Organic Synthesis

STATE OF THE ART 2011–2013

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TRISTAN LAMBERT

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and

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Preface

This volume is made up of the weekly *Organic Highlights* published online (http://www.organic-chemistry.org) in 2012 and 2013 and arranged by topic. These columns are still available online, with active links to the journal articles cited. This volume also includes a cumulated subject/transformation index for all five volumes in this series, going back to 2003. The leading references in these volumes together provide a thorough and easily used guide to modern organic synthesis.

This project originated with a discussion of the challenge of updating the class reference work *Comprehensive Organic Transformations: A Guide to Functional Group Preparations* by Richard C. Larock (2nd. edition; Wiley-VCH, 1999). Our objective was to provide immediate awareness of important new developments in organic synthesis, and at the same time to develop a readily accessible reference work. We were able to go far beyond functional group transformation, adding ring construction and control of relative and absolute configuration. The popularity of both the website (3500 subscribers worldwide) and of the previous volumes in this series attests to the success of this approach.

I often consult these volumes myself in my day-to-day work of teaching and research. These five volumes together (and the later biennial volumes that will follow) are a valuable resource that should be on the bookshelf of every practicing organic synthesis chemist.

Douglass F. Taber
Philadelphia, PA
March 5, 2014

Contents

Organic Synthesis
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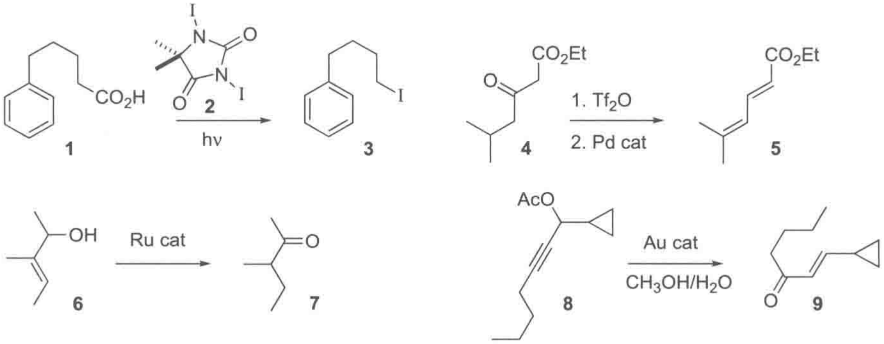
1. Functional Group Transformations

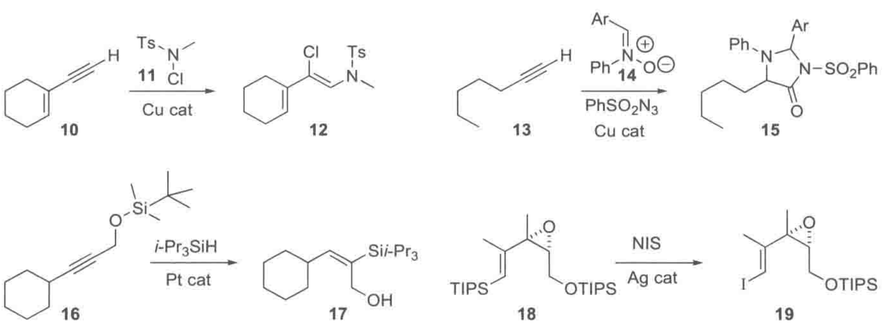
Douglass F. Taber
May 14, 2012

MARK GANDELMAN OF the Technion–Israel Institute of Technology devised (*Adv. Synth. Catal.* **2011**, *353*, 1438) a protocol for the decarboxylative conversion of an acid **1** to the iodide **3**. Doug E. Frantz of the University of Texas, San Antonio effected (*Angew. Chem. Int. Ed.* **2011**, *50*, 6128) conversion of a β-keto ester **4** to the diene **5** by way of the vinyl triflate.



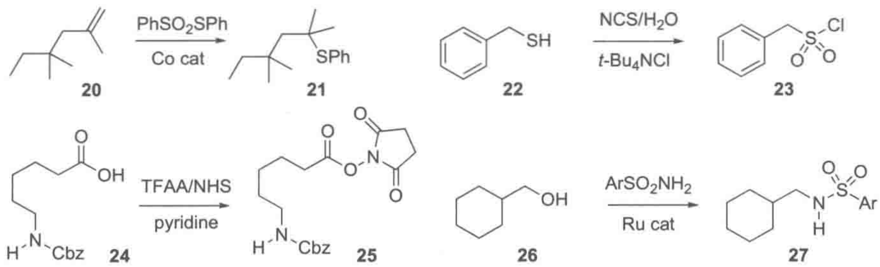
Pei Nian Liu of the East China University of Science and Technology and Chak Po Lau of the Hong Kong Polytechnic University (*Adv. Synth. Catal.* **2011**, *353*, 275) and Robert G. Bergman and Kenneth N. Raymond of the University of California, Berkeley (*J. Am. Chem. Soc.* **2011**, *133*, 11964) described new Ru catalysts for the isomerization of an allylic alcohol **6** to the ketone **7**. Xiaodong Shi of West Virginia University optimized (*Adv. Synth. Catal.* **2011**, *353*, 2584) a gold catalyst for the rearrangement of a propargylic ester **8** to the enone **9**.

Xue-Yuan Liu of Lanzhou University used (*Adv. Synth. Catal.* **2011**, *353*, 3157) a Cu catalyst to add the chloramine **11** to the alkyne **10** to give **12**. Kasi Pitchumani of Madurai Kamaraj University converted (*Org. Lett.* **2011**, *13*, 5728) the alkyne **13** into the α-amino amide **15** by reaction with the nitrone **14**.

