Tetrahedron Letters No.3, pp. 345-347, 1968. Pergamon Press. Printed in Great Britain.

# TOSYLHYDRAZONES IV.[1] STEREOCHEMISTRY OF THE REACTION OF TOSYLHYDRAZONES WITH METHYLLITHIUM.

Robert H. Shapiro
Department of Chemistry, University of Colorado
Boulder, Colorado 80302

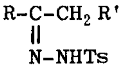
(Received in USA 21 August 1967)

In a previous communication we reported that aliphatic tosylhydrazones which contain α-hydrogens react with methyllithium in ether to give a quantitative yield of the unrearranged, less substituted olefin.[1] We have now examined the stereochemistry of this reaction and have made comparisons with the corresponding carbene and carbonium ion reactions. Phenyl benzyl ketone (desoxybenzoin) tosylhydrazone (I), phenyl ethyl ketone (propiophenone) tosylhydrazone (II), 1,3-diphenyl-1-propanone tosylhydrazone (III) and 1,3-diphenyl-2-propanone tosylhydrazone (IV) were chosen as model compounds since each, according to the precedents,[1] would give a mixture of geometric isomers of a single olefin upon reaction with methyllithium. The reactions proceeded quantitatively with $\geq$ 2 equivalents of methyllithium and were complete in less than 15 minutes at room temperature.

The stereochemical results are shown in the Table. Three sets of reaction products are shown on the right side of the Table in order to make a comparison of the methyllithium reaction with the sodium methoxide (5 equivalents, in diglyme) reaction (carbene process) as well as with the acid catalyzed dehydration of the corresponding alcohol (carbonium ion process).

# TABLE

## Stereochemistry of Olefin Formation from Tosylhydrazones of the Type

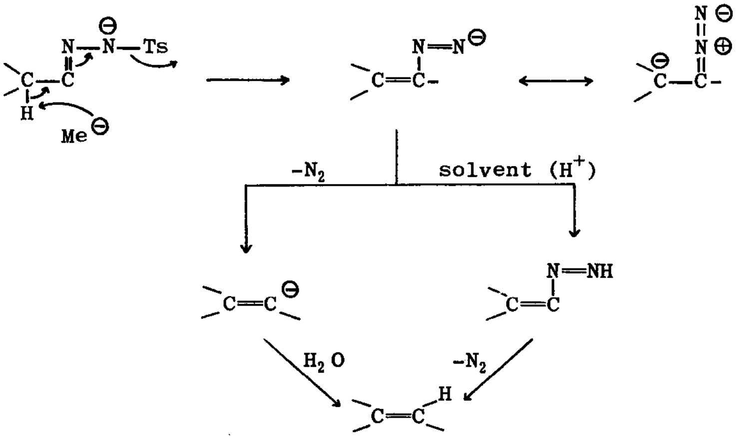


$$\underset{\text{N-NHTs}}{\overset{}{\text{R-}\underset{\|}{\text{C}}\text{-CH}_2\text{R}'}}$$

| Compound | R | R' | Olefin | MeLi/Et$_2$O | | Carbene Process | | Carbonium Ion Process | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | % cis | % trans | % cis | % trans | % cis | % trans |
| I | Ø | Ø | Stilbene | 14 | 86 | 3 | 97 | <1 | >99 |
| II | Ø | CH$_3$ | 1-Phenylpropene | 76 | 24 | 20 | 80 | 5 | 95 |
| III | Ø | CH$_2$Ø | 1,3-Diphenylpropene | 48 | 52 | 7 | 93 | --- | --- |
| IV | ØCH$_2$ | Ø | 1,3-Diphenylpropene | 86 | 14 | 3 | 97 | 28 | 72 |

Clearly the formation of cis-olefins is favored more by the methyllithium reaction than by either the carbene or carbonium ion process. Since the carbonium ion process leads to the formation of an equilibrium mixture and a small amount of equilibration could occur with the products under the carbene conditions (strong base, 140°),[2] the dominance of the trans-products in these reactions was expected. Both cis- and trans-stilbene are stable under the methyllithium reaction conditions. The question of the high cis to trans ratio resulting from the methyllithium reactions remains. If the reaction proceeds exclusively by way of a vinyl carbanion or covalently bonded lithium derivative,[1,3,4] complete equilibration to trans-stilbene would have been expected under our reaction conditions (ether, room temperature).[5] On the other hand if a diimide intermediate was intervening, nitrogen evolution should be observed after the addition of water, but it is not. However, the possibility that the unsaturated nitranion reacts with solvent exists. The fact remains that an $\alpha$-hydrogen is eliminated in the reaction[1] and this result is consistent with both mechanisms (see flow-sheet).

## Flow Sheet



The preference for the formation of cis-olefins cannot be explained by the routes shown in the flow sheet. Further work is progressing in order to determine the validity of the accepted routes.

Acknowledgment. The author wishes to express his gratitude to the National Science Foundation (Grant No. GP-5753) for support of this work.

## References

1. R.H. Shapiro and M.J. Heath, J. Am. Chem. Soc., in press.
2. D.J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, 1965, pp. 130-135.
3. M. Fischer, Z. Pelah, D.H. Williams and C. Djerassi, Ber., 98, 3236 (1965).
4. W. Kirmse, B.-G. von Bülow and ~~H. Sch~~epp, Ann., 691, 41 (1966).
5. D.Y. Curtin and J.W. Crump, J. Am. Chem. Soc., 80, 1922 (1958) and references contained therein.