

THE ROLE OF TOSYLHYDRAZONE STEREOCHEMISTRY
UPON THE REGIOSPECIFICITY OF OLEFIN FORMATION¹

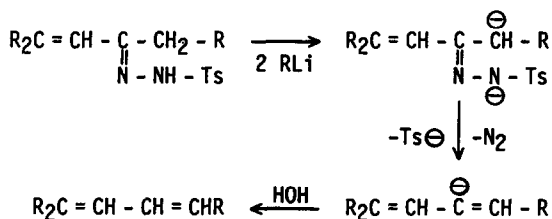
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(Received in USA 7 June 1976; received in UK for publication 9 July 1976)

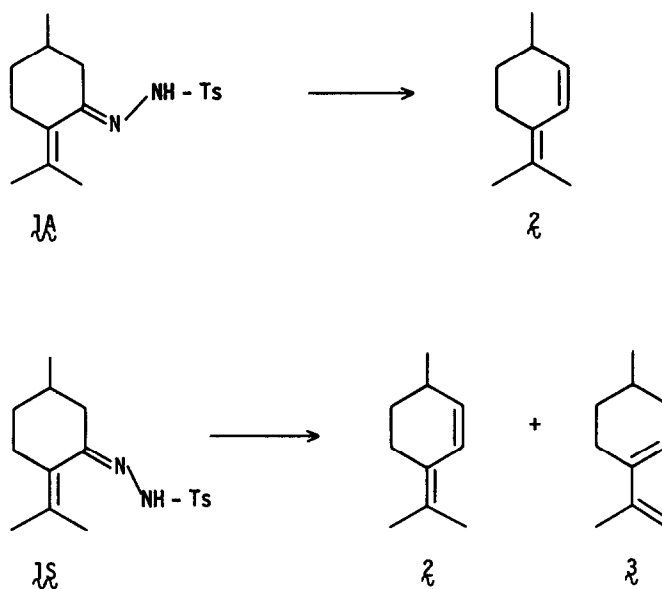
The alkyllithium induced decomposition of enone tosylhydrazones is known to occur in a regiospecific manner to form conjugated dienes where the position of the original carbon-carbon double bond is maintained.² These results demonstrate that only abstraction of the α' -proton of the conjugated tosylhydrazone occurs. Recently, it has been suggested,³ without experimental justification, that with alkane tosylhydrazones the



stereochemistry of the tosylhydrazone grouping could be the sole factor controlling the position of the newly formed double bond.

During the course of continuing studies of the photochemistry of 1,3-conjugated dienes, it was found possible to prepare, under carefully controlled conditions,⁴ either isomeric pulegone tosylhydrazone, λA or λS . These tosylhydrazones have been shown to be isomeric by spectroscopic and elemental analysis and the structures λA and λS have been established by x-ray crystallographic techniques.⁵ Earlier studies have

shown that decomposition in benzene of a pulegone tosylhydrazone of undefined stereochemistry yields only diene \mathcal{Z} . This present study reports preliminary results employing tosylhydrazones of defined stereochemistry.

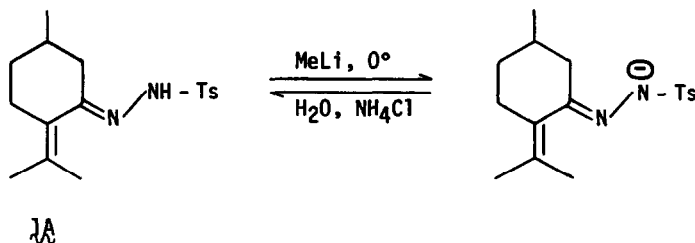


Decomposition of either $1A$ or $1S$ in benzene with ethereal methyllithium (benzene to ether ratio 20:1) gave rise to diene \mathcal{Z} , in agreement with previously published results.² While $1A$ is sparingly soluble in benzene, reaction of a suspension of $1A$ with methyllithium was found to be rapid, giving rise to \mathcal{Z} in greater than 80% isolated yield. In contrast, $1S$ is readily soluble in benzene but was found to react not as rapidly. The above data indicate that tosylhydrazone stereochemistry, therefore, does play a role in the overall reaction.

In view of the known solvent dependency of a great number of organometallic reactions, the decomposition of tosylhydrazones $1A$ and $1S$ was investigated in 1:1 benzene-ether. Once again, $1A$ gave rise to diene \mathcal{Z} in good yield. However, under identical conditions, decomposition of $1S$ gave rise to a mixture of dienes \mathcal{Z} and $\mathcal{3}$

in a 40:60 ratio. This remarkable result is the first experimental proof that tosylhydrazone stereochemistry can indeed direct the course of the decomposition reaction. To test further this finding, tosylhydrazones **1A** and **1S** were decomposed in *N,N,N',N'*-tetramethylethylenediamine (TMEDA), a solvent known to effect the state of aggregation of organometallic reagents and to modify their reactivities.⁶ Significantly, when the decomposition of **1A** was conducted in TMEDA with *n*-butyllithium, diene **2** was again cleanly produced. However, decomposition of **1S** under identical conditions gave a mixture of dienes **2** and **3** in a 10:90 ratio. This result clearly demonstrates that tosylhydrazone stereochemistry can have a decisive effect on the course of the decomposition reaction.

In order to probe further these tosylhydrazone decomposition reactions, the decomposition was conducted in tetrahydrofuran with ethereal methyllithium. In this solvent system both **1A** and **1S** yielded a mixture of dienes **2** and **3**. Under identical reaction conditions, **1A** gave **2** and **3** in an 80:20 ratio while **1S** gave the same dienes in a 20:80 ratio. The above data indicate that there are at least two competitive reaction pathways for the decomposition reaction. One of these pathways seems to be strongly stereochemically dependent while the other route appears to have little, if any, dependence on tosylhydrazone stereochemistry. The actual observed product ratios are thus a weighted average of these competitive processes. These combined results indicate that the decomposition reaction appears to be more complex than originally supposed. Furthermore, suitable control experiments demonstrated that tosylhydrazones **1A** and **1S** maintained their original stereochemistry when their monoanions were generated in benzene or THF. After one hour at zero degrees, the monoanions were quenched with saturated ammonium chloride solution and gave the original



tosylhydrazone in excellent yield with no detectable isomerization. These data indicate that stereochemical equilibration of isomeric tosylhydrazones, at least in this case, is not a likely factor in the decomposition reaction. A detailed study in order to reasonably interpret these results is now underway.

REFERENCES

1. This work was supported in Berkeley by Grant No. AM-00709, National Institute of Arthritic, Metabolic, and Digestive Diseases and in Chicago by Grant No. GM-20329, National Institute of General Medical Sciences.
2. W. G. Dauben, M. E. Lorber, N. D. Vietmeyer, R. H. Shapiro, J. H. Duncan, and K. Tomer, J. Am. Chem. Soc., **90**, 4762 (1968).
3. R. H. Shapiro, M. R. Lipton, K. J. Kolonko, R. L. Buswell, and L. A. Capuano, Tetrahedron Lett., 1811 (1975).
4. 1S , mp 111-113°, was prepared by refluxing the reactants 3 hr in acidic ethanol; 1A , mp 143-145°, was prepared simply by mixing the reactants in hot acidic ethanol.
5. The authors wish to thank Dr. J. F. Blount of Hoffmann-La Roche, Inc., for kindly performing the x-ray analyses.
6. The use of TMEDA as a solvent for organometallic reactions has been briefly reviewed; C. Agami, Bull. Soc. Chim. Fr., 1619 (1970).