**SYNLETT**

# Spotlight 466

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

# Allyl Alkyl Carbonates

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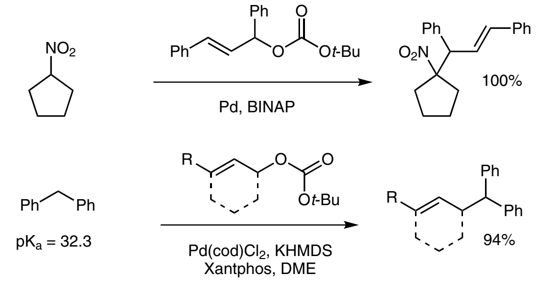
Dedicated to my family

## Introduction

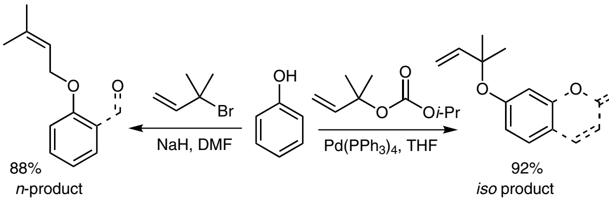
Allyl methyl carbonate is the simplest allyl alkyl carbonate. It was first synthesised by Hermann Otto Laurenz Fischer in 1929.[1] In general, a synthesis of these carbonates is possible in high yields starting from allyl alcohols, which can be converted with dialkyl dicarbonates[2] or alkyl chloroformates[3] under basic conditions (e.g., BuLi, pyridine) into the corresponding allyl alkyl carbonates. Allyl carbonates are highly versatile reagents, and they can be used both for nucleo- and electrophilic reactions. Furthermore, the introduction of allyl groups is of high synthetic value, because they can be easily transformed into other functional groups. Traditional allylation reagents, like allyl bromide, require the addition of a base. An advantage of allyl alkyl carbonates is that no additional base is needed because of the cleavage of the alkyl carbonate moiety into carbon dioxide and an alkoxide. This is the reason for the influence of the alkyl substituent (Me, *t*-Bu) on the reaction.

## Abstracts

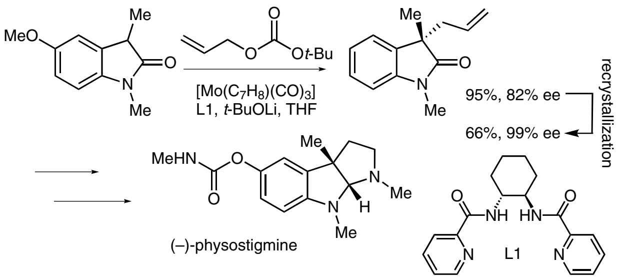
(A) *Allylic Alkylation of Nucleophiles; C–C Bond Formation*
Tsuji[4] and Trost[5] pioneered the palladium-catalysed allylation of nucleophiles. The allylic alkylation is a versatile method to construct C–C bonds, especially products with bulky quaternary carbon centres.[6,7] The allyl carbonate and palladium form an $\eta^3$-allylpalladium complex, which is attacked by a nucleophile. In general, C–H acidic compounds are used, but nucleophiles like diphenylmethane are also suitable.[8]



(B) *Allylic Alkylation of Nucleophiles; C–Het Bond Formation*
Various heteroatoms – with aliphatic as well as aromatic substituents – can be allylated by allyl alkyl carbonates[9–11] using catalysis by palladium or iron complexes.[12] While the reaction of 1,1-dimethylallyl bromide with phenol leads to the unexpected n-product due to an $S_N'$ reaction, [13] the analogue carbonate leads to the desired *iso* product.[14]



(C) *Asymmetric Alkylation of Nucleophiles; C–C Bond Formation*
The Trost asymmetric allylic alkylation, often referred to as AAA, is the enantioselective version of the Tsuji–Trost reaction. The AAA is catalysed by palladium or molybdenum. The enantioselectivity can be introduced by a chiral ligand, for example by a tetradentate Trost ligand.[15] Furthermore, branched asymmetric allylation products can be generated by iridium catalysis. The enantioselectivity can be introduced as described above.[16]



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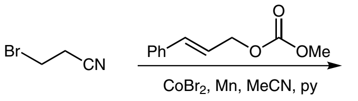
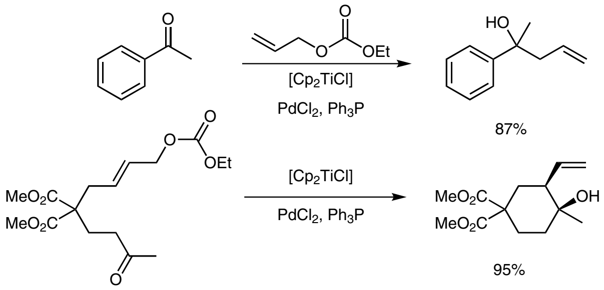
(D) *Reductive Allylation of Alkyl Halides*

The direct allylation of alkyl halides results in a C($sp^3$)–C($sp^3$) coupling. This catalysed reaction proceeds via an allyl alkyl cobalt intermediate. Manganese acts as reducing agent for the allyl copper complex.[17]



