Pergamon

Tetrahedron Letters 43 (2002) 3783–3784

TETRAHEDRON
LETTERS

Iodine-catalysed allylation of aldehydes with allyltrimethylsilane[†]

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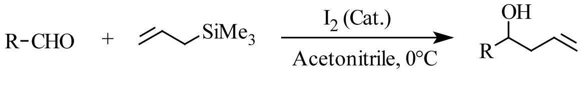
Received 22 August 2001; revised 18 February 2002; accepted 28 February 2002

Abstract—Iodine efficiently catalyses the allylation of both aromatic and aliphatic aldehydes with allyltrimethylsilane in acetonitrile at 0°C to afford the corresponding homoallyl alcohols in high yields in a short reaction time. © 2002 Elsevier Science Ltd. All rights reserved.

Allylation of aldehydes with allyltrialkylsilanes is one of the most powerful C–C bond forming reactions in organic synthesis. Generally, strong Lewis acids[1] such as $TiCl_4$, BF_3–OEt_2, $NbCl_5$ and $SnCl_4$ were known to catalyse these reactions. Recently, several metal triflates[2] such as $Sc(OTf)_3$, $Yb(OTf)_3$, $Zr(OTf)_4$ and $Hf(OTf)_4$ were found to be effective for this transformation. But in most of the cases either a long reaction time or drastic reaction conditions were employed. However, many of these Lewis acids are moisture sensitive and metal triflates are highly expensive. Therefore, the development of new reagents with greater efficiency, convenient procedures and delivering better yields is of interest.

In continuation of our interest in the applications of iodine for various transformations,[3] we herein report a mild convenient and rapid method using iodine as an efficient catalyst for allylation of both aromatic and aliphatic aldehydes with allyltrimethylsilane using a catalytic amount of elemental iodine (Scheme 1). The treatment of benzaldehyde with allyltrimethylsilane in the presence of 0.2 equiv. of iodine in acetonitrile afforded the corresponding homoallyl alcohol in 90% yield. Similarly several aliphatic and aromatic aldehydes reacted well at 0°C in acetonitrile to give the corresponding homoallyl alcohols in excellent yields. The reactions proceeded smoothly at 0°C with high selectivity. The products were isolated in high yields after a short reaction time (1 min). The generality of this reaction is evident from the results summarised in Table 1 which shows that a variety of aromatic and aliphatic aldehydes are converted into the corresponding homoallyl alcohols in high yields. The method does not involve anhydrous solvents or stringent reaction conditions and no additives or acidic promoters are required. Acetonitrile is the solvent of choice giving the best results. The method has the advantages of using inexpensive reagents, greater selectivity, operational simplicity, improved yields, enhanced rates and simple experimental work up procedures.



Scheme 1.

As to the role of iodine, it could be reacting with the formation of trimethylsilyl iodide, indeed this process is known,[4a] and it may be that it is the trimethylsilyl iodide which catalyses these reactions. To test this hypothesis, we carried out the reaction with various aliphatic and aromatic aldehydes and allyltrimethylsilane in the presence of trimethylsilyl iodide (0.2 equiv.) under otherwise identical conditions. The products obtained were identical to those obtained when iodine was employed. A comparable catalysis of the reaction between allylsilanes and acetals by trimethylsilyl iodide has been reported.[4b]

In conclusion, iodine is found to be a superior, efficient catalyst for the allylation of various aldehydes with allyltrimethylsilane under very mild and convenient conditions. The present procedure provides a novel, efficient and general methodology for the preparation of homoallyl alcohols in high yields. The procedure is very simple, quick and is one which may find use in organic synthesis.

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[†] IICT Communication No. 4617.

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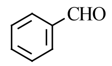
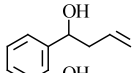
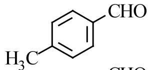
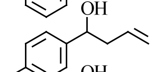
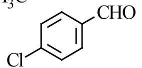
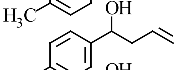
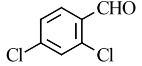
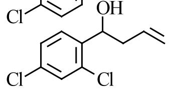
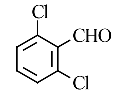
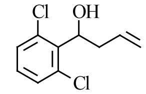
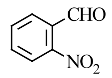
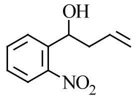
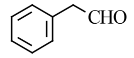
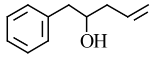
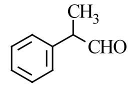
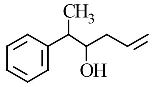
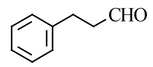
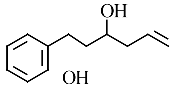
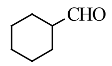
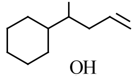
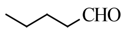
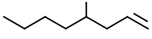
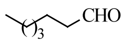
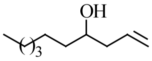
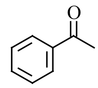
PII: S0040-4039(02)00439-2

Table 1. Conversion of aldehydes into homoallyl alcohols

Entry	Substrate	Product[a]	Time (sec.)	Yield (%)[b]
a)			50	90
b)			55	93
c)			60	92
d)			60	89
e)			70	86
f)			60	88
g)			65	85
h)			60	84
i)			60	86
j)			65	84
k)			60	82
l)			60	80
m)		No reaction	60	--

a) All the products were characterised by ^{1}H NMR and mass spectroscopy.
b) Isolated yields after column chromatography.

Typical procedure: To a stirred mixture of aldehyde (**a**, 0.106 g, 1 equiv.) and allyltrimethylsilane (0.19 ml, 1.2 equiv.) in dry acetonitrile at 0°C, iodine (0.05 g, 0.2 equiv.) was added. After 50 s the resulting mixture was quenched with aqueous sodium thiosulphate and extracted with diethyl ether (3×10 ml). The combined organic layers were dried over anhydrous sodium sulphate, and the solvent was evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel (Merck, finer than 200-mesh, hexane/ethyl acetate, 4:1) to afford pure product, characterised by ^{1}H NMR and mass spectroscopy.

Acknowledgements

P.K.C. and S.A. thank CSIR, New Delhi for the award of fellowships.

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