1163 (s), 1150 (w), 1127 (m), 1110 (w), 1065 (m),
1030 (s), 1005 (w), 982 (s), 975 (w), 862 (m), 840 (w),
825 (s), 800 (s), 790 (s), 775 (w), 760 (s), 735 (w),
715 (w), 710 (w), 690 (m), 660 (s), 635 (w), 575 (w),
563 (s), 550 (m), 510 (s) cm^{-1} .

6. Acetoxylation of H with $(\text{CH}_3\text{CO})_2\text{O}$ in chloroform

A mixture of H (0.509 g, 0.001 M) and $(\text{CH}_3\text{CO})_2\text{O}$ (15 ml) in chloroform (30 ml) was stirred at 25° for 40 h, and was reduced in volume in vacuo. The residue was extracted with chloroform. The chloroform extract was reduced to a small volume in vacuo. The isolated product was loaded on a silica gel packed column using petroleum ether ($60-80^\circ$). The fraction eluted with petroleum ether + benzene (1:1 v/v) afforded a yellow crystalline compound which was characterised as c (0.115 g, 20 %), from the analytical data. The residue insoluble in chloroform could not be characterised.

7. Acetoxylation of I with acetic anhydride in chloroform

A mixture of I (0.410 g, 0.001 M) and $(\text{CH}_3\text{CO})_2\text{O}$ (10 ml) in chloroform (20 ml) was stirred at 25° for 20 h, and was reduced in volume in vacuo. The residue was extracted with chloroform. The chloroform extract was reduced to a small volume in vacuo. The isolated product was loaded on

a silica gel packed column using petroleum ether (60-80°). The fraction eluted with petroleum ether + benzene (1:1 v/v) afforded a brown coloured liquid, e (0.09, 25 %). The insoluble green residue in chloroform was (0.174 g, 50 %), was characterised as anhydrous nickel acetate.

Product e, brown coloured liquid, b.p. 148.0 - 148.5°/710 mm. found, C, 65.9; H, 7.0; N, 6.1; $C_{13}H_{17}O_3N$ requires C, 65.4; H, 7.2; N, 5.9 %.

IR. ν_{\max} 3300 (bm), 2960 (m), 2941 (m), 2860 (m), 1786 (s), 1656 (s), 1600 (s), 1538 (m), 1495 (m), 1471 (m), 1458 (m), 1445 (m), 1385 (m), 1282 (s), 1231 (s), 1206 (s), 1160 (m), 1117 (m), 1099 (m), 1043 (m), 1013 (s), 978 (m), 920 (s), 900 (s), 855 (m), 847 (m), 815 (m), 800 (m), 765 (s), 730 (m), 601 (w), 518 (w), 432 (w) cm^{-1} .

8. Acetoxylation of J with $(CH_3CO)_2O$ in chloroform

J (0.415 g, 0.001 M) was treated with $(CH_3CO)_2O$ (12 ml) in chloroform (25 ml). The mixture was stirred at 25° for 24 hr, and was reduced in volume in vacuo. The residue was extracted with chloroform. The chloroform extract was reduced to small volume in vacuo. The isolated product was loaded on a silica gel packed column using petroleum ether (60-80°).

The fraction eluted with petroleum ether + benzene (1:1 v/v) afforded a brown liquid which was characterised as e.

3. Results

The reaction of A with acetic anhydride, $(\text{CH}_3\text{CO})_2\text{O}$ afforded two products a and B. The elemental analysis of a fitted well with that of the expected monoacetoxy derivative of salicylaldehyde. Infrared spectrum of a displayed two strong and sharp bands at 1700 cm^{-1} and 1740 cm^{-1} , which were assigned to C = O group of CHO and OCOCH_3 respectively. A broad band was observed at 3150 cm^{-1} due to intramolecularly H-bonded OH group. The medium intensity bands observed at 2960 cm^{-1} and 2870 cm^{-1} clearly indicated the presence of aliphatic group. The medium intensity band was observed at 1450 cm^{-1} due to C- CH_3 deformation mode.

