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# A NOVEL METHOD FOR REDUCTIVE REMOVAL OF TOSYLOXY AND MESYLOXY GROUPS.

Yasuo Fujimoto and Takashi Tatsuno
RIKAGAKU KENKYUSHO(The Institute of Physical and Chemical Research)
Wako-Shi, Saitama, Japan 351.

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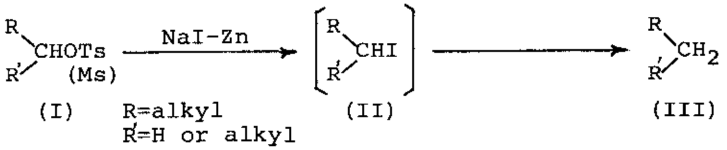
Transformation of a primary or secondary hydroxy group to a methyl or methylene group is frequently encountered in the field of organic synthesis. For this purpose, reductive removal of a tosyloxy(or mesyloxy) group with a variety of metal hydride reagents$^{1),2),3)}$ has often been used.

In this paper, we describe a convenient method for the reductive removal of a primary or secondary tosyloxy(or mesyloxy) group. The present method involves two reactions: the tosylate(or mesylate)(I) is converted into the iodide intermediate(II), which is then reduced to the corresponding methyl or methylene derivative(III) with zinc powder in an aprotic solvent such as glyme DMF, DMSO, or HMPA.

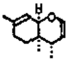
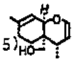
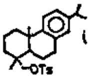
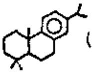
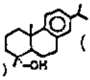
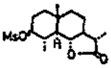
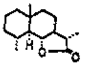
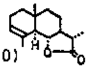
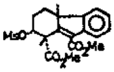
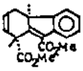


The experiments summarized in Table I indicated that (i) the reductive cleavage of a primary or secondary tosylate was *achieved in excellent yield* by refluxing with 5 eq. of sodium iodide and 10 eq. of zinc powder in glyme (entries 1, 2, 3, 4 and 10); (ii) when lithium bromide was used in place of sodium iodide, the reduction of cyclododecanol tosylate(4) to cyclododecane required 25 hr for a 50% yield(entry 5); (iii) the sterically hindered mesylate(5) and tosylate(6) were also reduced to the corresponding methyl derivatives(5a and 6a) in good yield(entries 6 and 8), while treatment of 5 and 6 with lithium aluminum hydride predominantly produced the alcohols(5b and 6b)(entries 7 and 9); (iv) the secondary tosylate(4) and mesylate(7) having hydrogen atoms on the β-carbon gave the elimination products(4b and 7b) together with the reduction products(entries 4 and 11); (v) the highly hindered mesylate(8) afforded only elimination product(8a).

The typical experimental procedures are as follows.
A mixture of 84.8 mg(0.2 mmol) of 1-octadecanol tosylate(2), 150 mg(1.0 mmol) of sodium iodide, 130 mg(10.0 mmol) of zinc powder and 2.0 ml of glyme was refluxed for 1.5 hr under stirring. The reaction mixture was filtered

(or centrifuged) to remove excess sodium iodide and zinc powder. Then, the filtrate was poured into water and extracted with n-pentane. The organic layer was washed with saturated salt solution, dried over sodium sulfate, and concentrated under reduced pressure. The residual oil was purified by silica gel column chromatography(n-hexane) to give 46 mg of n-octadecane.

Table 1[a]

| Entry | Substrate | Reagent | Solvent | Temp.°C | Time,hr | Product | Yield,% |
|---|---|---|---|---|---|---|---|
| 1 | $CH_3(CH_2)_9OTs$(1) | NaI-Zn | glyme | 83 | 1.5 | $CH_3(CH_2)_8CH_3$(1a) | 90[b] |
| 2 | $CH_3(CH_2)_{17}OTs$(2) | NaI-Zn | glyme | 83 | 1.5 | $CH_3(CH_2)_{16}CH_3$(2a) | 90 |
| 3 | $CH_3\underset{OTs}{CH}(CH_2)_5CH_3$(3) | NaI-Zn | glyme | 83 | 1.5 | $CH_3(CH_2)_6CH_3$(3a) | 89[b] |
| 4 | cyclododecanol tosylate (4) | NaI-Zn | glyme | 83 | 5.0 | $(CH_2)_{12}$(4a) + $C_{12}H_{22}$(4b)<br>(85 :15) | 95[b] |
| 5 | (4) | LiBr-Zn | glyme | 83 | 25.0 | 4a + bromocyclododecane (4c)<br>(55 : 45) | 90 |
| 6 |  (5) | NaI-Zn | glyme-HMPA | 83 | 3.0 |  (5a) | 70 |
| 7 | (5) | $LiAlH_4$ | ether | 35 | 24.0 | 5a +  (5b)<br>(45 : 55) | 90 |
| 8 |  (6) | NaI-Zn | HMPA | 105 | 3.0 |  (6a) | 72 |
| 9 | (6) | $LiAlH_4$ | ether | 35 | 24.0 | 6a +  (6b)<br>(5 : 95) | 90 |
| 10 |  (7) | NaI-Zn | glyme | 83 | 1.5 |  (7a) | 90 |
| 11 | (7) | NaI-Zn | DMF or DMSO | 70 | 3.0 | 7a +  (7b)<br>(60 : 40) | 95 |
| 12 |  (8) | NaI-Zn | HMPA | 105 | 3.0 |  (8a) | 51 |

[a] Experiments performed on 1-2 mmol scale. [b] Yields determined by vpc.

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## References:

1) $NaBH_3CN$ reduction: R. O. Hutchins, B. E. Maryanoff and C. A. Milewski, Chem. Comm., 1097(1971).

2) $LiAlH_4$ reduction: S. S. Pizey, Synthetic Reagents, Vol. I, p. 236, John Wiley & Sons Ltd., England.

3) Copper(I) Complex reduction: S. Masamune, P. A. Rossy and G. S. Bates, J. Am. Chem. Soc., 95, 6452(1973).