Sodium Metaperiodate: a Mild Oxidizing Agent for the Generation of Di-imide from Hydrazine

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Summary Di-imide, generated by the sodium metaperiodate oxidation of hydrazine is a particularly useful reducing system for compounds which contain readily oxidized functional groups.

RECENTLY, we had to convert the thiophen derivative (I) into its dihydro-analogue (II) by reduction. Catalytic procedures were ineffective presumably because of catalyst poisoning by (I). Di-imide reductions, carried out by oxidation of hydrazine with hydrogen peroxide[1] or ferricyanide,[2] while effective in reducing the double bond of (I) also caused oxidation of the sulphide function to its corresponding sulphone (III). Other non-oxidative methods of generating di-imide proved to be either difficult experimentally or not amenable to use on a small scale.[3]

In looking for other mild oxidative methods of generating di-imide from hydrazine, our attention was drawn to a report of the potassium periodate oxidation of substituted hydrazines.[4] We found that sodium metaperiodate efficiently converts hydrazine into di-imide in a variety of aqueous organic solvent systems.

The use of sodium metaperiodate and hydrazine permits the quantitative di-imide reduction of thiophen (I) into (II) without concomitant formation of either sulphone (III) or sulphoxide (IV). A variety of other unsaturated compounds has been reduced by this method (Table). In a typical procedure, 2·5 mmol of sodium metaperiodate in 5 ml of water was added dropwise (1 h) to a mixture of olefin

TABLE

Substrate	Product	Yield (%)
Azobenzene	Hydrazobenzene	95
Acenaphthylene	Acenaphthene	91
Cinnamic acid	3-Phenylpropionic acid	87
Ethyl cinnamate	3-Phenylpropionic acid	80
Phenylpropiolic acid	3-Phenylpropionic acid	85
Maleic anhydride	Succinic anhydride	95

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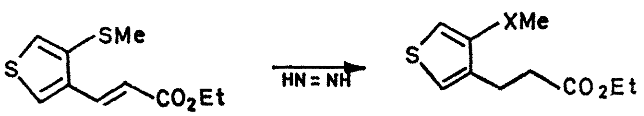
(I)

(II; X = S)
(III; X = SO_2)
(IV; X = SO)

(0·5 mmol), hydrazine hydrate (100%, 20 mmol), 2 drops of saturated copper sulphate, and 2 drops of glacial acetic acid dissolved in dimethyl sulphoxide (3 ml).‡

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‡ Tetrahydrofuran, acetic acid, dioxan, ethanol, methanol, and glyme have been used as solvents for these reactions.

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[4] D. J. Cram and J. S. Bradshaw, *J. Amer. Chem. Soc.*, 1963, **85**, 1108.