SYNLETT Spotlight 11

This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

(4-Tolylsulfonyl)hydrazones

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Heidi R. Vollmer was born in Pittsburgh, Pennsylvania. She received a B.S. in chemistry and a B.A. in German at the University of Utah. She was involved in undergraduate research in organic chemistry with Dr. Frederick G. West and is currently working on her D.Phil with Professor Sir Jack E. Baldwin and Dr. Victor Lee at the University of Oxford.

(4-Tolylsulfonyl)hydrazones and aldehyde tosylhydrazones are versatile synthetic intermediates. They are used to make stereospecific alkenes, undergo synthetically useful fragmentations, and are used in C-C σ -bond formation. Furthermore, aldehyde tosylhydrazones are more stable than their parent aldehydes, because they do not undergo autoxidation, self-condensation, and hydration.¹

Preparation: Ketones and aldehydes condense readily with p-toluenesulfonyl hydrazide to form tosylhydrazones.¹⁻³

Abstracts

Reaction of tosylhydrazones with n-butyllithium leads to olefinic products via carbene intermediates in the Bamford-Stevens reaction.⁴ Deprotonation to make the dianion results in vinyl lithium intermediates, which give the less-substituted alkene in the Shapiro-Heath reaction.^{1,5}

Tosylhydrazones of certain α,β -epoxyketones undergo fragmentation to yield a ketone and acetylene.⁶ This fragmentation can also be applied to the formation of medium-sized rings.²

Silylated aldehyde tosylhydrazones can be induced to decompose by sigmatropic rearrangement of proposed allylic diazene intermediate to form alkenes.³

C-C sigma bonds can be constructed by the reductive coupling of aldehyde tosylhydrazones with alkyl lithium reagents.⁷

References

- (1) Adlington, R. M.; Barrett, A. G. M., *Acc. Chem. Res.*, **1983**, 16, 55.
- (2) Tanabe, M.; Crowe, D. F.; Dehn, R. L., *Tetrahedron Lett.*, **1967**, 40, 3943.
- (3) Myers, A. G.; Kukkola, P. J., *J. Am. Chem. Soc.*, **1990**, 112, 8208.
- (4) Bamford, W. R.; Stevens, T. S., *J. Chem. Soc.*, **1952**, 4735.
- (5) Shapiro, R. H.; Heath, M. J., *J. Am. Chem. Soc.*, **1967**, 89, 5734; Shapiro, R. H., *Org. React. (N.Y.)*, **1975**, 23, 405.
- (6) Eschenmoser, A.; Felix, D.; Ohloff, G., *Helv. Chim. Acta*, **1967**, 50, 708.
- (7) Myers, A. G.; Movassaghi, M., *J. Am. Chem. Soc.* **1998**, 120, 8891.

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