Three strong bands were observed at 1190 cm^{-1} , 1205 cm^{-1} and 1210 cm^{-1} . This region is associated with the CO stretching mode of ester group and phenol OH deformation mode. Similarly the assignment of two bands observed between 1370 cm^{-1} and 1375 cm^{-1} is difficult. It is associated with OH deformation mode, CO stretching mode and C- CH_3 deformation mode. The strong characteristic band at 765 cm^{-1} was presumably due to the presence of three adjacent hydrogen atoms on the benzene ring. Thus the elemental analysis and

infrared spectrum suggested that the compound a was 3-acetoxysalicylaldehyde. The ^1H n.m.r. spectrum of a substantiated this structural assignment.

A signal observed at 2.35 p.p.m. was due to protons present in the acetoxy group. The signal due to OH proton was comparatively broad at 10.95 ppm. The signal due to CHO proton was comparatively at high field (8.4 ppm).

The absence of carboxylic group in compound a was clarified from the following observation : C = O group frequency of hydrogen bonded carboxylic group was generally observed in the region 1650 cm^{-1} to 1670 cm^{-1} , and the chemical shift of COOH proton was expected between 10 to 14 ppm; and the spectra of a did not show any of these characteristic bands / signals.

The compound B containing nickel was characterised as anhydrous nickel acetate from elemental analysis and infrared spectrum.

A similar acetoxylation reaction using complex C containing copper (II) also afforded the organic compound which was characterised as a. From this reaction a green crystalline metal complex of copper (II) was separated. Its elemental analysis suggested that it was a complex with substituted salicylaldehydato group containing acetoxy group. Its infrared

spectrum displayed two strong bands at 1760 cm^{-1} and 1670 cm^{-1} , indicating the presence of OCOCH_3 group and the coordinated CHO group. The bands observed at 2960 cm^{-1} and 2870 cm^{-1} substantiated the presence of CH_3 group. The ligand separation from the complex D afforded only one organic compound which was characterised as from the elemental analysis, m.p., infrared spectrum and ^1H n.m.r. spectrum. These results suggested that the complex D contained 3-acetoxy salicylaldehyde as the coordinated ligand.

These interesting results obtained from the acetoxylation reaction of salicylaldehydato complexes prompted us to carry out the similar reactions of the complexes with 2-hydroxyacetophenone, 2'-hydroxychalcone and N-n-butylsalicylaldimine. The reaction with acetic anhydride and bis(2-hydroxyacetophenonato) nickel (II) yielded an organic compound b; its elemental analysis suggested that it was an acetoxy derivative of 2-hydroxyacetophenone. The infrared spectrum of b displayed two strong and sharp bands at 1760 cm^{-1} and 1670 cm^{-1} , which were assigned to the carbonyl group present in OCOCH_3 and COCH_3 groups respectively. Two well resolved strong bands were observed at 1215 cm^{-1} and 1192 cm^{-1} ; this region is assigned to C-O group present in ester and phenol. The strong and sharp band observed at 770 cm^{-1} suggested the presence of three adjacent hydrogen atoms in the aromatic ring.

A strong and comparatively broad band was observed at 3230 cm^{-1} which was assigned to OH stretching mode. These results suggested that the compound b was 2-hydroxy-3-acetoxyacetophenone. This structural assignment was confirmed from its ^1H n.m.r. spectrum. Two signals of equal intensity, each corresponding to three protons were observed at 2.55 ppm and 2.25 ppm. These were tentatively assigned to the protons of COCH_3 and OCOCH_3 groups respectively. A broad signal corresponding to one proton was observed at 11.00 ppm, and was assigned to the proton of phenol. The complex multiplet observed in the region 7.00 to 7.8 ppm resembles the structure observed for 3-acetoxysalicylaldehyde (a).

The acetoxylation of complex F containing copper (II), separated the organic compound which was also characterised as b. The compounds containing metal ion obtained from these two reactions could not give reproducible elemental analysis. From the strong band observed at 1760 cm^{-1} in the infrared spectrum of the complex clearly indicated the presence of OCOCH_3 group. The ^1H n.m.r. spectrum of the ligand separated of this complex showed the presence of more than two CH_3 groups. The aromatic ligands present in these complexes therefore contained an acetoxy group. The detailed analysis was however difficult due to the limitations in the purification of these compounds.

