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Acylation of Phenols with Salicylic Acid Using Polyphosphoric Acid

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Acylation of 2-naphthol (**2**), 1-naphthol (**6**) and resorcinol (**11**) with salicylic acid (**1**) in the presence of PPA affords salicylate esters (**4, 7, 13 and 14**), 1,2-benzoxanthone (**5**), 3, 4-benzoxanthone (**8**), 3-hydroxyxanthone (**12**), 2-salicyloyl-1-naphthol (**9**) and 11-hydroxy-12*H*-benzo[*b*]xanthen-12-one (**10**). Compounds (**4, 5, 7, 8, 12, 13 and 14**) are identical with those obtained by heating a mixture of phenyl salicylate (**3**) and phenols (**2, 6 and 11**).

During the past few years we have been studying the reaction between phenols and organic acids in the presence of various acids including PPA. In view of the recent report on the condensation of phenols with cinnamic acids in the presence of PPA[1], we wish to place on record our results on the condensation of various phenols with salicylic acid.

A mixture of salicylic acid (**1**) and 2-naphthol (**2**) was heated with PPA under the reaction conditions used for the preparation of phenyl salicylate (**3**)[2] to give 2-naphthyl salicylate (**4**)[3] and 1, 2-benzoxanthone (**5**)[3].

As anticipated the reaction of 1-napthol (**6**) and **1** in the presence of PPA gave 1-naphthyl salicylate (**7**)[3] and 3, 4-benzoxanthone (**8**)[3] in addition to an orange red solid which was separated into alkali soluble and alkali insoluble compounds. The alkali soluble fraction gave 2-salicyloyl-1-naphthol (**9**)[4] while the alkali insoluble fraction afforded hydroxybenzoxanthone (**10**)[4-6].

In the above two reactions of **1** and naphthols (**2** and **6**) with PPA, ester was the major product in the case of **2** while benzoxanthone was the major product in the case of **6**. This behaviour of 1-naphthol (**6**) and 2-naphthol (**2**) may be attributed to the fact that the electron density on C-2 of **6** is more in comparison to that on C-1 of **2**. As a result cyclodehydration leading to **8** is the main reaction of **6** and esterification giving **4** is the major reaction of **2**.

When resorcinol (**11**) was heated with **1** in the presence of PPA, 3-hydroxyxanthone (**12**)[3], resorcinol disalicylate (**13**)[3] and resorcinol monosalicylate (**14**)[3] were obtained.

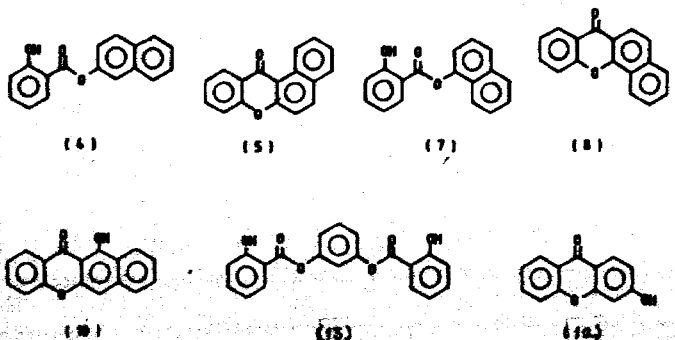
Melting points reported are uncorrected. Petroleum ether refers to the fraction b.p. 60-80°.

Reaction of naphthols (**2** *and* **6**) *with salicylic acid* (**1**): *General procedure*

A mixture of **1** (4.14 g, 0.03 mol) and 2-naphthol (**2**; 4.32 g, 0.03 mol) was added to the freshly prepared PPA [from P_2O_5 (10 g) and orthophosphoric acid (6 ml), stirred vigorously at 95° for 1 hr] and the reaction mixture was stirred at 90-95° for 24 hr. The cooled reaction product was diluted with cold water, extracted with benzene, the organic extract washed with saturated solution of $NaHCO_3$, dried ($MgSO_4$) and concentrated. The residue (5.63 g) was chromatographed over silica gel. Elution with pet ether-benzene (2:1) afforded 2-naphthyl salicylate (**4**)[3] (3 g, 53%) which recrystallized from pet ether in silvery white flakes, m.p. 95°.

Further elution with pet ether-benzene (1:9) gave 1,2-benzoxanthone (**5**)[3] (0.45 g, 8%) which recrystallized from pet ether-benzene (1:1) in white needles, m.p. 144°.

Similar reaction of **6** afforded after work-up a residue which was subjected to column chromatography. Elution with pet ether-benzene (3:1) gave upon concentration of the fraction, an orange red solid (1 g,



20%), m.p. 198-202° which was dissolved in benzene and extracted with 10% NaOH. The alkali phase was neutralized with dil HCl to give 2-salicyloyl-1-naphthol (**9**; 0.6 g, 12%), crystallized from pet ether in yellow flakes, m.p. 112° [lit. m.p. 111-13° (hexane)[4]] (Found: C, 76.6; H, 4.8. Calc. for $C_{17}H_{12}O_3$: C, 77.2; H, 4.5%). The organic extract was washed with water, dried ($MgSO_4$) and concentrated to give 11-hydroxy-12*H*-benzo[*b*]xanthen-12-one (**10**; 0.35 g, 7%), recrystallized from benzene in orange coloured fine needles, m.p. 205°[lit. m.p. 205-9° (hexane-chloroform)[4], 198-203° (C_6H_{12})[5], 200°(EtOH)[6]]. The IR, UV and PMR data of **9** and **10** were compatible with their structures.

Further elution of the column with pet ether-benzene (3:2) gave 1-naphthyl salicylate (**7**)[3] (0.2 g, 4%), which recrystallized from pet ether in white flakes, m.p. 83°.

Finally after washing out the unreacted **6** from the column, the fraction with pet ether-benzene (1:9) gave 3, 4-benzoxanthone (**8**)[3] (3 g, 60%), which recrystallized from pet ether-benzene (1:1) in white needles, m.p. 157°.

Resorcinol disalicylate (**13**), *resorcinol monosalicylate* (**14**) *and* 3-*hydroxyxanthone* (**12**)

A mixture of **1** (8.28 g, 0.06 mol) and resorcinol (**11**; 3.3 g, 0.03 mol) was reacted with freshly prepared PPA as before. The cooled reaction product was diluted with water, extracted with benzene, washed with saturated solution of $NaHCO_3$, extracted with 10% NaOH and neutralized with dil HCl to give a mixture of phenolic compounds, which were separated by column chromatography. Elution with pet ether-benzene (3:2) gave **13**[3] (0.112 g, 11.2%), which recrystallized from pet ether in silvery white flakes, m.p. 102°.

Elution with benzene-diethyl ether (19:1) gave **14**[3] (0.065 g, 6.5%), which recrystallized from benzene in white needles, m.p. 136°.

No further recovery of the organic material was possible by further elution of the column with more polar solvents. However, refluxing the heterogeneous mixture of the adsorbent and benzene followed by immediate filtration and evaporation of the solvent, gave **12**[3] (0.6 g, 60%), which recrystallized from benzene in yellow crystals, m.p. 246°, methyl ether, m.p. 129°.

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