

## ORGANIC TELLURIDE-MEDIATED REACTION OF TOSYL AZIDE WITH CARBONYL COMPOUNDS

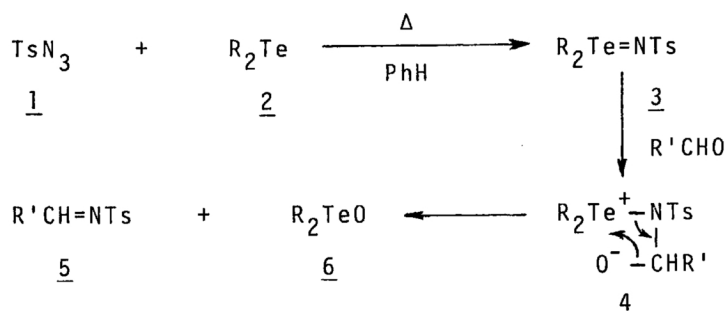
Hitomi SUZUKI,\* Syoko TAKEDA, and Yasuaki HANAZAKI

Department of Chemistry, Faculty of Science,  
Ehime University, Bunkyo-cho, Matsuyama 790

Organic telluride induces the reaction of tosyl azide with aldehydes to afford the corresponding N-tosylimines in various yields. Tellurilimine has been suggested as a probable intermediate.

Tosyl azide (1,  $\text{TsN}_3$ ) does not react with carbonyl compounds even at prolonged refluxing conditions in benzene. However, when dialkyl telluride (2) is added to the reaction system, the azide decomposes slowly with evolution of nitrogen gas and, when carbonyl component is aromatic aldehyde, N-tosylarylideneimine (5,  $\text{R}' = \text{Ar}$ ) is obtained as a major product. Aliphatic aldehyde with no  $\alpha$ -hydrogen atom reacts similarly to afford 5, but aldehydes bearing  $\alpha$ -hydrogens lead to a complex mixture of unidentified products. The reaction is moderately facilitated in the presence of copper powder and the yields of imines 5 are much improved. Ketones fail to react under similar conditions.

Ease of the formation of imine 5 is subject to polar effect; strongly electron-withdrawing group apparently suppresses the reaction (Table 1). When dialkyl telluride is replaced by less basic diaryl telluride, the reaction becomes sluggish and incomplete. Addition of triphenylphosphine, instead of telluride, to the reaction mixture results in rapid decomposition of azide and N-tosylimino-phosphorane is obtained as the only product.



Scheme 1.

The telluride-mediated formation of imine 5 may reasonably be explained by the intermediacy of tellurilimine (3) as depicted in Scheme 1. Thus, telluride 2 attacks on azide 1 to form 3, which then reacts with carbonyl compound to yield adduct (4). The zwitter-ionic intermediate 4 collapses in a way as indicated to form imine 5 and telluroxide (6). The supposed tellurilimine 3 can also be generated by the reaction of dialkyl telluride with chloramine-T,<sup>1)</sup> followed by treatment with potassium t-butoxide. It is trapped in the presence of aldehyde to give

Table 1. N-Tosylimines 5 obtained from tosyl azide and aldehydes<sup>a)</sup>

Aldehyde	RCHO	Reaction time/h	N-Tosylimine Mp $\theta_m$ /°C	RCH=NTs Yield/%
Benzaldehyde		18	115-116	52
2-Methoxybenzaldehyde		18	110-111	77
4-Methoxybenzaldehyde		20	131-132	82
3,4-Methylenedioxybenzaldehyde		15	115-116	76
4-Chlorobenzaldehyde		17	174-175	40
4-Nitrobenzaldehyde		18	212-213	28
2-Methyl-2-phenylpropionaldehyde		16	96-98	44

a) The reaction was carried out in the presence of copper powder. Products were identified by mass, IR, and <sup>1</sup>H NMR spectra as well as by conversion into sulfonamide and aldehydes. Yields refer to the isolated compounds and are not optimized.

the same imine as that obtained via the azide route. Attempts to isolate 3, however, failed due to its liability to undergo hydrolytic decomposition.

Although tellurilimine was described as early as in 1960's,<sup>2)</sup> its chemistry has received little attention until recently. N-Tosyldiaryltellurilimines are moisture-sensitive crystalline solids, usually obtained by the condensation of diaryl telluroxide with sulfonamides,<sup>3)</sup> or by oxidation of diaryl telluride with t-butyl hypochlorite, followed by treatment with N-sodiosulfonamides.<sup>4)</sup> Thus, the present reaction may provide an alternative way to generate reactive tellurilimines in situ under mild conditions.

A general procedure is as follows: A mixture of tosyl azide (1.3 mmol), diisobutyl telluride (1.3 mmol),<sup>5)</sup> carbonyl compound (1.0 mmol), and benzene (20 ml) was heated in the presence of copper powder (1.3 mmol) under nitrogen. The progress of the reaction was monitored by TLC. After appropriate hours, 0.5 mol dm<sup>-3</sup> hydrochloric acid (20 ml) was added and organic phase was extracted with dichloromethane, dried over sodium sulfate, and evaporated in vacuo. The residue was purified by chromatography on silica gel with hexane-ether (5:1) as eluent,<sup>6)</sup> and then recrystallized from appropriate solvent to give N-tosylimine.

#### References

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- 5) Diisobutyl telluride was chosen because of its handling ease.
- 6) The purification must be done rapidly, since the product is labile on silica gel.

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