From the acetoxylation reactions of complexes with 2'-hydroxychalcone no complex containing chalcone derivative could be separated, instead the acetate of the respective metal ion was obtained. The organic compound c obtained from these reactions was characterised as acetoxy derivative of 2'-hydroxychalcone from the elemental analysis, infrared spectrum and ^1H n.m.r. spectrum (infrared bands associated with acetoxy group 1775 cm^{-1} , 1195 cm^{-1} ; δ $-\text{OCOCH}_3$, 2.38 ppm). A similar reaction of nickel (II) complex with 2-hydroxychalcone could not give any observable reaction with acetic anhydride. This observation suggested that the acetoxylation reaction required a chelated aromatic ligand. (2-Hydroxychalcone would act as a monodentate ligand). We are therefore tempted to assume that during the acetoxylation reaction of coordinated 2'-hydroxychalcone, the OCOCH_3 group entered the chelated aromatic ring. Due to the complex nature of the ^1H n.m.r. spectrum between 7.1 to 7.9 ppm, it was difficult to analyse the exact position of OCOCH_3 group in the aromatic nucleus. We have tentatively proposed the position of OCOCH_3 group at 3'-position on the basis of the experience of the acetoxylation reaction of metal complexes containing salicylaldehyde and 2-hydroxyacetophenone. The infrared spectrum of the acetoxy derivative of 2'-hydroxychalcone showed a strong band at 790 cm^{-1} suggesting the presence of three adjacent hydrogen atoms in the aromatic ring.

The reaction of acetic anhydride with the coordinated salicylaldehyde and 2-hydroxyacetophenone was expected to be similar to the corresponding coordinated imines. It would be interesting to analyse whether the imine group would remain stable towards hydrolysis during these reactions. The acetoxylation of complexes I and J gave a metal containing compound, which could not be characterised with confidence. The organic compound separated from these two reactions gave comparable elemental analysis and identical infrared and ^1H n.m.r. spectrum, (e). Infrared spectrum of e showed a broad band at 3300 cm^{-1} assigned to a intramolecularly hydrogen bonded OH group. Three bands observed in the region 2960 to 2860 cm^{-1} suggested the presence of a bulky alkyl group. A strong band observed at 1780 cm^{-1} suggested the presence of C = O group and a strong broad band observed at 1230 cm^{-1} indicated the overlap of C-O stretching modes. The band observed at 1655 cm^{-1} was assigned to C = N group. The band observed at 766 cm^{-1} was presumably due to the presence of three adjacent hydrogen atoms on the benzene ring. The ^1H n.m.r. spectrum observed in the aromatic region between 7.1 p.p.m. to 7.8 p.p.m. resembled the pattern observed for a.

The comparison of the intensity of these signals associated with three protons with that observed in the upfield region between 0.88 to 3.13 ppm indicated that there

were twelve aliphatic protons. A singlet observed at 2.35 ppm associated with three protons was assigned to OCOCH_3 . A triplet observed at 0.88 ppm was associated with the CH_3 group present in the butyl group. A complex multiplet was observed between 1.4 ppm to 1.8 ppm associated with four protons at β (beta) and gamma position in the butyl group. A triplet observed at 3.13 ppm was associated with $\alpha\text{-CH}_2$ group. A singlet observed at 9.95 ppm was associated with the $\text{CH} = \text{N}$ group. A singlet associated with OH proton was broad at 11.2 ppm. These observations suggested that the compound e was 3-acetoxy, N-n-butylsalicylaldimine.

These unique reactions indicated that the imine group remained stable under the experimental conditions used for the acetoxylation reaction (i.e. in the presence of acetic acid possibly formed during the reaction).

The reaction of nitro acetic acid with complexes A and C yielded an organic compound, which was characterised as a from its melting point, elemental analysis, infrared spectrum and ^1H n.m.r. spectrum. No nitro derivative was separated from these reactions. The similar reactions of imine complexes I and J with nitro acetic acid yielded organic compound, which was also characterised as a; no acetoxy derivative of the imine could be separated from these reactions.

