

SYNLETT
Spotlight 288Potassium Dodecatungstocobaltate
Trihydrate: $K_5CoW_{12}O_{40} \cdot 3H_2O$

Compiled by M. Venu Chary



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

M. Venu Chary was born in Uddemarry, Andhra Pradesh, India, in 1976. He obtained his M.Sc. in Organic Chemistry from Kakatiya University, Warangal, in 2001. After working for one year as Junior Chemist in Thioxazo Biotech Laboratory Pvt. Ltd., Hyderabad, he joined the Indian Institute of Chemical Technology as Junior Research Fellow. He is currently working towards his Ph.D. under the supervision of Dr. D. Subhas Bose on the total synthesis of (–)-circumdatin H. His research interests focus on the synthesis of bioactive natural products, process development work, and development of new synthetic methodologies.

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Dedicated to my mentor Dr. D. Subhas Bose for his constant encouragement.

Introduction

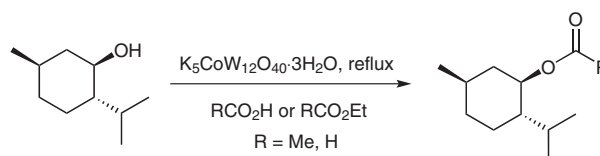
Heteropolyoxometalates as stable inorganic porphyrins have attracted much attention in the last two decades. The versatility of these catalysts has been demonstrated in various organic transformations due to their weak superacidity, redox properties, low toxicity, stability, inexpensiveness, water tolerance and reusability.¹ Potassium dodecatungstocobaltate (PDTC) is apparently a perfect outer-sphere one-electron oxidant, due to the presence of a sheath of chemically inert oxygen atoms, which protects the central ion from undesired inner-sphere substitution reactions.² For this reason, electron transfer with PDTC typically leads to selective reactions and clean chemistry. Habibi et al. introduced this reagent for the acetylation, formylation, tetrahydropyranylation of alcohols, and de-

tetrahydropyranylation of ethers.³ Further PDTC was successfully used in various organic transformations including esterification and transesterification, regeneration of carbonyl compounds from oximes, and synthesis of substituted 3,4-dihydropyrimidin-2(1*H*)-ones, quinolines, dihydroquinolines, pyridines, imidazoles and xanthenes.

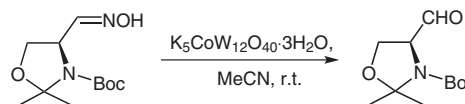
For the preparation of PDTC, cobaltous acetate and sodium tungstate were initially treated with acetic acid and water at pH ~7 to give sodium tungstodicobalt(II)ate. The sodium salt was then converted into the potassium salt by treatment with potassium chloride. Finally, the cobalt(II) complex was oxidized to the cobalt(III) complex by potassium persulfate in sulfuric acid. Crystallization in MeOH yielded PDTC as light blue solid.^{2,5}

Abstracts

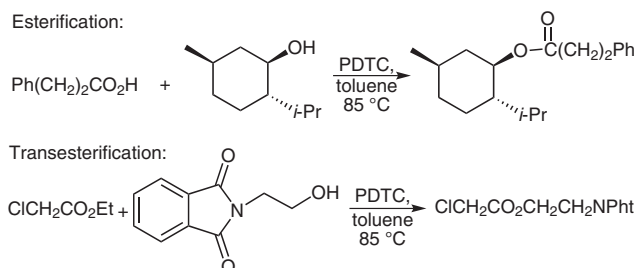
(A) *Acetylation and Formylation of Alcohols*: PDTC is used as a catalyst for the stereospecific acetylation and formylation of various alcohols.³



