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Communication

Solvent-Free, Microwave-Assisted Conversion of Tosylates into Iodides*

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A highly efficient method for the conversion of primary tosylates into the corresponding iodides is outlined. The method involves heating a neat mixture of the tosylate and solid sodium iodide in a microwave cavity. Reaction times are short, usually about 60 minutes, delivering high yields. This procedure is especially useful for the in situ generation of volatile primary iodides, and for most of the primary iodides, the crude product is sufficiently pure.

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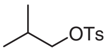
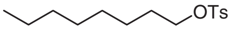
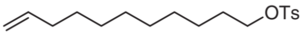
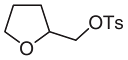
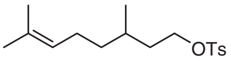
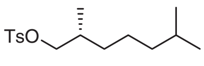
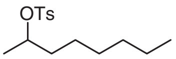
We recently reported a new approach to chiral isoprenoid natural product synthesis based on the reductive alkylation of chiral lactones.[1] From this work it transpired that we required a method for the rapid conversion of tosylates into iodides. The current method involves treatment of a tosylate with excess sodium iodide in refluxing acetone solution.[2] Reaction times are typically around 12 hours. It seemed likely that the use of microwave irradiation would reduce the reaction time. Indeed we found this to be the case and also discovered that no solvent was required.

$$\underset{\textbf{1a–g}}{\mathrm{R-OTs}} \xrightarrow{\text{3 equiv. NaI, neat}} \underset{\textbf{2a–g}}{\mathrm{R-I}}$$

Scheme 1. Conversion of tosylates to iodides.

The conversion of tosylates into iodides employing, for example, a modified Finkelstein reaction[3] (i.e. refluxing tosylates and NaI in acetone for several hours) is a well-established procedure.[2] In order to reduce the reported reaction times, we

Table 1. Conversion of tosylates to iodides under solvent-free microwave irradiation
Each tosylate was reacted with 3 equiv. of NaI

Tosylate	Temperature [°C]	Power [W]	Time [min]	Scale [mmol]	Yield [%]
 (**1a**)	120	100	30	0.4	>99
 (**1b**)	120	120	45	0.3	95
 (**1c**)	140	150	30	0.2	95
 (**1d**)	115	100	90	0.2	94
 (**1e**)	120	120	45	0.3	98
 (**1f**)	120	110	45	0.2	94
 (**1g**)	115	100	60	0.3	75

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*In memory of Professor Roger Brown, a great scientist, artist, and a wonderful friend.

explored the use of microwave irradiation (Scheme 1). After some exploration of conditions an optimised set of conditions was developed. This involved heating a tosylate with three equiv. of NaI at 100–150 W in a sealed 10 mL microwave vial in a microwave reactor irradiating for 0.5–2 h, during which time the temperature was maintained at 100–140°C. A variety of tosylates were subjected to this treatment and the results are collected in Table 1.

It was found all the primary tosylates gave iodides in >94 % yields, whilst conversion of a secondary tosylate to the corresponding iodide, also succeeded although competing elimination reduced the yield to 75 %.

Thus the conversion of primary tosylates to iodides under solvent-free, microwave irradiation condition gives the corresponding iodides in high yields with relatively short reaction time. This procedure is especially useful for the in situ generation of volatile primary iodides in excellent yields (>94 %), because the solids (remaining NaI and the by-product sodium *p*-toluenesulfonate) can be easily filtered off and the liquid iodide products could be collected easily.

Experimental

NaI (3 equiv.) was added to neat primary tosylate in a 10 mL microwave vial, which was sealed and heated under microwave irradiation in a CEM Discover^{TM} microwave reactor, and subjected to 100–150 W irradiations for 30–90 min. Following reaction, CH_2Cl_2 was added to the mixture, and the solid was removed by filtration. The solvent was removed under vacuum to yield the product. Primary iodides were mostly pure according to NMR spectroscopy, while for the secondary iodide, the yield was somewhat reduced due to by-product formation.

Supplementary Material

Experiment procedures and characterisations of the products are available on the Journal's website.

References

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