4. Discussion :

The treatment of salicylaldehyde with acetic anhydride did not show any reaction. The treatment of salicylaldehyde metal (II) complexes with acetic anhydride at room temperature yielded 3-acetoxy salicylaldehyde. This observation suggested that the coordinated metal ion played a definite role in this reaction, yielding a stereo specific derivative of salicylaldehyde. The approach of the two reactant molecules was shown in Fig. 1, (1). The probable direction of polarisation under the electrophilic influence of the metal ion was also shown in Fig. 1. The metal complex being square planar, the approach of acetic anhydride group would be in a plane tilted with the xy plane. Such an approach polarises coordinated salicylaldehyde group and acetic anhydride molecule, which would yield an intermediate with a substitution of acetoxy group at 3-position and an unstable anion $\text{CH}_3\text{C}=\text{O}^-$. This reaction would be followed by first reaction yielding a metal complex with 3-acetoxy salicylaldehyde and acetaldehyde. Acetaldehyde being unstable in air, it was partially oxidised to acetic acid. When the complex (4) was labile under the acetic acid condition, 3-acetoxy salicylaldehyde would be separated and the metal was separated as acetate. Salicylaldehyde and its derivatives were expected to be comparatively stable towards air oxidation due to intramolecular hydrogen bonding. This mechanism was substantiated by the separation of complex with

