Reaction of Magnesium Iodide with Tosylates

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Summary Alkyl iodides are obtained in good yield from the reaction of MgI_2 with tosylates; depending on the structure of the starting material the mechanism is S_N1 or S_N2; in several cases, elimination products are observed.

In a recent publication we reported that in ether at room temperature MgI_2 reacts with the tosylates of benzyl alcohol and butan-2-ol to give the corresponding iodo-derivatives.[1] We have studied the generality and the stereochemistry of this reaction.

TABLE

Starting tosylates	Reaction products	Yields (%)
3β-Tosylcholestane	3α-Iodocholestane	95
trans-4-t-Butyl-1-tosylcyclohexane	*cis*-1-Iodo-4-t-butylcyclohexane	77
	4-t-Butylcyclohexene	14
cis-4-t-Butyl-1-tosylcyclohexane	*cis*-1-Iodo-4-t-butylcyclohexane	3
	trans-1-Iodo-4-t-butylcyclohexane	15
	4-t-Butylcyclohexene	55
(+)-2-Tosyloctane	(−)-2-Iodo-octane	94
2-Tosyladamantane	2-Iodoadamantane	96
trans-2-Methyl-1-tosylcyclohexane	*trans*-1-Iodo-2-methylcyclohexane + *cis*-1-iodo-2-methylcyclohexane + 1-iodo-1-methylcyclohexane + other products	Relative proportions of the 1-iodo-2-methyl cyclohexanes: *trans*: 55% *cis*: 45%

The reaction seems to be general for the tosylates of primary and secondary alcohols. Addition of an ethereal solution of the tosylate to a stirred solution of MgI_2 in the same solvent, followed by 10 min stirring and rapid hydrolysis at 0° gives the alkyl iodide in excellent yield.

The following alkyl iodides were obtained: n-butyl (95%); isobutyl (80%); s-butyl (84%); cyclohexyl (80%); cyclopentyl (85%); benzyl (98%). The reaction is complete before hydrolysis as shown by t.l.c. control but this step is necessary in order to eliminate the excess of MgI_2 and to obtain pure products. The yields given are calculated from crude products but t.l.c. and n.m.r. indicate the absence of impurities. This reaction is particularly useful for the transformation of cyclic alcohols to cyclic iodides for which the NaI–acetone procedure requires drastic conditions.[2]

The results of the stereochemical study are given in the Table: the reaction proceeds with inversion in the case of equatorial cyclohexyl tosylates but the axial ones give mainly elimination. In the case of (+)-2-tosyloctane, the rotatory power of the (−)-iodide obtained ($[\alpha]_D^{17} -48°$) is close to that given in the literature for the optically pure compound.[3]

The reaction is not S_N2 in every case: Schleyer and his co-workers[4] have shown that 2-tosyladamantane probably reacts by an S_N1 process. Furthermore, the results obtained with the tosylate of *trans*-2-methylcyclohexanol are better explained by an assisted ionisation of the C–O ester bond. In this last case, it was impossible to separate the products of the reaction and the structural assignments were made from the n.m.r. spectrum of the mixture.

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