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Spotlight 375

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

Silver Carbonate

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Introduction

Silver carbonate, Ag_2CO_3, is a odorless, yellow to yellow-grey powder poorly soluble in water. Upon heating, it gradually decomposes to silver oxide, Ag_2O, and CO_2 close to its melting point of 210 °C. Silver carbonate is commercially available, but can also be readily accessed through the reaction of cheaper silver nitrate with sodium carbonate in water (Scheme 1).[1]

$$2\,AgNO_3 + Na_2CO_3 \xrightarrow{H_2O,\ r.t.} Ag_2CO_3 + 2\,NaNO_3$$

Scheme 1 Silver carbonate is easily obtained from silver nitrate and sodium carbonate

Silver carbonate can also be used to prepare other silver salts. One such salt, particularly useful in catalysis is silver bis(trifluoromethanesulfonyl)imide, derived from the reaction of silver carbonate and triflimide (Scheme 2).[2]

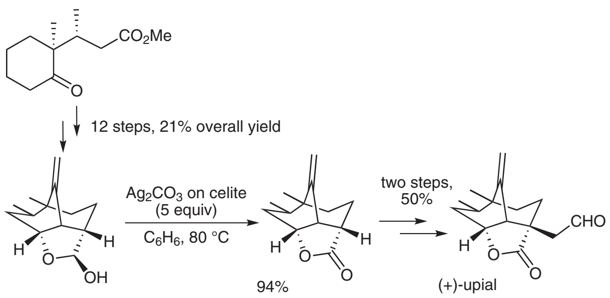
$$Ag_2CO_3 + 2\,HNTf_2 \xrightarrow{H_2O,\ 65\ °C} 2\,AgNTf_2 + H_2O + CO_2$$

Scheme 2 Silver carbonate can also be used for the preparation of other useful silver salts

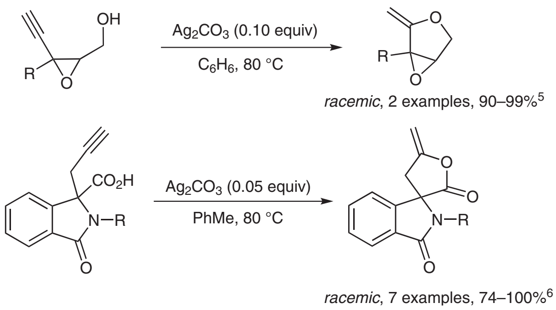
Silver carbonate has found a myriad of different uses in organic chemistry, notably as oxidizing agent (Fetizon's reagent), as catalyst for alkyne activation, as halogen scavenger and as base and/or oxidant of choice for various transition-metal-catalyzed reactions. Selected applications of silver carbonate in these diverse contexts will be presented here.

Abstracts

(A) *Oxidation of Alcohols:*
Fetizon's reagent (silver carbonate on celite) is known to be a mild oxidizing agent capable of converting alcohols into aldehydes and ketones.[3] Here, this reagent is applied in the complex setting of an enantioselective total synthesis of (+)-upial.[4] The desired lactone was obtained from the corresponding lactol in excellent 94% yield.



(B) *5-Exo-dig Cyclization of Alcohols and Carboxylic Acids:*
Alcohols containing a proximal acetylenic part[5] and isoindolones containing γ-acetylenic carboxylic acid moieties[6] can be efficiently cyclized using a catalytic amount of Ag_2CO_3.



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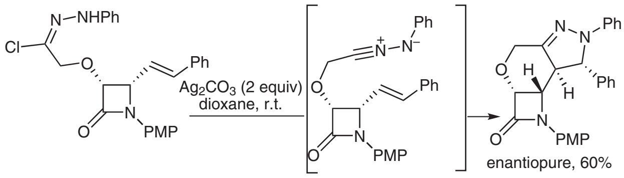
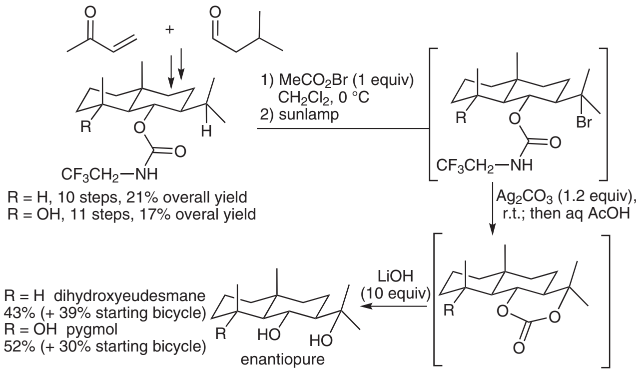
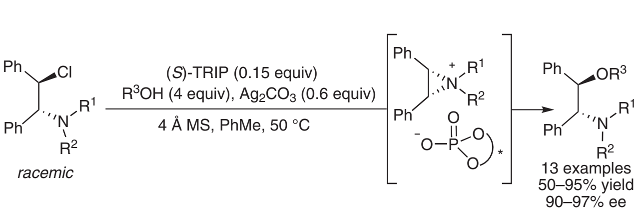
(C) *Halogen Scavenger; Generation of Nitrilimines:*
The azeto[3′,4′:2,3]pyrano[4,5-*c*]pyrazole skeleton holds potential interest as a β-lactamase-resistant antibiotic. An enantioselective route towards one member of this class was developed from the intramolecular [3+2] cycloaddition of a nitrilimine and a proximal alkene. The nitrilimine was generated via chlorine abstraction from the parent hydrazonoyl chloride using silver carbonate.[7]