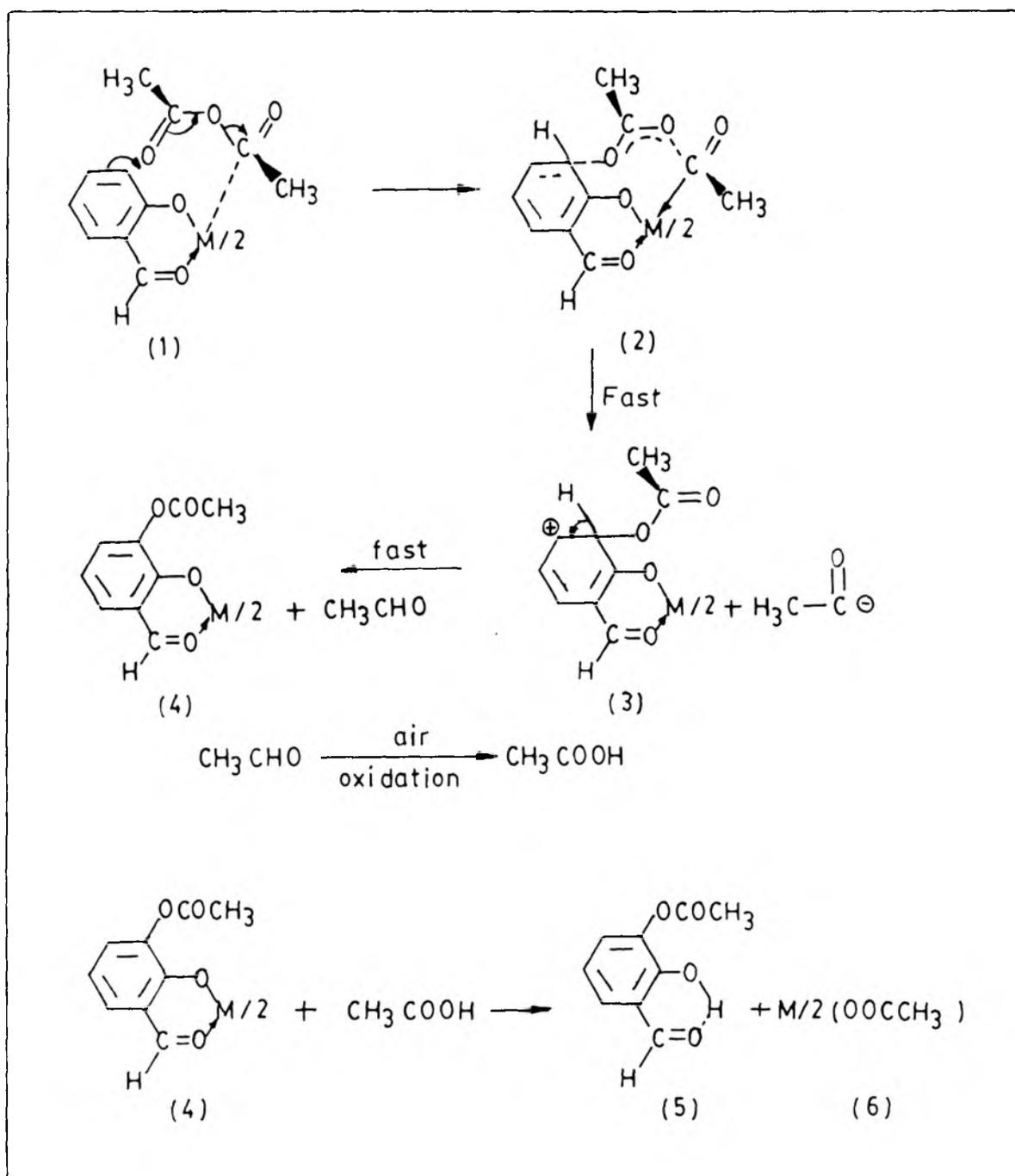


Fig.1: Mechanism of acetoxylation reaction of salicylaldehyde metal(II) complexes by acetic anhydride.

formula (4), when the reaction between bis(salicylaldehydato) copper (II) and acetic anhydride was carried out. When *M* was nickel (II) a complex of the type (4) could not be separated indicating that M-L bond in nickel complex was labile as compared to that in a complex containing copper (II). The participation of site 3 in the coordinated salicylaldehyde group was obvious from the steric preference as shown in species (1).

The acetoxylation reaction of the complex containing 2-hydroxy acetophenone, 2'-hydroxychalcone and N-n-butylsalicylaldehyde could be explained using a mechanism that suggested for the acetoxylation reaction of salicylaldehydato metal complex. It was obvious that the acetoxy group entered at 3'-position in an aromatic ring coordinated with the metal ion and not in the second aromatic ring present in a complex with 2'-hydroxychalcone.

From the acetoxylation reaction of imine, 3-acetoxy-salicylaldehyde was obtained. This result indicated that the imine group was stable in an acetic acid medium. From the reaction of dinitrogen tetroxide (N_2O_4) with the salicylaldehyde complex the derivative of salicylaldehyde complex was separated and no derivative of imine was obtained.

The suggested mechanism for the nitration reaction

involved the formation of nitrous acid. Since nitrous acid is stronger than acetic acid, the imine group might not be stable in the nitrous acid medium, while it was stable in the acetic acid medium.

The reactions discussed above were carried out at room temperature (27-30 °C). When the mixture of bis(salicylaldehydato)metal (II) complex and acetic anhydride was stirred in an ice bath no observable reaction took place even after 72 hours. However when reaction was carried out in the presence of cupric nitrate in ice bath the 3-acetoxy derivative of salicylaldehyde was obtained within an hour. This reaction seemed to be different from a direct reaction of the metal complex with acetic anhydride. The mixture of cupric nitrate and acetic anhydride was used as a nitrating agent and it was proposed that acetyl nitrate was formed. Thus the reaction carried out in the present work at ice bath temperature was the reaction between metal complex and acetyl nitrate and not between metal complex and acetic anhydride. The probable mechanism for the reaction between salicylaldehydato complex and acetyl nitrate was probably similar to that between salicylaldehydato complex and acetic anhydride. The probable mechanism was given in Fig. 2. Since no nitro derivative of salicylaldehyde was obtained from this reaction it was proposed that the nitrogen end of the acetyl nitrate

