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$PbBr_2$/Al-Promoted Reductive Addition of 1,1,1-Trichloro-2,2,2-trifluoroethane (Flon) to Aldehydes

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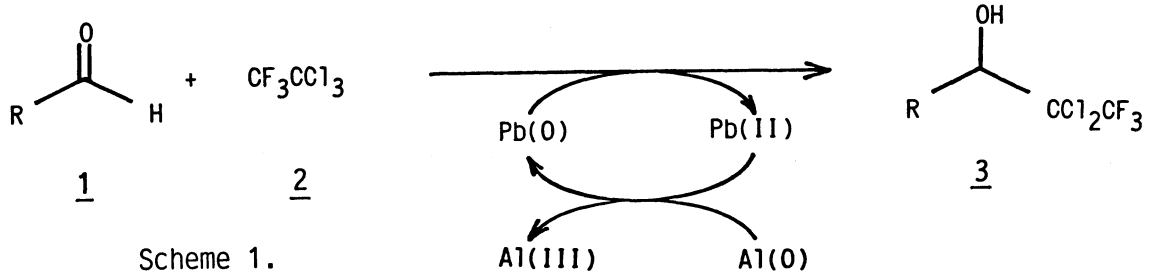
Introduction of CF_3CCl_2 unit into aldehydes with CF_3CCl_3 has been performed successfully by the action of catalytic $PbBr_2$ and Al foils in DMF.

Introduction of fluorine-substituted alkyl groups into organic molecules is a promising strategy for the synthesis of the fluorine-substituted analogues of bioactive compounds.[1] In view of remarkable activity of the fluorine-substituted analogues, various perfluoroalkyl metals (Rf-Mtl) have been intensively studied as a potent reagent for this purpose.[2]

Recently, Hiyama and co-workers have reported an operationally simple and efficient procedure for the introduction of CF_3CX_2 unit (X= Br, Cl) into aldehydes with CF_3CX_2ZnX (X= Br, Cl) generated by treatment of CF_3CX_3 with catalytic CuCl and Zn powder in DMF.[3] This prompted us to report our own studies on the reductive addition of CF_3CCl_3 to aldehydes in a catalytic $PbBr_2$/Al foils/DMF system.



1 2 3

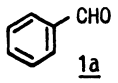
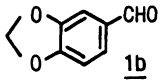
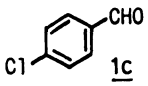
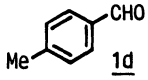
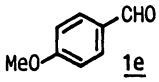
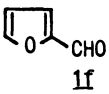
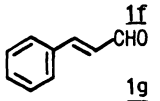
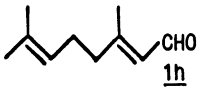
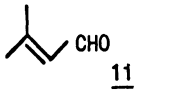
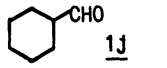
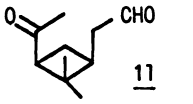
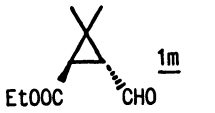
Scheme 1.

A typical experimental procedure (Entry 2 in Table 1) is as follows: Into a stirred mixture of $PbBr_2$ (0.1 mmol) and finely cut Al foils (1 mmol) in DMF (5 ml) were added benzaldehyde (**1a**, 1 mmol) and CF_3CCl_3 (**2**, 2 mmol) and the stirring was continued at ambient temperature until most of **1a** was consumed (2 h). Usual workup of the mixture afforded the adduct **3a** (91%). The representative results are shown in Table 1. Aromatic aldehydes were smoothly converted to the adducts **3** (Entries 1- 7). The reaction took place even at 4 °C though prolonged reaction time was required to complete the reaction (Entries 5- 7). Upon the reaction with α,β-unsaturated aldehydes, 1,2-addition took place exclusively (Entries 8- 10). Aliphatic aldehydes were less effective; indeed excess CF_3CCl_3 was required to achieve moderate yields of the adducts **3** (Entries 10, 13, and 14). Under similar conditions, ketones, e.g., acetophenone, cyclohexanone, and ethyl 2-oxopropionate, were recovered intact.

As demonstrated above, the combination of catalytic $PbBr_2$ and Al foils is a

promising promoter for the reductive addition to aldehydes (1 → 3), and almost comparable with CuCl/Zn.[3] The presence of both $PbBr_2$ and Al foils is indispensable since neither Pb, $PbBr_2$, nor Al foils alone effected the aldehyde addition at all. The detailed mechanism is still unclear, but it is likely that the in situ generated Pb(0) on the Al foils (Scheme 1) is effective for the formation of organometal (CF_3CCl_2PbCl) as well as the subsequent addition to aldehydes.

Table 1. Reaction of CF_3CCl_3 with Aldehydes in a $PbBr_2$/Al/DMF System[a]

Entry	1	2 (equiv.)	Time h	Yield[b] %
1	 1a	1.2	3	83
2	1a	2	2	91
3	 1b	2	2	91
4	 1c	2	2	89
5	 1d	2	10[c]	91
6	 1e	2	10[c]	88
7	 1f	2	4[c]	72
8	 1g	2	2	91
9	 1h	2	12	77
10	1h	4	6	92
11	 11	2	3	63
12	 1j	2	2	50
13	 1k	4	6[c]	48
14	 11	4	6[c]	62[d]
15	 1m	2	10	49[e]

a) Carried out in the manner as described in the text unless otherwise noted. b) Isolated yields. c) Carried out at 4 °C. d) The keto carbonyl was retained intact. e) Aldehyde 1m (18%) was recovered.

References

1) "Biomedical Aspects of Fluorine Chemistry," ed by R. Filler and Y. Kobayashi, Elsevier Biomedical Press, Amsterdam (1982); F. A. Smith, CHEMTECH, 1973, 422; R. Filler, ibid., 1974, 752.

2) For example: P. G. Gassman and N. J. O'Reilly, Tetrahedron Lett., 26, 5243 (1985); L. S. Chen, G. J. Chen, and C. Tamborski, J. Fluorine Chem., 26, 341 (1984); T. Kitazume and N. Ishikawa, J. Am. Chem. Soc., 107, 5186 (1985); S. Benefice, H. Blancou, and A. Commeyras, Tetrahedron, 40, 1541 (1984); and references cited therein. Any perfluoroalkylleads have not hitherto disclosed.

3) M. Fujita, T. Morita, and T. Hiyama, Tetrahedron Lett., 27, 2135 (1986).

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