SYNLETT Spotlight 406

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

Phenylisocyanate

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Introduction

Isocyanates are useful intermediates for a variety of reactions including nucleophilic additions with alcohols and amines to produce carbamates and ureas, respectively. They also participate in cycloadditions to generate heterocycles and polymerizations to produce commodities such as polyurethane. The high yields and lack of by-products associated with isocyanate chemistry has led to widespread application of isocyanates in the pharmaceutical, agrochemical and polymer industries.1

Phenylisocyanate is a colorless liquid with strong odor and causes lachrymation. Typically phenylisocyanate is generated either from aniline by reacting with phosgene or phosgene equivalents, such as diphosgene or triphosgene or via thermal dissociation of carbamic acid derivatives. Phenylisocyanate can also be generated from non-amine precursors via the rearrangement of phenyl azide (Curtius rearrangement) and hydroxamic acids (Lossen rearrangement).2

Abstract

(A) Parcher et al. have described a methodology for the synthesis of 5-amino-4-imidazolecarboxylates, which participate efficiently in the synthesis of purine analogues. The authors have shown that the treatment of 2-cyanoglycine ethyl ester with phenylisocyanate in the presence of a catalytic amount of triethylamine provided the desired imidazol-2 one in excellent yields.3

(B) Kondo et al. reported that the rhodium(I) complex RhCl(PPh3)2, generated by the combination of [RhCl(C2H4)2] with a fourfold amount of Ph3P, effectively catalyzed the cyclocotrimerization of alkynes and isocyanate to give selectively 2-pyridones and/or pyrimidine-2,4-diones, by controlling the molar ratio of alkynes and isocyanates.4
(C) Coskun and Parlar have reported that the cycloaddition of substituted nitrone with phenylisocyanate proceeds smoothly in a short time with high yields to give the corresponding 1,2,4-oxadiazolidinone.5

(D) Awadallah has described that aryl benzoyl hydrazones react readily with phenylisocyanate at room temperature to give the corresponding substituted 2,3-dihydro-1,3,4-oxadiazoles.6

(E) Zhang et al. have presented a study detailing the thermal reactions of phenylisocyanate and vinyl aziridines. These reactions afforded interesting heterocyclic products in addition to the expected vinyl-substituted imidazolidinones.7

(F) Chen and co-workers have reported a ‘one-flask’ synthesis of guanidine hydrochlorides. They have carried out the reaction of NaN(TMS)2 with phenylisocyanate followed by addition of primary or secondary amines in the presence of a catalytic amount of AlCl3 in one flask to provide the corresponding guanidines in good yields.8

(G) Veronese et al. described the reaction of a tricarbonyl substrate with phenylisocyanate in the presence of 2 mol% transition metal acetylacetonate at room temperature to obtain 1:1 adduct in high yields. Formation of the compound clearly indicated the C–C bond formation between one intercarbonylic and one isocyanato carbon atom.9

(H) Khandan-Barani et al. have reported the synthesis of dihydro-1H-pyrrole from the reaction between alkyl/aryl isocyanide and di-alkyl acetylenedicarboxylate in the presence of phenylisocyanate in good yields.10

(I) Miura et al. showed that one molecule of acrylate reacts with two molecules of isocyanate in the presence of nickel(0)/SIPr catalyst to give 1,3,5-trisubstituted hydantoin.11

References

(6) Awadallah, A. D. Islamic Univ. J. 2006, 14, 129.