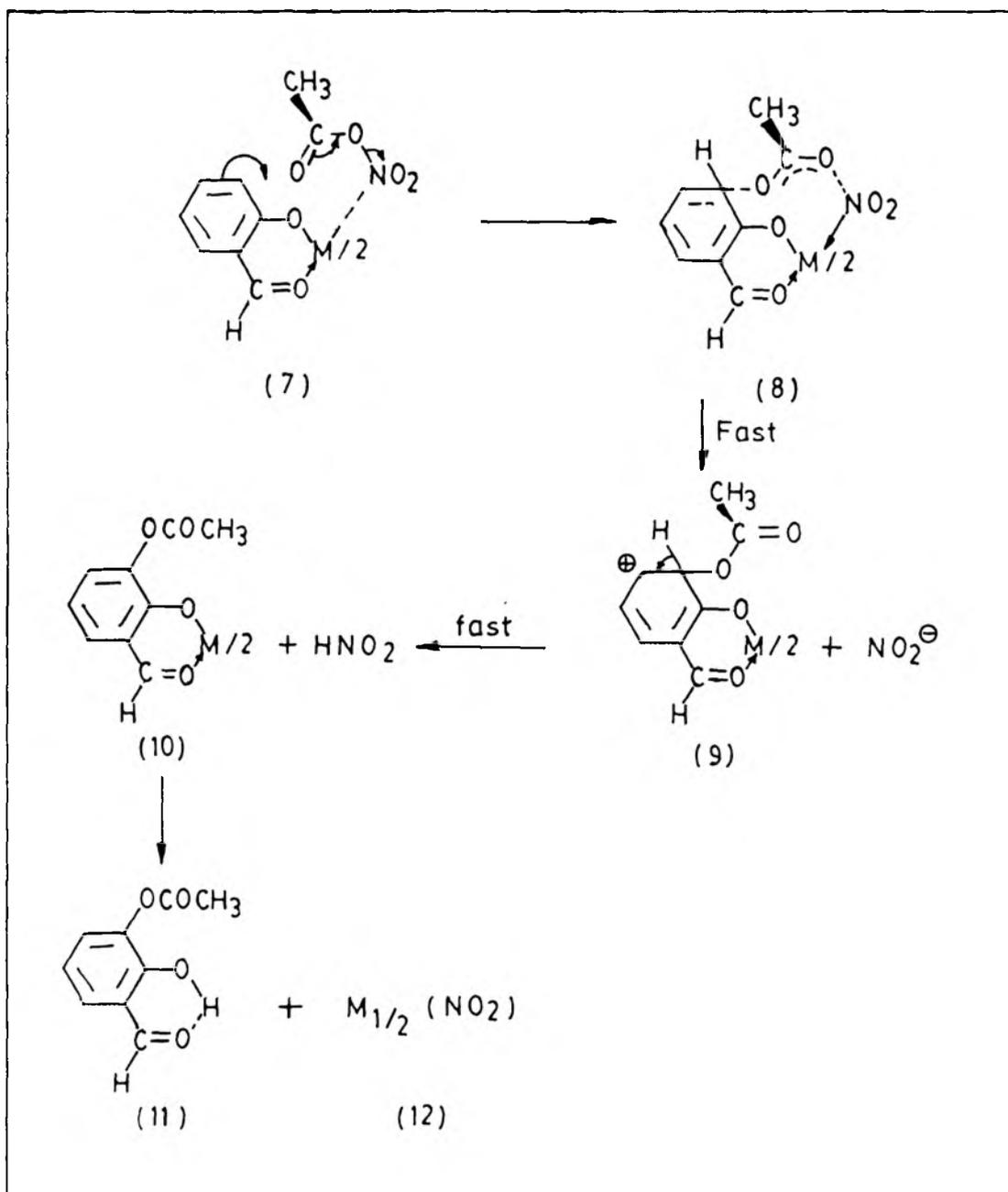


Fig.2: Mechanism of acetoxylation reaction of salicylaldehyde metal(II) complexes by acetyl nitrate.

preferred coordination with metal ion over the carbon ion, due to the obvious preferred direction of the polarisation of the acetyl nitrate. Since nitrous acid formed during these reactions was stronger than acetic acid formed during the direct reaction of acetic anhydride with the metal complex and since metal complex (10) was labile in the nitrous acid medium, no complex of the type (10) could be separated from this reaction. This reaction also indicated the role of the metal ion in directing the reaction of acetyl nitrate with the coordinated ligand.

5. References :

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