

SYNLETT Spotlight

Triphenylphosphine/Carbon Dioxide

Compiled by Jolanta Robak



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

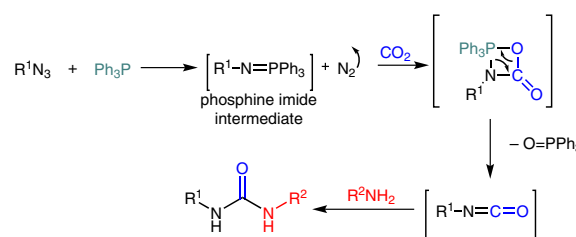
Jolanta Robak was born in Ciechanów, Poland, in 1987. She received a B.Sc. in biology and chemistry in 2012 and her a in organic chemistry in 2011 from the University of Łódź. She is currently working towards her Ph.D. under the supervision of Professor Bogusław Kryczka and Dr. Stanisław Porwański at the same university. Her research interests focus on the synthesis of (thio)urea carbohydrate organocatalysts and their asymmetric reactions.

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Introduction

This paper reviews a relatively new procedure for the direct and general synthesis of urea compounds.¹ 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.² This ‘one-flask’ synthesis of urea derivatives in-

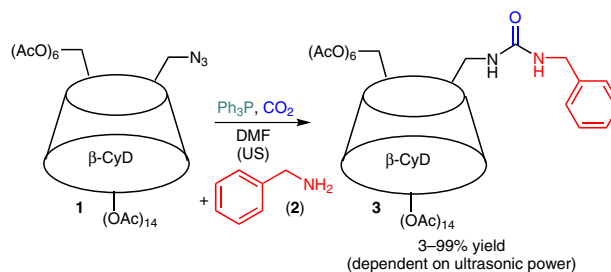
cludes the reaction of azides with triphenylphosphine followed by the reaction of the phosphine imide intermediates with carbon dioxide and amines (Scheme 1).³



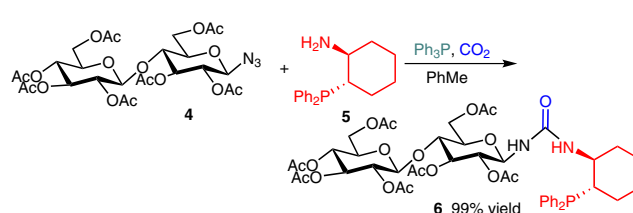
Scheme 1

Abstracts

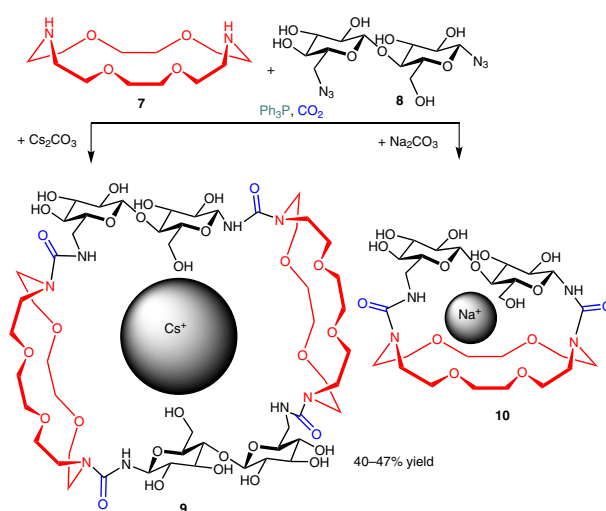
(A) Marsura and co-workers have described a Staudinger–aza-Wittig reaction on a monoazido-*O*-peracetylated β -cyclodextrin.⁴ In this synthesis the authors mixed 6^A-azido-6^A-deoxy-per-*O*-acetylated- β -cyclodextrin (**1**) with Ph_3P in presence of CO_2 and benzylamine (**2**) in anhydrous DMF. The mixture was treated with ultrasound. Compared to standard conditions, product **3** was obtained in higher yield and a shorter reaction time.



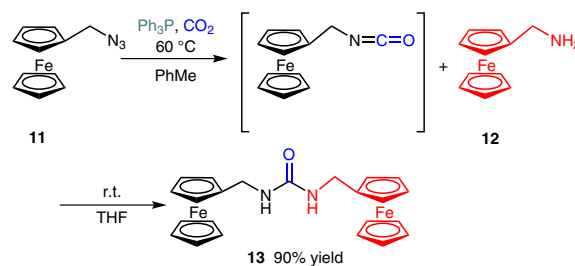
(B) A combination of Ph_3P and CO_2 can be used for the synthesis a chiral urea from saccharide **4** and cyclohexane derivative **5**. Bifunctional urea **6**, containing a glycosyl and a diphenylphosphinyl scaffold, was synthesized in good yield. The obtained organocatalyst was shown to be effective in asymmetric Morita–Baylis–Hillman and aza-Henry reactions.⁵



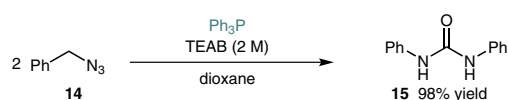
(C) The Staudinger–aza-Wittig reaction has been used to prepare sugar-ureido cryptands. Cryptates were synthesized by a one-pot reaction from 1,6'-diazido-1,6'-dideoxy- β -D-cellobiose (**8**) and tert-oxadiazacyclooctadecane (**7**) by using a tandem Staudinger–aza-Wittig reaction in anhydrous DMF. The structure of cyclic products **9** and **10** (2:2 or 1:1) was under control by a Cs^+ or Na^+ template effect.⁶



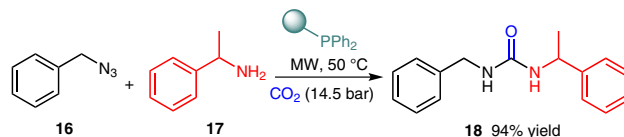
(D) A bisferrocenyl–substituted urea has been obtained by a one-pot process involving sequential addition of Ph_3P and then CO_2 to azide **11**, and treatment of the isocyanate intermediate with ferrocenylmethyl amine **12**. Product **13** showed high anion coordination properties, especially for the dihydrogenphosphate anion (H_2PO_4^-).⁷



(E) Yagodkin and co-workers described the reaction of benzylazide (**14**) with Ph_3P in dioxane in the presence of triethylammonium bicarbonate (TEAB) as a source of CO_2 .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

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