Aluminium Triiodide Mediated Reductive Dehalogenation of α-Halocarbonyl Compounds and Trapping of the Aluminium Enolate Intermediate *via* Aldol Reaction

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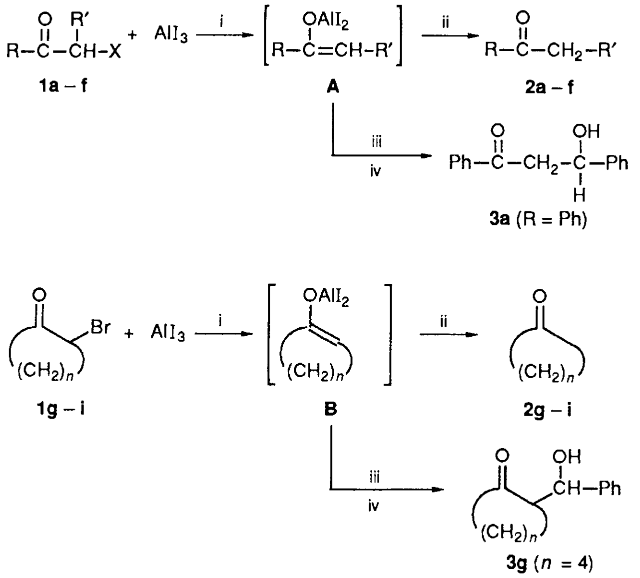
Aluminium triiodide has been conveniently used for reductive dehalogenation and aldol condensation of α-halocarbonyl compounds *via* aluminium enolate.

Selective reduction of the carbon–halogen bond is of considerable interest and great importance in synthetic organic chemistry.[1,2] Much attention has been paid to the reductive dehalogenation of α-haloketones using Si, Fe, Te, P, Sn and heterocyclic compounds[3–6] but there has been no report on the use of aluminium reagents as dehalogenating agents in organic synthesis. Because of renewed interest in the chemistry of aluminium,[7–9] we anticipated that the inexpensive aluminium reagent should lead to very useful synthones. More recently the metal enolate induced aldol condensation has become one



1a, R = Ph, X = Br, R′ = H	**2a**, R = Ph, R′ = H
1b, R = p-BrC$_6$H$_4$, X = Br, R′ = H	**2b**, R = p-BrC$_6$H$_4$, R′ = H
1c, R = p-ClC$_6$H$_4$, X = Cl, R′ = H	**2c**, R = p-ClC$_6$H$_4$, R′ = H
1d, R = Ph, X = Br, R′ = Ph	**2d**, R = R′ = Ph
1e, R = PhNH, X = Cl, R′ = H	**2e**, R = PhNH, R′ = H
1f, R = p-ClC$_6$H$_4$NH, X = Cl, R′ = H	**2f**, R = p-ClC$_6$H$_4$NH, R′ = H
1g, n = 4	**2g**, n = 4
1h, n = 3	**2h**, n = 3
1i, n = 5	**2i**, n = 5

Scheme 1 *Reagents and conditions:* i, MeCN, 80 °C; ii, H$_2$O; iii, PhCHO, 80 °C; iv, H$_2$O

of the most important tools for stereocontrolled carbon–carbon formation.[10–12] However, the utility of aluminium promoted aldol reactions has received scant attention possibly due to the lack of an effective procedure for converting carbonyl compounds into aluminium enolates.[13] In this Communication we report the utility of aluminium triiodide as a mild and selective reagent for efficient reductive dehalogenation and aldol condensation of α-halocarbonyl compounds *via* facile generation of an aluminium enolate intermediate.

In a typical experiment 2-bromoacetophenone (1 mmol) was slowly added to a mixture of freshly prepared AlI$_3$ (2 mmol)[14] and MeCN (25 ml) under an atmosphere of nitrogen. The mixture was refluxed for 1 h, poured onto cold water, stirred and then extracted with CH$_2$Cl$_2$ (3 × 20 ml). The CH$_2$Cl$_2$ layer was washed with Na$_2$S$_2$O$_3$ solution (20%) dried over anhydrous K$_2$CO$_3$ and then concentrated to give crude acetophenone, which was purified by column chromatography (silica gel, Merck, Kiselgel 60, 70–230 mesh, 1 × 20 cm, CH$_2$Cl$_2$–hexane 1 : 3 v/v) to give pure product (92%, b.p. 202 °C). Products from the reaction of similar substrates and ω-haloacetanilides were purified by column chromatography and identified by comparison of (IR, NMR, m.p.) with authentic samples. The results obtained are summarized in Table 1.

In order to investigate the participation of the intermediate aluminium enolate **A**, the reaction mixture obtained from 2-bromo-acetophenone **1a** and AlI$_3$, was treated with benzaldehyde and a cross-aldol product **3a** was isolated in high yield (80%). The product **3a** was identified using spectral analysis and comparison of m.p. with an authentic sample.[10] Similarly the aluminium enolate **B** obtained from 2-bromo cyclohexanone **1g** following treatment with AlI$_3$ could conveniently react with benzaldehyde to afford the aldol product **3g** in 75% yield. Interestingly, the reported aldol condensation required no promotion of any extra Lewis acid catalyst[10] and the self-condensed aldol product was isolated[15] only as a minor by-product (*ca.* 4%).

Thus, the AlI$_3$-mediated aldol condensation of **1a** or **1g** clearly revealed the facile formation of aluminium enolate **A** and **B**, however, the enolate intermediates could not be isolated, rather, decomposed products were obtained. Monitoring of the reaction of **1a** with AlI$_3$ by NMR spectroscopy has shown the appearance of vinylic proton signals due to intermediate **A** at δ 4.35 and 4.92 (J 1.7 H).

Table 1 Reductive dehalogenation of α-haloketones with AlI$_3$

Compound, **1**	Product, **2**	t/h	m.p. (b.p.)[a]/°C	Yield(%)[b]
a	**a**	1	82(12)	92
b	**b**	1	50–52	90
c	**c**	1	232(760)	88
d	**d**	1.5	60–61	80
e	**e**	2	113–115	92
f	**f**	2	177–179	94
g	**g**	1.5	47(15)	84
h	**h**	1.5	131(760)	91
i	**i**	1.5	179(760)	85

[a] B.p.(mmHg); [b] Isolated yields. All products exhibited NMR, IR, and mass spectra consistent with the assigned structures.

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