

THE IODINATION OF AROMATIC COMPOUNDS

II. THE IODINATION OF AROMATIC ETHERS AND OF 2-NAPHTHOL

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Summary

A rapid process for the iodination of aromatic ethers is described, the ether in 95 per cent. ethanol being treated with iodine and mercuric oxide at an elevated temperature. Anisole and the 2-alkoxy-naphthalenes give high yields of iodo-compounds by this process.

1-Iodo-2-naphthol is readily prepared by the action of iodine and alkali or iodine and mercuric oxide on 2-naphthol.

A mechanism is suggested for the iodination of phenols and ethers in the presence of mercuric oxide.

I. INTRODUCTION

Although low temperatures and anhydrous solvents are usually employed in the direct iodination of aromatic ethers by means of iodine and mercuric oxide it is now found that in the presence of water and by the use of an elevated temperature the reaction period is reduced very considerably without decrease in the yield and purity of the product. The marked decrease in the iodination of the phenol ethers, the rates decreasing in the order $\text{CH}_3\text{O}- > \text{C}_2\text{H}_5\text{O}- > \text{HOOC}\cdot\text{CH}_2\text{O}- > \text{C}_6\text{H}_5\cdot\text{CH}_2\text{O}-$, is not nearly so apparent with the 2-naphthol ethers, all of which are readily iodinated (Table 1).

II. EXPERIMENTAL

(i) *Preparation of p-Iodo-anisole*.—Iodine (19.9 g.) is added in four portions during 10 minutes, with vigorous agitation between each addition, to a suspension of mercuric oxide (13.1 g.) in a 95% ethanol solution (60 cc.) of anisole (8.5 g.), the temperature of the reaction mixture being maintained at 50–60 °C. After shaking for a further five minutes the temperature is raised to the boiling point of alcohol and the insoluble mercury compounds are removed by filtration and washed with boiling alcohol (30 cc.). On cooling, the filtrate, which deposits a mass of crystals, is poured into water (350 cc.) containing potassium iodide (3.0 g.). The light yellow, crystalline precipitate (17.2 g.) which separates is collected and recrystallized from 85% ethanol, colourless plates, melting at 51 °C. (lit. 50–51 °C.), being obtained (15.2 g., i.e. 83% of the theoretical yield).

The iodo ethers which have been prepared by this method are set out in Table 1.

1-Iodo-2-naphthyl benzyl ether, colourless plates, melting at 86–7 °C. from alcohol, and 1-iodo-2-naphthyl ethyl ether, colourless elongated prisms, melting at 75 °C. from petroleum ether, have not been previously described. The position of attachment of the iodine was proved by the synthesis of each from 1-iodo-2-naphthol by alkylation in the usual manner.

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(ii) *Iodination of 2-Naphthol*.—1-Iodo-2-naphthol is an unstable substance for which only one satisfactory synthesis has been described(1). Although Messinger and Vortmann(2) isolated a highly coloured, amorphous product of indefinite composition by treating 2-naphthol in aqueous alkaline solution at 50 °C. with iodine, crystalline 1-iodo-2-naphthol is readily obtained in almost quantitative yields when slightly less than the theoretical quantity of iodine reacts with 2-naphthol in ice-cold, alcoholic potassium hydroxide solution.

Iodine (3.48 g.) is added gradually during 15 minutes to an agitated, alcoholic solution (10 cc.) of 2-naphthol (2.0 g.) and potassium hydroxide (1.60 g.) maintained at 5 °C. The flocculent, off-white precipitate which separates when the yellow, alcoholic solution is poured into dilute, aqueous sulphuric acid (80 cc.) is collected, washed thoroughly with water, and recrystallized from acetic acid. Colourless needles, melting at 94 °C., are obtained (3.44 g., i.e. 94% of the theoretical yield).

TABLE 1

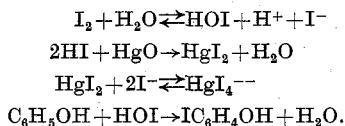
THE IODINATION OF AROMATIC ETHERS IN ALCOHOLIC SOLUTION AT 50–60 °C. IN THE PRESENCE OF MERCURIC OXIDE

Ether	Reaction Period (min.)	Product	Yield (%)	Melting Point (°C.)	Melting Point (lit. °C.)
Anisole	15	<i>p</i> -Iodo-anisole	83	51	50–1
Phenetole	40	<i>p</i> -Iodo-phenetole	67	28–9	29
Phenyl benzyl ether ..	60	<i>p</i> -Iodophenyl benzyl ether	Small	62	62
Veretrole	25	4-Iodo-veratrole	60	172–4/ 32 mm.	
Phenoxy-acetic acid	30	4-Iodo-phenoxy-acetic acid	62	156	155–6
2-Methoxy-naphthalene	20	1-Iodo-2-methoxy-naphthalene	89	88	88
2-Ethoxy-naphthalene	20	1-Iodo-2-ethoxy-naphthalene	82	75	
2 - Benzyloxy - naphthalene	20	1 - Iodo - 2 - benzyloxy - naphthalene	80	86–7	
2-Naphthoxy-acetic acid	30	1-Iodo-2-naphthoxy-acetic acid	71	174	d., 145, melts, 203–10

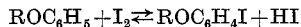
1-Iodo-2-naphthyl acetate, not previously described, prepared by the action of fused sodium acetate and acetic anhydride on 1-iodo-2-naphthol, is obtained from alcohol as small, colourless, brittle crystals, melting at 69 °C.

1-Iodo-2-naphthol is readily obtained by the following process: Iodine (3.50 g.) is added cautiously during 30 minutes to a mixture of mercuric oxide (2.35 g.) and 2-naphthol (2.0 g.) in alcohol at 5 °C., the reddish colour of iodine being allowed to disappear before each new addition is made. Vigorous agitation is continued for 10 minutes after completing the addition of iodine, the insoluble mercury compounds then being filtered off and washed with cold alcohol (5 cc.). The light yellow precipitate which separates when the alcoholic filtrate is poured into water (175 cc.) is collected, washed with dilute potassium iodide solution and water, and dried (3.70 g.). This product is dissolved in excess of glacial acetic acid with gentle warming. On cooling, tufts of colourless needles, melting at 93.5 °C. (lit. 93–4 °C.), separate (1.54 g.). On adding water to the warmed filtrate and cooling, long colourless needles, melting at 93 °C., separate (1.91 g.). The yield of 1-iodo-2-naphthol is therefore 92%.

In the presence of mercuric iodide the rate of reaction between iodine and 2-naphthol is accelerated considerably. The iodination of phenols in the presence of mercuric oxide therefore probably follows the course:



Since *p*-iodo-anisole and 1-iodo-2-methoxy-naphthalene are recovered quantitatively when equimolecular quantities of the iodo-ether and hydrogen iodide are agitated in alcoholic solution at 60 °C. for 30 minutes, the suggestion(3, 4) that the function of mercuric oxide in the iodination of aromatic ethers is to prevent the reversal of the reaction



is untenable. It is probable that the active agent is hypoiodous acid and that the role of mercuric oxide in the iodination of ethers is similar to that in the iodination of phenols.

III. REFERENCES

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