

**HYPERVALENT IODINE AS GOOD LEAVING GROUP:
OXIDATIVE REARRANGEMENT OF 1-iodo-2-methoxy-2-arylalkanes.**

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Summary - A new example of the good leaving group properties of hypervalent iodine is reported: oxidative rearrangement of 1-iodo-2-methoxy-2-arylalkanes **1** (R=alkyl) provides, via 1,2-aryl shift, alkyl benzyl ketones **3** in good yields.

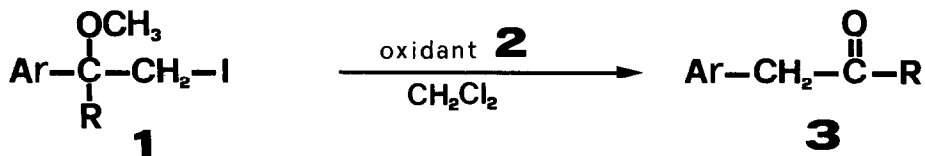
Treatment of alkyl iodides with peroxy acids has been the subject of several recent papers.¹⁻⁴

This oxidation results in the formation of iodoso intermediates (R₁O_n), in which n is an integer sufficiently large that the system in question, will undergo nucleophilic substitution or elimination.¹⁻²

Recently, Higgins and Thomas reported⁵ that the oxidation of α-iodoalkyl aryl acetals gives rise to the formation of esters of 2-arylalkanoic acids; hypervalent iodine intermediates have been proposed to account for this behaviour.⁵⁻⁶

This prompts us to report our results⁷ on the oxidative rearrangement of 1-iodo-2-methoxy-2-arylalkanes.

As a matter of facts, **1** (R=alkyl) are converted into the corresponding alkyl benzyl ketones **3** when reacted with peracids or with hydrogen peroxide.



Thus, treatment of 10 mmol of **1** (R=CH₃, Ar=phenyl) with 13 mmol of m-chloroperbenzoic acid (m-CPBA) in dichloromethane at 30°C, for 1 h, afforded 1-phenyl-propan-2-one **3** (R=CH₃, Ar=phenyl) in 93% yield (see Table).

m-CPBA is used in slight excess with respect to **1** when electron donating group are present on the aromatic ring of **1**. In the case of aromatic ring, bearing electron withdrawing groups, a larger excess of m-CPBA has to be used (Table).

Other organic peracids (i.e. peracetic, performic, permaleic, etc.) or mixture of anhydrous hydrogen peroxide and of organic carboxylic acids (acetic or trifluoroacetic) or mixture of 60% hydrogen peroxide and of anhydrides (maleic, acetic) in dichloromethane gave results similar to those obtained with m-CPBA. It is worth noting that 1-iodo-2-methoxy-2-arylethanes **1** (R=H), under analogous reaction conditions, gave rise to a substantial amount of the elimination products.

The reported reactivity is ascribed to the formation of hypervalent iodine species (R₁O_n, n ≥ 1) which thanks to its good leaving group properties promote 1,2-aryl shift in **1**.

Table: Synthesis of alkyl benzyl ketones **3** by oxidation of 1-iodo-2-methoxy-2-aryllkanes **1** with *m*-CPBA.

Ar	R	<i>m</i> CPBA (mmol)	3 (yield %) ^b	1 (conversions %) ^c
phenyl	CH ₃	10	88	90
phenyl	" ₃	13	93	100
3-methylphenyl	"	11	81	90
4-methylphenyl	"	11	92	95
4-methoxyphenyl	"	11	90	95
4-biphenyl	"	11	90	96
4-chlorophenyl	"	11	50	58
4-chlorophenyl	"	25	80	92
4-fluorophenyl	"	30	73	100
phenyl	<i>n</i> -butyl	11	85	90

- a) Typical procedure: a solution of *m*-CPBA (11 mmol) in CH₂Cl₂ (25 mL) was added, at 0°C, to a solution of **1** (10 mmol) in dichloromethane (25 mL). The reaction mixture was kept at 0°C for 1 h. The mixture was poured into 10% aqueous sodium carbonate solution; the organic layer was separated, washed with aqueous sodium thiosulphate solution, and dried on sodium sulphate. The solvent was evaporated under reduced pressure and the crude **3** was purified by column chromatography (SiO₂, hexane: AcOEt-95 : 5 as eluent).
- b) Yields are based on the introduced **1** and are calculated on isolated pure products. Products **3** were identified by comparison with authentic samples.
- c) Conversions are calculated on the reaction crude by G.L.C. using biphenyl as internal standard (OV 17-10% Chromosorb AVTMCs; 150°C → 220°C, 5°C/min).

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