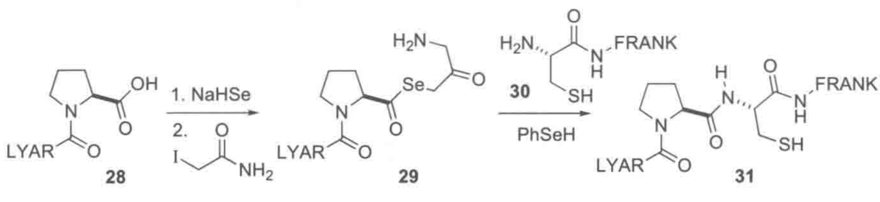


Katsuhiko Tomooka of Kyushu University effected (*J. Am. Chem. Soc.* **2011**, *133*, 20712) hydrosilylation of the propargylic ether **16** to the alcohol **17**. Matthew J. Cook of Queen's University Belfast (*Chem. Commun.* **2011**, *47*, 11104) and Anna M. Costa and Jaume Vilarrasa of the Universitat de Barcelona (*Org. Lett.* **2011**, *13*, 4934) improved the conversion of an alkenyl silane **18** to the iodide **19**.

Vinay Girijavallabhan of Merck/Kenilworth developed (*J. Org. Chem.* **2011**, *76*, 6442) a Co catalyst for the Markovnikov addition of sulfide to an alkene **20**. Hojat Veisi of Payame Noor University oxidized (*Synlett* **2011**, 2315) the thiol **22** directly to the sulfonyl chloride **23**. Nicholas M. Leonard of Abbott Laboratories prepared (*J. Org. Chem.* **2011**, *76*, 9169) the chromatography-stable O-Su ester **25** from the corresponding acid **24**. Diego J. Ramón of the Universidad de Alicante coupled (*J. Org. Chem.* **2011**, *76*, 5547) the alcohol **26** with a sulfonamide to give the protected amine **27**.



Whereas short (up to about 40) oligopeptides are readily prepared by bead-based synthesis, longer oligopeptides and proteins are prepared by convergent coupling of the oligopeptides so prepared using thioester-based native chemical ligation. Some C-terminal amino acids, however, including proline, do not work well. Thomas Durek of the University of Queensland showed (*Angew. Chem. Int. Ed.* **2011**, *50*, 12042) that the *selenyl* ester **29** participated more efficiently.

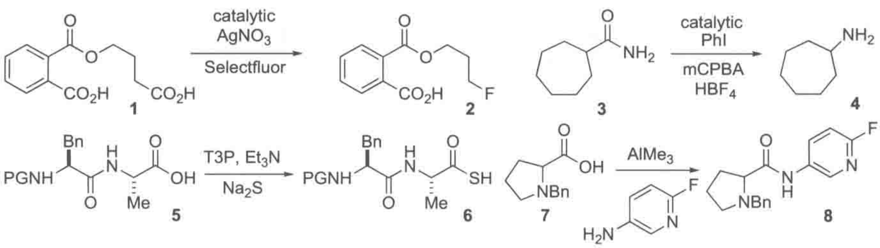


2. Functional Group Interconversion

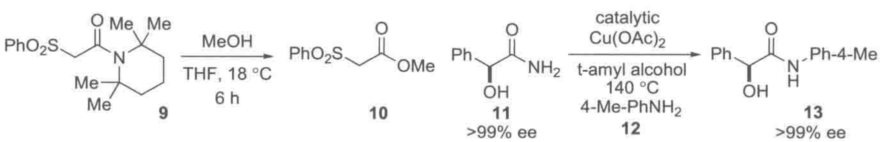
Tristan H. Lambert
October 22, 2012

CHAOZHONG LI OF the Shanghai Institute of Organic Chemistry reported (*J. Am. Chem. Soc.* **2012**, *134*, 10401) the silver nitrate catalyzed decarboxylative fluorination of carboxylic acids, which shows interesting chemoselectivity in substrates such as **1**. A related decarboxylative chlorination was also reported by Li (*J. Am. Chem. Soc.* **2012**, *134*, 4258). Masahito Ochiai at the University of Tokushima has developed (*Chem. Commun.* **2012**, *48*, 982) an iodobenzene-catalyzed Hofmann rearrangement (e.g., **3** to **4**) that proceeds via hypervalent iodine intermediates.

The dehydrating agent T3P (propylphosphonic anhydride), an increasingly popular reagent for acylation chemistry, has been used (*Tetrahedron Lett.* **2012**, *53*, 1406) by Vommina Sureshbabu at Bangalore University to convert amino or peptide acids such as **5** to the corresponding thioacids with sodium sulfide. Jianqing Li and co-workers at Bristol-Myers Squibb have shown (*Org. Lett.* **2012**, *14*, 214) that trimethylaluminum, which has long been known to effect the direct amidation of esters, can also achieve the direct coupling of acids and amines, such as in the preparation of amide **8**.



The propensity of severely hindered 2,2,6,6-tetramethylpiperidine (TMP) amides such as **9** to undergo solvolysis at room temperature has been shown (*Angew. Chem. Int. Ed.* **2012**, *51*, 548) by Guy Lloyd-Jones and Kevin Booker-Milburn at the University of Bristol. The reaction proceeds by way of the ketene and is enabled by sterically induced destabilization of the usual conformation that allows conjugation of the nitrogen lone pair with the carbonyl. Matthias Beller at Universität Rostock has found (*Angew. Chem. Int. Ed.* **2012**, *51*, 3905) that primary amides may be transamidated via copper(II) catalysis. The conditions are mild enough that an epimerization-prone amide such as **11** undergoes no observable racemization during conversion to amide **13**.



A photochemical transamidation has been achieved (*Chem. Sci.* **2012**, *3*, 405) by Christian Bochet at the University of Fribourg that utilizes 385-nm light to activate a