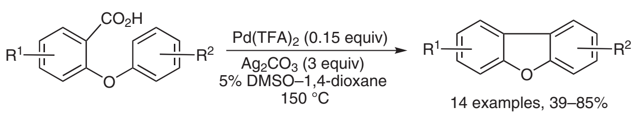
(D) *Halogen Scavenger; C–H Oxidation Strategy:*
In landmark work,[8] a C–H oxidation strategy was employed for the synthesis of eudesmane terpenes. The syntheses of two of them, dihydroxyeudesmane and pygmol, feature as key steps the selective bromination of the more reactive tertiary carbon from the isopropyl sidechain, followed by a cyclization event assisted by silver carbonate. After hydrolysis of the cyclic carbonate formed, the corresponding diol is obtained in a very selective manner.



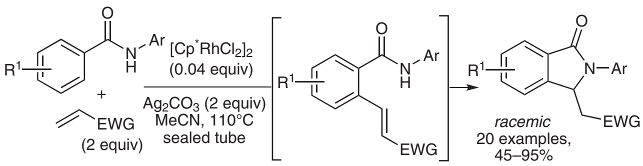
(E) *Halogen Scavenger: Aziridinium Ion Formation:*
A chiral anion phase-transfer catalysis was established by taking advantage from the low solubility of silver carbonate and the generally high solubility of (*S*)-TRIP salts in organic solvents. Silver carbonate abstracts the chlorine atom to generate an aziridium phosphate ion pair,[9] whose chiral anion directs the enantioselective nucleophilic aziridinium ring opening to afford the corresponding amino ethers in good yields and excellent enantioselectivities.[10]



(F) *Base/Oxidant for Decarboxylative Cross-Coupling:*
An efficient, regio- and chemoselective palladium-catalyzed intramolecular arylation of benzoic acid derivatives by means of a decarboxylation/C–H activation sequence using silver carbonate as base and oxidant of choice has been described.[11]



(G) *Oxidant for Olefination–Michael Addition Sequence:*
The use of dinuclear rhodium species $[Cp^*RhCl_2]_2$ as catalyst and Ag_2CO_3 as oxidant allows direct access to Heck cross-coupled products without the need for prior arene functionalization.[12] The styrene product obtained undergoes spontaneous Michael addition under the reaction conditions to afford the corresponding cyclized products in good yields.[13]



References

(1) For a detailed protocol see: Xu, C.; Liu, Y.; Huang, B.; Li, H.; Qin, X.; Zhang, X.; Dai, Y. *Appl. Surf. Sci.* **2011**, *257*, 8732.
(2) For a detailed protocol see: Vij, A.; Zheng, Y.; Kirchmeier, R. L.; Shreeve, J. M. *Inorg. Chem.* **1994**, *33*, 3281.
(3) Tojo, G.; Fernández, M. *Oxidation of Alcohols to Aldehydes and Ketones*; Springer Science; Business Media: New York, **2006**.
(4) Takahashi, K.; Watanabe, M.; Honda, T. *Angew. Chem. Int. Ed.* **2008**, 131.
(5) Other examples using stoichiometric amounts of Ag_2CO_3 have also been reported: Pale, P.; Chuche, J. *Eur. J. Org. Chem.* **2000**, 1019.
(6) Rammah, M. M.; Othman, M.; Ciamala, K.; Strohmann, C.; Rammah, M. B. *Tetrahedron* **2008**, *64*, 3505.
(7) (a) Del Buttero, P.; Molteni, G.; Pilati, T. *Tetrahedron: Asymmetry* **2010**, *21*, 2607. In this same context, see also: (b) Lee, K. J.; Choi, J.-K.; Yum, E. K.; Cho, S. Y. *Tetrahedron Lett.* **2009**, *50*, 6698.
(8) Chen, K.; Baran, P. *Nature* **2009**, *459*, 824.
(9) This can be seen as a particular case of a more general concept coined as asymmetric counteranion-directed catalysis. For a leading reference, see: Mayer, S.; List, B. *Angew. Chem. Int. Ed.* **2006**, *45*, 4193.
(10) Hamilton, G.; Kanai, T.; Toste, F. D. *J. Am. Chem. Soc.* **2008**, *130*, 14984.
(11) (a) Wang, C.; Piel, I.; Glorius, F. *J. Am. Chem. Soc.* **2009**, *131*, 4194. For an intermolecular version, see: (b) Zhang, F.; Greaney, M. F. *Org. Lett.* **2010**, *12*, 4745.
(12) For a leading reference in this area see: Murai, S.; Kakiuchi, S.; Sekine, S.; Tanaka, Y.; Kamatani, A.; Sonoda, M.; Chatani, N. *Nature* **1993**, *366*, 529.
(13) Wang, F.; Song, G.; Li, X. *Org. Lett.* **2010**, *12*, 5430.