

A RADICAL DEOXYGENATION OF PRIMARY ALCOHOLS BY USE OF  
TRI-n-BUTYLTIN HYDRIDE - SODIUM IODIDE, AND ITS  
APPLICATION TO A RADICAL CYCLIZATION

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Primary alcohols are deoxygenated to hydrocarbons via tosylates with tri-n-butyltin hydride-sodium iodide under mild radical conditions; the method is useful for the preparation of cyclic compounds from acyclic ones possessing primary hydroxyl and olefinic groups by reductive cyclization.

Barton et al., developed an elegant method for the radical deoxygenation of a secondary hydroxyl group via O-alkyl dithiocarbonate derivatives.<sup>1)</sup> The method, however, could not be applied to a primary hydroxyl group. We wish to report here the facile radical deoxygenation of primary alcohols. Thus, we found tosylates (1) reacted with tri-n-butyltin hydride (1.2 eq) and sodium iodide (2 eq) in refluxing 1,2-dimethoxyethane (DME) to produce the corresponding hydrocarbons (Table 1).

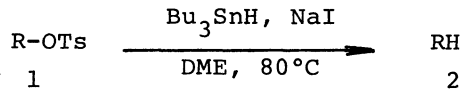
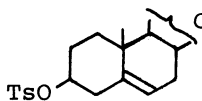
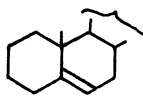
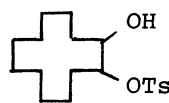
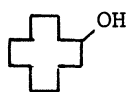
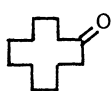


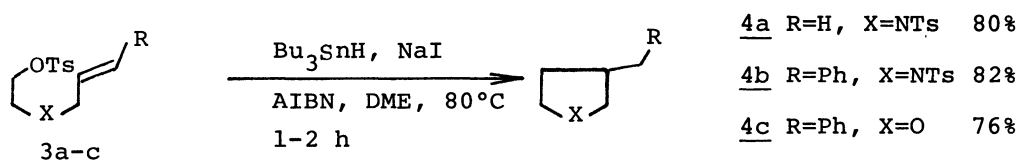
Table 1. Deoxygenation of Alcohols via Tosylates<sup>2)</sup>

Tosylate ( <u>1</u> )	React. time (h)	Product ( <u>2</u> )	Yield (%) <sup>a</sup>
n-C <sub>8</sub> H <sub>17</sub> OTs	1	n-C <sub>8</sub> H <sub>18</sub>	100
n-C <sub>10</sub> H <sub>21</sub> OTs	1	n-C <sub>10</sub> H <sub>22</sub>	80 (73 <sup>b</sup> )
PhCH <sub>2</sub> CH <sub>2</sub> OTs	0.5	PhCH <sub>2</sub> CH <sub>3</sub>	93
PhCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OTs	0.5	PhCH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	99
	5		64 <sup>b</sup>
	4		56
			20

<sup>a</sup> GLC yield. <sup>b</sup> Isolated yield. <sup>c</sup> Tosylate derived from cholesterol.

The present method is especially useful for the reductive deoxygenation of primary alcohols, although the tosylate derived from cholesterol affords the desired deoxygenated product in a reasonable yield. The monotosylate of a 1,2-diol gave the desired monoalcohol in moderate yield. This is a first example of the mono-deoxygenation of the 1,2-diol group without protection of another hydroxyl group.

In order to clarify the mechanism, we examined the homolytic carbocyclization starting from tosylates.



Thus, the tosylates 3a-c gave the five-membered cyclic products 4a-c in good isolated yields as shown above. The results indicate clearly that the deoxygenation or cyclization proceeds via radical species such as the species 5, which are derived from alkyl iodides formed in situ in the reaction system.<sup>3)</sup>

The present reaction offers a synthetically useful method for the preparation of cyclic compounds starting from alcohols, since the reaction requires no use of active halogenating reagents, and also no isolation of generally unstable and hazardous alkyl iodides.<sup>4)</sup>

A typical experimental procedure is as follows.

To a refluxing solution of tosylate 3b (0.30 g, 0.62 mmol), NaI (0.2 g, 1.33 mmol), and a catalytic amount of azobisisobutyronitrile (AIBN) in DME (5 ml), was added dropwise tri-*n*-butyltin hydride (0.24 g, 0.83 mmol). The mixture was refluxed for 1 h. A usual work up gave the crude product, which was purified by column chromatography on silica gel eluted with hexane followed by chloroform to give pure 4b (0.16 g, 82%)

#### References

- 1) D.H.R. Barton and S.W. McCombie, *J. Chem. Soc., Perkin Trans. 1*, 1975, 1574.
- 2) All new compounds obtained here had satisfactory spectral and analytical data.
- 3) Y. Ueno, K. Chino, M. Watanabe, O. Moriya, and M. Okawara, *J. Am. Chem. Soc.*, 104, 5564 (1982).
- 4) The reduction of tosylates with Zn-NaI has been reported. Y. Fujimoto and T. Tatsuno, *Tetrahedron Lett.*, 1976, 3325. The method is useful for the deoxygenation, however, such reagent gave a cyclized product in a poor yield (22-30%). S. K. Pradhan, J. N. Kolhe, and J.S. Mistry, *Tetrahedron Lett.*, 23, 4481 (1982). Tosylates are deoxygenated to hydrocarbons with  $\text{LiAlH}_4$ . The method, however, often gives the corresponding alcohols. L.J. Dolby and D.R. Rosencrantz, *J. Org. Chem.*, 28, 1888 (1963).

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