**Introduction**

*p*-Toluenesulfonyl isocyanate (tosyl isocyanate or TsNCO) is a colorless liquid that reacts violently with water and with basic and protic solvents. Reactions should be carried out with care and only in a fumehood, since TsNCO is corrosive and lachrymatory. It is easily soluble in inert media such as chlorinated, aromatic and ethereal solvents. It is now commercially widely available but can also be synthesised in about 93% yield as shown in Scheme 1.1

The reactivity of the isocyanate carbon is greatly improved by the sulfonyl group nearby. TsNCO is remarkably heat-stable and can be distilled in vacuo without decomposition.

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**Abstracts**

(A) Murai and co-workers showed that nucleophilic attack by TsNCO at the central carbon of a platinum π-allyl system leads to the substitution of the oxygen atom by the *p*-toluenesulfonyl N group in high yield.2 This was the first example of stoichiometric nucleophilic substitution at a central π-allyl carbon.

(B) Willis et al. used TsNCO to react with mononuclear iron η¹-allyls, propargyls and allenyls and afford [2+3] cycloaddition products.3 The iron allenyl system gave the cycloadduct shown.
(C) Supuran et al.\(^4\) showed that the reaction of TsNCO with primary amines, amino acids or dipeptides afforded a novel class of compounds that possess powerful antitumor activity. Some functional groups had to be protected in order to avoid unwanted reactions. The product 4-toluenesulfonylureido derivatives were obtained in yields varying from 36% up to 95%. Secondary amines were reacted with TsNCO in a similar manner by Nussbaumer et al.\(^5\) to target several hormone dependant diseases.

(D) McFarland and co-workers reported the use of TsNCO in a ring enlargement process (from 3- to 5-membered).\(^6\) TsNCO cyclised with an epoxide to give the corresponding toluenesulfonyl 2-oxazolinone. One of the C–O bonds of the epoxide is broken during the process and the N–C group from the tosyl isocyanate is inserted. The less sterically hindered isomer I is favoured over II.

(E) Holmes et al. reported that the thermal reaction of methyl glyoxylate with TsNCO gave an imino ester via [2+2] cycloaddition, followed by cycloreversion with expulsion of carbon dioxide.\(^7\)

(F) Sharpless and Xu reported that the reaction of an ene diol with TsNCO, catalysed by Pd(0), afforded enantiomerically enriched oxazolidin-2-ones via [2+3] cycloaddition.\(^8\)

References