SYNLETT Spotlight

Triphenylphosphine/Carbon Dioxide

Compiled by Jolanta Robak

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Introduction

This paper reviews a relatively new procedure for the direct and general synthesis of urea compounds. A typical method to generate urea bonds is the reaction of amines with highly toxic phosgene. This class of compounds can also be obtained by using the Staudinger–aza-Wittig reaction, also known as the ‘phosphine imide’ reaction. This methodology is based on iminophosphorane chemistry and leads to the efficient formation of amide or urea bonds, very important for safer ‘phosgene-free’ chemistry. This ‘one-flask’ synthesis of urea derivatives includes the reaction of azides with triphenylphosphine followed by the reaction of the phosphine imide intermediates with carbon dioxide and amines (Scheme 1).

Abstracts

(A) Marsura and co-workers have described a Staudinger–aza-Wittig reaction on a monoazido-O-peracetylated β-cyclodextrin. In this synthesis the authors mixed 6-Azido-6-deoxy-per-O-acetylated-β-cyclodextrin (1) with Ph3P in presence of CO2 and benzylamine (2) in anhydrous DMF. The mixture was treated with ultrasound. Compared to standard conditions, product 3 was obtained in higher yield and a shorter reaction time.

(B) A combination of Ph3P and CO2 can be used for the synthesis a chiral urea from saccharide 4 and cyclohexane derivative 5. Bifunctional urea 6, containing a glycosyl and a diphenylphosphinyl scaffold, was synthesized in good yield. The obtained organocatalyst was shown to be effective in asymmetric Morita–Baylis–Hillman and aza-Henry reactions.
(C) The Staudinger–aza-Wittig reaction has been used to prepare sugar-ureido cryptands. Cryptates were synthesized by a one-pot reaction from 1,6′-diazido-1,6′-dideoxy-β-D-cellobiose (8) and tert-oxadiazacyclooctadecane (7) by using a tandem Staudinger–aza-Wittig reaction in anhydrous DMF. The structure of cyclic products 9 and 10 (2:2 or 1:1) was under control by a Cs⁺ or Na⁺ template effect.6

(D) A bisferrocenyl–substituted urea has been obtained by a one-pot process involving sequential addition of Ph₃P and then CO₂ to azide 11, and treatment of the isocyanate intermediate with ferrocenyl-methyl amine 12. Product 13 showed high anion coordination properties, especially for the dihydrogenphosphate anion (H₂PO₄⁻).7

(E) Yagodkin and co-workers described the reaction of benzylazide (14) with Ph₃P in dioxane in the presence of triethylammonium bicarbonate (TEAB) as a source of CO₂.8

(F) Cravotto and co-workers synthesized urea derivatives via microwave-assisted Staudinger–aza-Wittig reaction with polymer-bound diphenylphosphine. With this method, the authors could conduct the reaction at any temperature and gas pressure. The best results were obtained in acetonitrile under a high carbon dioxide pressure.9

References