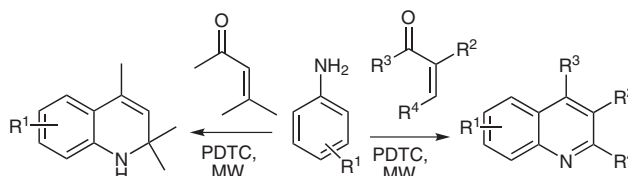
(B) *Regeneration of Carbonyl Compounds from Oximes*: Bose et al. reported an environmentally benign selective method for the regeneration of carbonyl compounds from oximes and *N,N*-dimethyl hydrazones. This protocol can be readily applied to large-scale processes with high efficiency and selectivity. In addition, stereochemical integrity at the aldehyde-bearing carbon was retained.⁴



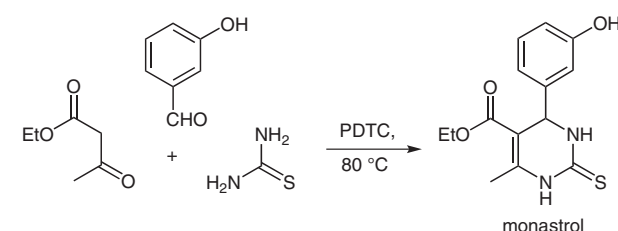
(C) *Esterification and Transesterification*: Esterification of various carboxylic acids with alcohols and transesterification of carboxylic esters using PDTC was achieved in good to excellent yields. The esterification process worked well with primary, secondary, tertiary, benzylic and homoallylic alcohols with the reactivity of the alcohols decreasing in the order of primary>secondary>tertiary, and neither isomerization of the substrate nor racemization were observed.⁵



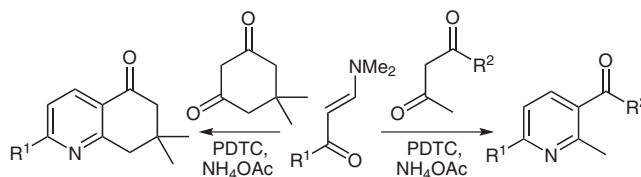
(D) *Skraup and Friedländer Reaction*: A mild and efficient solvent-free method has been developed by two different approaches for the synthesis of quinoline and dihydroquinoline derivatives in high yields using PDTC under microwave irradiation: (i) one-pot reaction of anilines with alkyl vinyl ketones (Skraup reaction); (ii) Friedländer reaction between various acetophenones and 2-aminoacetophenone.⁶



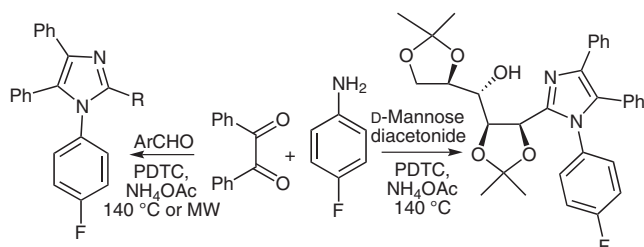
(E) *Biginelli Reaction*: An eco-friendly synthesis of 3,4-dihydropyrimidin-2(1H)-ones is achieved by a three-component condensation reaction of an aldehyde, β -keto ester and urea in the presence of PDTC under solvent-free conditions. The scope of this method was utilized for the synthesis of mitotic kinesin EG5 inhibitor monastrol.⁷



(F) *Synthesis of Pyridines and Tetrahydroquinolin-5-ones*: Regio-selective one-pot, three-component condensation of enamines, β -dicarbonyl compounds and ammonium acetate in the presence of PDTC in refluxing isopropanol as well as under solvent-free conditions^{8a} and microwave irradiation^{8b} afforded 2,3,6-trisubstituted pyridines and novel 2,7,7-trisubstituted-5,6,7,8-tetrahydroquinolin-5-ones in excellent yields.



(G) *Synthesis of 1,2,4,5-Tetrasubstituted Imidazoles*: 1,2,4,5-Tetrasubstituted imidazoles were obtained by four-component condensation of benzyl or benzoin, aldehydes, amines and ammonium acetate using PDTC.^{9a} By the use of sugar aldehydes C-glycosyl tetrasubstituted imidazoles were achieved.^{9b}



References

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