

SYNLETT Spotlight 337

2-Bromoacetophenone

Compiled by Shyamalee Gogoi



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

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Introduction

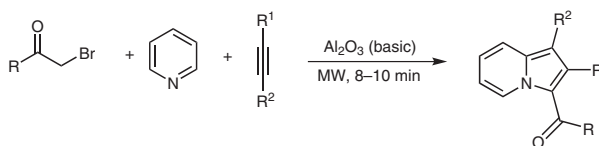
2-Bromoacetophenone (C_8H_7BrO , mp 48–51 °C), also known in the literature either as ω -bromoacetophenone or phenacyl bromide, is a crystalline powder with a very sharp odor. It is a highly toxic and corrosive compound and a powerful lachrymator. Further, the reagent is harmful if swallowed or inhaled and causes irritation to skin and mucous membranes. 2-Bromoacetophenone is a stable compound, but incompatible with strong bases and strong oxidizing agents. The versatile reagent is a useful precursor of many organic compounds and is primarily used as an intermediate in pharmaceuticals and other fine

chemical industries. It can be prepared by bromination of acetophenone in dry ether using $AlCl_3$ as catalyst.¹ 2-Bromoacetophenone reacts slowly with moisture to form HBr. Contact with metals should be avoided as mild corrosion occurs.

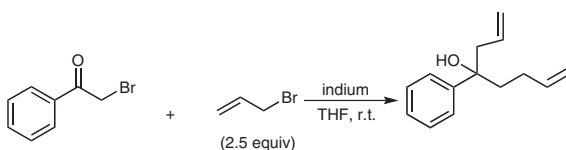
2-Bromoacetophenone has found wide applications in organic synthesis including the syntheses of indolizines, pyridines, dihydrofuran derivatives, etc. It is also a very useful reagent for the identification of organic acids as it easily converts them into the corresponding crystalline phenacyl esters. This versatile reagent was first reported in 1871.²

Abstracts

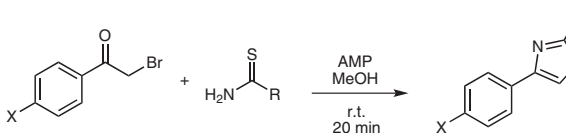
(A) Boruah and co-workers³ reported an efficient synthesis of indolizines in excellent yields via a microwave-mediated, one-pot, three-component reaction of 2-bromoacetophenone, pyridine, and acetylene, catalyzed by basic Al_2O_3 .



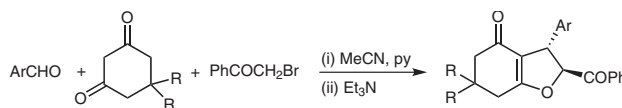
(B) Yadav et al. reported vic-diallylation and dipropargylation of 2-bromoacetophenone with allyl and propargyl indium reagents, generated in situ from metallic indium and allyl or propargyl bromide to produce 4-aryl-octa-1,7-dien-4-ol derivatives in good yields.⁴



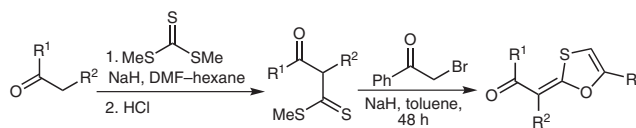
(C) Das et al.⁵ developed a convenient method for the rapid and high-yielding synthesis of thiazoles and amino thiazoles by treatment of 2-bromoacetophenone with thioamides or thiourea in the presence of ammonium-12-molybdophosphate (AMP) at room temperature.



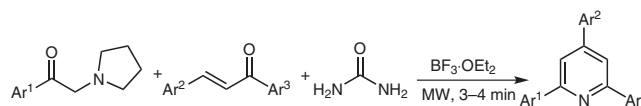
(D) An efficient synthetic procedure for fused 2,3-dihydrofuran derivatives was developed by Chao-Guo Yan and co-workers⁶ with the assistance of pyridinium ylide. A sequential one-pot, two-step tandem reaction starting from pyridine, aromatic aldehyde, dimedone or 4-hydroxy coumarin and 2-bromoacetophenone with triethylamine as catalyst proceeded smoothly in acetonitrile.



(E) Anabha and co-workers⁷ reported the synthesis of substituted 2-ylidene-1,3-oxathioles from aroyl dithiocarboxylates and 2-bromoacetophenone in good yields. The aroyl dithiocarboxylates were prepared by treatment of active methylene ketones with trithiocarbonate in the presence of sodium hydride.



(F) An efficient method for the synthesis of 2,4,6-triarylpyridines has been accomplished via microwave-promoted and $\text{BF}_3 \cdot \text{OEt}_2$ -catalyzed one-pot reaction of ω -pyrrolidinoacetophenone with chalcone. ω -Pyrrolidinoacetophenone was prepared via condensation of 2-bromoacetophenone with pyrrolidine in refluxing methanol.⁸



References

- (1) Cowper, R. M.; Davidson, L. H. *Org. Synth., Coll. Vol. II* **1943**, 480.
- (2) Emmerling, A.; Engler, C. *Ber.* **1871**, 4, 147.
- (3) Bora, U.; Saikia, A.; Boruah, R. C. *Org. Lett.* **2003**, 5, 435.
- (4) Yadav, J. S.; Subba Reddy, B. V.; Biswas, S. K.; Sengupta, S.; Vishnumurthy, P. *Tetrahedron Lett.* **2008**, 49, 1034.
- (5) Das, B.; Reddy, V. S.; Ramu, R. *J. Mol. Catal. A: Chem.* **2006**, 252, 235.
- (6) Wang, Q. F.; Hou, H.; Hui, L.; Yan, C.-G. *J. Org. Chem.* **2009**, 74, 7403.
- (7) Samuel, R.; Asokan, C. V.; Suma, S.; Chandran, P.; Retnamma, S.; Anabha, E. R. *Tetrahedron Lett.* **2007**, 48, 8376.
- (8) Borthakur, M.; Dutta, M.; Gogoi, S.; Boruah, R. C. *Synlett* **2008**, 3125.