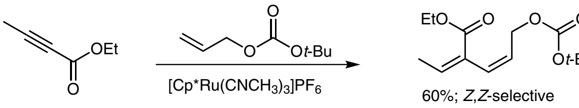
(E) *Barbier-Type Allylation*

Allyl ethyl carbonate can be used for the allylation of aldehydes and ketones in good yield. Furthermore, crotylation, prenylation, and intramolecular allylation are also possible with the corresponding carbonate. The Barbier-type allylation is mediated by a bimetallic system of titanium/palladium and highly accelerated by manganese dust. Initially, palladium undergoes an oxidative addition with allyl carbonate. Single electron transfer (SET) of the $\eta^3$-allylpalladium complex forms a palladium(I) intermediate. This species fragments further to an allyl radical, which can form the nucleophilic $\eta^3$-allyltitanocene(IV) complex.[18]



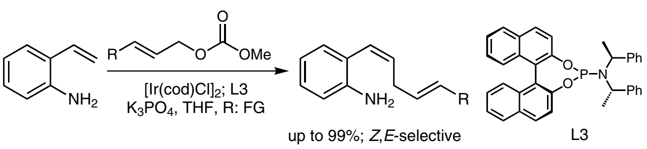
(F) *Alder-ene Reaction*

1,4-Dienes can be formed by the Alder-ene reaction of allyl carbonates and alkynes. The *E*/*Z*-selectivity could be increased by the use of a permethylated cyclopentadienyl ruthenium complex.[19]



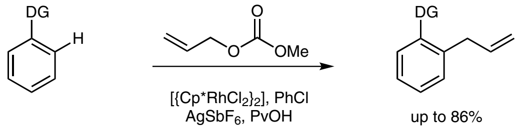
(G) *Allylation of Styrenes via a Heck-Type Reaction*

The iridium-catalysed reaction of 2-vinylanilines and allyl carbonates leads to *Z*,*E*-dienes. This method is a *cis*-selective supplement to the Heck reaction, which affords the *trans* products. The authors discuss an amine-assisted iridium-catalysed vinyl C–H bond activation to form the reactive intermediate.[20]



(H) *Direct C–H Allylation of Arenes*

The allylation of arenes is catalysed by a permethylated cyclopentadienyl ruthenium complex. The reaction proceeds via C–H activation and is directed by *N*,*N*-diisopropylacetamide.[21]



## References

(1) Fischer, H. O. L.; Feldmann, L. *Chem. Ber.* **1929**, *62*, 858.
(2) Lemke, M.-K.; Schwab, P.; Fischer, P.; Tischer, S.; Witt, M.; Noehringer, L.; Rogachev, V.; Jäger, A.; Kataeva, O.; Fröhlich, R.; Metz, P. *Angew. Chem. Int Ed.* **2013**, *52*, 11651.
(3) Trost, B. M.; Miller, J. R.; Hoffman, C. M. Jr. *J. Am. Chem. Soc.* **2011**, *133*, 8165.
(4) Tsuji, J.; Takahashi, H.; Morikawa, M. *Tetrahedron Lett.* **1965**, *6*, 4387.
(5) Trost, B. M.; Fullerton, T. J. *J. Am. Chem. Soc.* **1973**, *95*, 292.
(6) Dickschat, A. T.; Behrends, F.; Surmiak, S.; Weiß, M.; Eckert, H.; Studer, A. *Chem. Commun.* **2013**, *49*, 2195.
(7) Maki, K.; Kanai, M.; Shibasaki, M. *Tetrahedron* **2007**, *63*, 4250.
(8) Sha, S.-C.; Zhang, J.; Carroll, P. J.; Walsh, P. J. *J. Am. Chem. Soc.* **2013**, *135*, 17602.
(9) Schmidt, B.; Nave, S. *Adv. Synth. Catal.* **2006**, *348*, 531.
(10) Dieskau, A. P.; Plietker, B. *Org. Lett.* **2011**, *13*, 5544.
(11) Deska, J.; Kazmaier, U. *Chem. Eur. J.* **2007**, *13*, 6204.
(12) Plietker, B. *Angew. Chem. Int. Ed.* **2006**, *45*, 6053.
(13) Patent: US4515801 A1, Bayer Aktiengesellschaft, **1985**
(14) Beare, K. D.; McErlean, C. S. P. *Tetrahedron Lett.* **2013**, *54*, 1056.
(15) Trost, B. M.; Zhang, Y. *Chem. Eur. J.* **2011**, *17*, 2916.
(16) Gärtner, M.; Jäkel, M.; Achatz, M.; Sonnenschein, C.; Tverskoy, O.; Helmchen, G. *Org. Lett.* **2011**, *13*, 281.
(17) Qian, X.; Auffrant, A.; Felouat, A.; Gosmini, C. *Angew. Chem. Int. Ed.* **2011**, *50*, 10402.
(18) Millán, A.; Campaña, A. G.; Bazdi, B.; Miguel, D.; Álvarez de Cienfuegos, L.; Echavarren, A. M.; Cuerva, J. M. *Chem. Eur. J.* **2011**, *17*, 3985.
(19) Trost, B. M.; Martos-Redruejo, A. *Org. Lett.* **2009**, *13*, 1071.
(20) He, H.; Liu, W. B.; Dai, L. X.; You, S. L. *J. Am. Chem. Soc.* **2009**, *131*, 8346.
(21) Wang, H.; Schröder, N.; Glorius, F. *Angew. Chem. Int. Ed* **2013**, *52*, 5386.