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IODOBENZENE DICHLORIDE II - AN EFFICIENT REAGENT FOR DEOXIMATION

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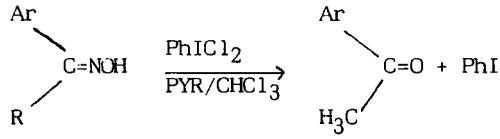
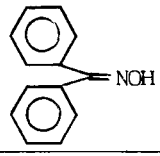
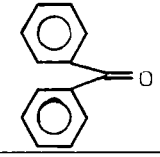
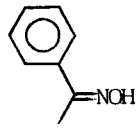
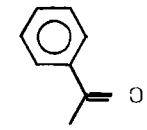
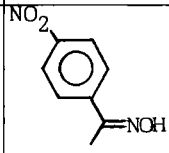
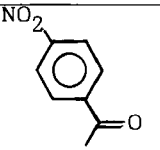
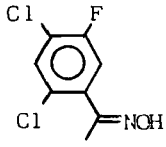
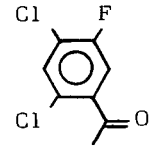
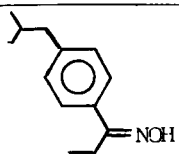
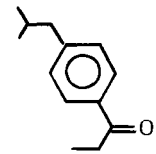
Summary : Reaction of Aromatic and Aralkyl ketoximes with iodobenzene dichloride leads to the formation of corresponding ketones in good yields in a single pot reaction.

The cleavage of oximes to aldehydes or ketones (scheme) is of considerable practical interest since oximes can be prepared from noncarbonyl compounds[2-6] where deoximation could lead to a new route for the preparation of carbonyl compounds. A number of methods have been reported for the deoximation of aldoximes and ketoximes[7-11] and search for newer methods is of continued interest[12]. Hypervalent iodine compounds have been extensively studied in recent years for bringing about various transformations[13]. We report here a simple method of conversion of aromatic and aralkyl ketoximes to ketones using iodobenzene dichloride. The treatment of several aromatic and aralkyl ketoximes with iodobenzene dichloride in presence of pyridine gave the corresponding ketones in good yield, under very mild conditions. (Scheme & Table).



Scheme

TABLE

Sl. No.	Oxime	Reaction Conditions	Product	Yield
1		3 h/10°C		80%
2		3 h/10°C		75%
3		3 h/10°C		76%
4		3 h/10°C		65%
5		3 h/10°C		80%

To test the generality of the reaction a representative set of aromatic ketoximes were deoximated (Table). This method when applied to aldoximes gave corresponding nitrile oxides.[14] Aliphatic ketoximes did not give the ketones but gave a deep blue coloured solution on treatment with iodobenzene dichloride suggestive of the formation of chloronitroso compound.[15]

Experimental

One equivalent of iodobenzene dichloride and two eq. of pyridine are used in all the reactions. $CHCl_3$ is the solvent used in all the reactions. Products were characterised by comparison with authentic samples (IR, ^1H NMR, Glc). All yields refer to isolated yields isolated by column chromatography on silicagel.

Deoximation of benzophenoneoxime (Typical Procedure)

To a stirred solution of benzophenoneoxime (1.97 g; 0.01 M) in chloroform (35 ml), cooled in ice-ice water, pyridine (1.58 g; 0.02 M) is added. To this stirred solution iodobenzene dichloride (2.74 g; 0.01 M) is added in portions during 15 min, while maintaining the temperature around 10°C. Stirring at about 10°C is continued for 3 h. Water (15 ml) or dilute hydrochloric acid (5%, 15 ml; more convenient procedure) is added and stirred for 10 min. Organic layer separated and washed with water till washings are neutral. Chloroform layer briefly dried over anhydrous sodium sulfate and solvent distilled off under reduced pressure. Residue subjected to high vacuum distillation to isolate the pure ketone.

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