ACETYLATION OF PHENOLS USING ACETIC ACID

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THE use of acetic acid in the acetylation of the lower alcohols is well known. The acid has also been used for the acetylation of aliphatic hydroxy acids.¹ Its ability to introduce the acetyl group into the aromatic nucleus to produce acetophenones has been recently shown by Kosolapoff.² However, its use for the acetylation of phenols does not seem to have been investigated,³ though a reference was made by Dusart and Bardy to the formation of phenyl acetate by the action of fuming hydrochloric acid at 180° on a mixture of acetic acid and phenol.⁴ Under the conditions adopted by these authors, it is doubtful whether acetic acid actually exists as such, since, in the presence of dehydrating agents, it is known to be converted into acetic anhydride⁵ or acetyl chloride, if hydrogen chloride is also present.⁶

The scope of the employment of glacial acetic acid for the acetylation of phenols has now been studied. The condensation has been carried out in the presence of phosphorus pentoxide under different conditions and the following results are obtained (table). Under the conditions of our experiments there is no indication of the formation of any acetic anhydride, and the acetylation seems to have been effected by the direct elimination of a molecule of water between the phenol and acetic acid.

No.	Phenol	Glacial acetic acid	Phosphorus pentoxide	Tempe- rature	Duration of reaction in hours	Yield of the acetyl deri- vative in g.
1 2 3 4 5 6 7 8 9	9.4 g.(0.1 mole) """"""""""""""""""""""""""""""""""""	6.0 g. (0.1 mole) "" "" 12.0 g. (0.2 mole) 18.0 g. (0.3 mole)	7 g (0.05 mole) " 14 g. (0.1 mole) 7 g. (0.05 mole) "	0° C. 35° 100° 100° 100° 100° 100° 100°	24 24 1 2 3 1 2 1 1	3.0 5.5 5.5 5.5 5.5 5.0 5.0 4.5 4.5

From the above results, the condensation seems to take place best when (1) the reactants are present in equimolecular proportions, (2) the condensing

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agent is in half molecular amounts and (3) the heating is for one hour at 100° C. Since the mixture of the reactants with phosphorus pentoxide at the room temperature produces considerable local heating and consequent decomposition, the procedure followed has been to add a cooled mixture of the reactants to well-cooled phosphorus pentoxide, further cooling the mixture in ice-water during addition. Adopting this procedure the acetylation of various simple phenols has been carried out and the acetyl derivatives are produced in 10 to 40 per cent. yields.

Though only an equimolecular amount of acetic acid takes part in the condensation, its presence in excess does not seriously affect the yields. In the case of solid phenols, consequently, acetic acid has been taken in excess to keep the phenol in solution.

Zinc chloride also effects the condensation, though the yields are lower than when phosphorus pentoxide is used.

EXPERIMENTAL

Phenyl acetate.-Dry phenol (9.4 g., 0.1 mole) and glacial acetic acid $(6 \cdot 0 \text{ g.}, 0 \cdot 1 \text{ mole})$ were mixed in a dry conical flask and cooled to zero degrees in ice. Similarly phosphorus pentoxide (7 g., about 0.05 mole) was cooled in a dry acetylation flask provided with an air-condenser and anhydrous calcium chloride tube, and the mixture of phenol and acetic acid was then carefully added to it. During the addition the mixture was shaken vigorously and cooled to avoid local development of heat and consequent decomposition. It was then kept on a water-bath the temperature of which was slowly raised to the boiling point during the course of half an hour. Heating was continued for an hour longer. The mixture was then cooled and treated with crushed ice (200 g.). When it attained the laboratory temperature, it was extracted twice with ether. From the combined ether extract (200 c.c.), the unreacted phenol was removed by extraction with 10 per cent. sodium hydroxide (50 c.c.). The ether solution was then washed with water and dried over anhydrous sodium sulphate. On the removal of the solvent, phenyl acetate was obtained, and purified by redistillation. B.P. 196° C. The yield was 5.5 g.

Using anhydrous zinc chloride as the condensing agent in place of phosphorus pentoxide, the yield of phenyl acetate was 3.0 g. from 9.4 g. of phenol.

m-Tolyl acetate.—The same procedure as in the case of phenyl acetate was followed. From 10 g. of *m*-cresol, 6 g. of glacial acetic acid and 7 g. of phosphorus pentoxide, heating for an hour on the boiling water-bath, $4 \cdot 7$ g. of the ester boiling at 212° C. was obtained.

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Resorcinol diacetate.—By adopting the general procedure described above, the acetylation of resorcinol was tried. From 11 g. of resorcinol and 12 g. of glacial acetic acid, only 1.5 g. of diacetyl resorcinol, boiling at 278° C., was obtained.

Since there was the chance for mono-acetylation also to take place, the alkaline extract from the ethereal solution containing the reaction products was diluted with water to 200 c.c., acidified with hydrochloric acid and then extracted with ether, when a small amount of resorcinol monoacetate, (0.5g.), b.p. 183° C., was obtained [Found: C, 63.35; H, 5.41; C₆H₄ (OH) (OCO CH₃) requires C, 63.15 and H, 5.26%]. The oil was somewhat soluble in water and freely in alkalis and the aqueous solution gave a purplish violet colour with ferric chloride.

Catechol diacetate.—When the mixture of catechol (11 g.) and acetic acid (12 g.) was added to phosphorus pentoxide (7 g.) as before and heated for an hour on a boiling water-bath, 1 g. of the diacetyl derivative, melting at 63° C., was obtained. Mixed m.p. with the sample obtained from catechol through the action of acetic anhydride and anhydrous sodium acetate was undepressed. No lower product of acetylation could be isolated.

Pyrogallol triacetate.—The reaction between pyrogallol and glacial acetic acid was carried out as in the previous case. Only 1 g. of the triacetyl derivative, m.p. 165° C., was obtained from 12.6 g. of pyrogallol and 18 g. of glacial acetic acid.

a-Naphthyl acetate.—From 14.5 g. of a-naphthol and 12 g. of glacial acetic acid, 3 g. of the acetate was obtained. It melted at $48-49^{\circ}$ C.

 β -Naphthyl acetate. 4.0 g. of the acetate, m.p. 70° C., was obtained from 14.5 g. of β -naphthol and 12 g. of glacial acetic acid.

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SUMMARY

Acetylation of phenols with glacial acetic acid in presence of phosphorus pentoxide gives the O-acetyl derivatives in yields of 10 to 40 per cent.

References

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