

STEREOSPECIFIC DISPLACEMENTS OF p-TOLUENESULFONATE
AND IODIDE IONS WITH ORGANOLITHIUM REAGENTS

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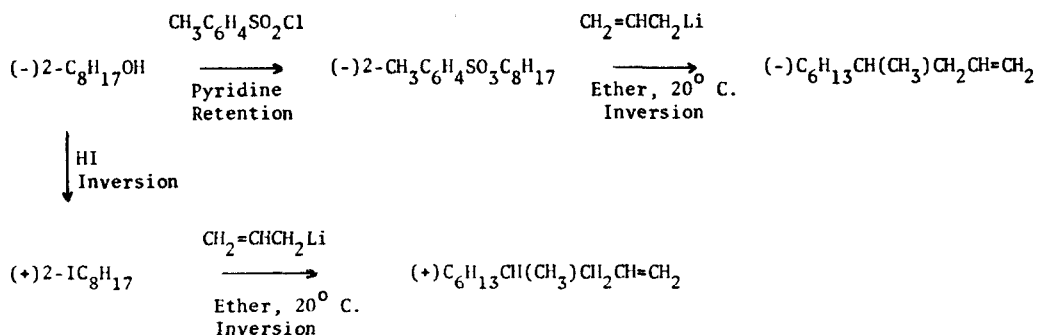
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Several recent studies have shown that Wurtz type coupling reactions between alkyllithium reagents and alkylhalides proceed by two one-electron transfer processes rather than a direct nucleophilic displacement.¹ However, certain charge delocalized organolithium reagents displace the bromide and chloride leaving groups from secondary carbon with a high degree of stereospecificity indicating typical S_N2 type displacement.²

We have found that alkyllithium also displaces both the p-toluenesulfonate and iodide leaving groups from secondary carbon with a high degree of stereospecificity, 93% and 90% inversion of configuration, respectively.³ 2-Octyl tosylate was prepared from (-)-2-octanol, [α]_D -8.0° (neat), and treated with alkyllithium in ethyl ether solvent at 20° C. to give (-)-4-methyl-1-decene, [α]_D -5.25° (neat), n_D²⁵ 1.4246 (Lit.⁶ [α]_D -7.0° (neat), n_D²⁵ 1.4246) in at least 60% yield.⁷ (+)-2-Iodoctane, α_D +45.8° (neat), coupled with alkyllithium to give (+)-4-methyl-1-decene, [α]_D +4.5° (neat), n_D²⁵ 1.4244, in at least a 65% yield.⁷



The relative configuration of 2-octyl tosylate, 2-iodooctane, and 4-methyl-1-decene can be rigorously shown. (-)-2-Bromooctane has been related to (-)-4-methyl-1-decene,⁶ and

(+)-2-bromooctane, (+)-2-iodooctane, and (+)-2-octanol have the same configuration.⁸ Therefore, both reactions with allyllithium must proceed with inversion of configuration.

The high degree of stereospecificity of these reactions is expected if the coupling reactions are proceeding by an S_N2 pathway involving a rate controlling transition state similar to that suggested by Eastham and Gibson.⁹

A similar high degree of stereospecificity with yields of at least 60% was also observed for the reactions of another charge-delocalized organolithium reagent, benzylolithium, with 2-octyl tosylate and 2-iodooctane. All charge delocalized organolithium reagents, however, do not appear to react with such high yields with tosylates since Meyers and coworkers¹⁰ indicate that the yield of coupled product for the reaction of the lithio salt of 2,4,4,6-tetramethyl-5,6-dihydro-1,3(4H)-oxazine with butyl tosylate was very low. The good yields of coupled products make allyllithium an attractive reagent for extending carbon chains by three carbons as well as adding a versatile functional group.

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References

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