

Bismuth Mediated Organic Reaction: The Formation of β, γ -Unsaturated Ketones

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Abstract: Allyl bromide reacts with acid chlorides to give β, γ -unsaturated ketones in moderate yields in THF at the presence of BiCl_3/Al .

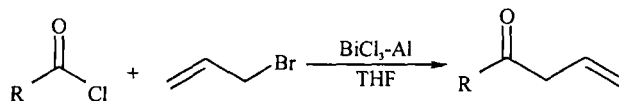
Key words: bismuth, β, γ -unsaturated ketones, synthesis

CLC number: O621.3, **Document Code:** B, **Article ID:** 1672-1292(2002)04-0013-03

0 Introduction

The organic reactions mediated by metals have aroused much interest. Of these metals, the application of bismuth in organic synthesis has been paid special attention^[1]. Many studies focused on Barbier-type reaction of allylic halides to carbonyl compounds or aldimines mediated by bismuth^[2~4]. It was viewed that the reaction proceeds through an allylic bismuth intermediate. Bismuth was also used in the cross coupling reaction of carbonyl compounds^[5] and the synthesis of heterocyclic compounds^[6], *etc.* We have reported a bismuth mediated reaction for the formation of C-Se bond^[7]. In these reactions, bismuth was usually generated from the reduction of BiCl_3 *in situ* by some active metals such as Zn, Al, Fe, *etc.*, then it acted to organic compounds to promote the reactions. The weaker activity of bismuth avoided some side reactions, so it may make the reactions with high yields. Another advantage of this type of reaction is that the most reaction can take place in the presence of water, which makes the operation very convenient. These facts show that bismuth has great potential in organic synthesis. The further studies on it, and exploring its new applied area will have great significance.

β, γ -Unsaturated ketones have high versatility and wide applicability in natural product synthesis^[8], so the reaction conditions for the synthesis of this class of compounds need to be as mild as possible. Some methods by the reaction of allylic organometallics of metals such as tin^[9], titanium^[10], mercury^[11] with acyl halides have been reported, but these reactions are of limited application. Besides, some of these procedures entail the problems of corrosivity and effluent pollution. Now we wish to report a new bismuth mediated reaction. The coupling reaction of allyl bromide with acid chloride gives β, γ -unsaturated ketones with moderate yields.



Received date: 2002-10-28.

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1 Experimental

1.1 Instruments

IR spectra were recorded on a Bruker IFS-48 spectrophotometer. ^1H NMR spectra were obtained from solution in CDCl_3 on a JEOL FX-90Q spectrometer, with TMS as an internal standard. The solvents were purified with general procedure.

1.2 General procedure



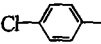
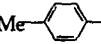
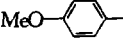

To a suspension of 0.8 mmol BiCl_3 and 2.5 mmol aluminum powder in 5 mL THF under nitrogen atmosphere, 1.2 mmol allyl bromide were added. After stirring for 20 min, 1 mmol acid chloride was added dropwise. The reaction mixture was sonicated or refluxed for 8 h, 10 mL saturated NH_4Cl solution was added. The mixture was extracted with diethyl ether. The extracts were combined and washed with brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The pure product was obtained by TLC (1:4 diethyl ether/petroleum ether).

2 Results and discussion

2.1 Results

All the products are colorless oil. They are known compounds.

Table 1 The yields of the reaction and the structural data of the products

Entry	R	Yields/ %	^1H NMR	IR/ cm^{-1}
1		52	3.72 (2H, d, $J=7\text{Hz}$), 5.10~5.32 (2H, m), 6.02~6.13 (1H, m), 7.40~7.95 (5H, m)	3 085, 1 715, 1 620
2		60	3.70 (2H, d, $J=7\text{Hz}$), 5.12~5.30 (2H, m), 6.08~6.20 (1H, m), 7.32~7.95 (4H, m)	3 076, 1 712, 1 634, 765
3		65	3.68 (2H, d, $J=7\text{Hz}$), 5.02~5.30 (2H, m), 6.03~6.22 (1H, m), 7.46 (2H, d, $J=9\text{Hz}$), 7.85 (2H, d, $J=9\text{Hz}$)	3 062, 1 715, 1 625, 758
4		48	3.32 (3H, s), 3.70 (2H, d, $J=7\text{Hz}$), 5.12~5.32 (2H, m), 6.00~6.10 (1H, m), 7.20 (2H, d, $J=9\text{Hz}$), 7.75 (2H, d, $J=9\text{Hz}$)	3 080, 1 708, 1 632
5		45	3.71 (2H, d, $J=7\text{Hz}$), 3.85 (3H, s), 5.18~5.38 (2H, m), 6.05~6.12 (1H, m), 6.98 (2H, d, $J=9\text{Hz}$), 7.90 (2H, d, $J=9\text{Hz}$)	3 068, 1 712, 1 620, 1 245
6	$(\text{CH}_3)_2\text{CH}-$	40	1.12 (6H, d, $J=6\text{Hz}$), 2.72 (1H, m), 3.50 (2H, d, $J=7\text{Hz}$), 4.92~5.18 (2H, m), 5.97~6.10 (1H, m)	3 075, 1 710, 1 625
7		55	1.28~1.70 (10H, m), 2.85 (1H, m), 3.58 (2H, d, $J=7\text{Hz}$), 5.00~5.22 (2H, m), 6.08~6.20 (1H, m)	3 075, 1 718, 1 630

2.2 Discussion

The reaction is very sluggish at room temperature, but it can be promoted by sonication or heating. Using TLC to monitor the course of the reaction, it was revealed that to all of the reactants we used, the reaction can finish within about 8 h, and it gives moderate yields. To aliphatic acid chlorides (entries 6, 7), the yields are lower than aromatic acid chlorides. Another feature of this reaction is that for the yields the reactants with electron withdrawing group are higher than that for the reactants with electron donating

group, i. e., the lower electron density of the carbonyl carbon is favored to the reaction. So we can presume that the reaction may proceed through an allylic bismuth bromide intermediate. This nucleophilic organobismuth intermediate makes substitution to acid chloride to generate allylic ketone products. This intermediate is not as active as general Grignard reagent, so no further addition product of allylic bismuth intermediate to allylic ketone was isolated. The further identification to the mechanism is being made in our laboratory. Also, as a new "one pot" reaction for the synthesis of β, γ -unsaturated ketone, though the yield is not very satisfactory, it has some advantages such as mild conditions, simple operation. Therefore it is of great significance in organic synthesis.

[References]

- [1] Suzuki H, Ikegami T, Matano Y. Bismuth in Organic Transformations[J]. Synthesis, 1997: 249.
- [2] Wada M, Ohki H, Akiba K. A Grignard-Type Addition of Allyl Unit to Aldehydes by Using Bismuth and Bismuth Salt [J]. Bull Chem Soc Jpn, 1990, 63: 1738.
- [3] Bhuyan P J, Prajapati D, Sandhu J S. Metallic Bismuth and Tantalum Mediated C-Allylation of Aldimines with Allyl Bromide[J]. Tetrahedron Lett, 1993, 34: 7975.
- [4] Wada M, Ohki H, Akiba K J. Bismuth Chloride-Aluminium Promoted Allylation of Aldehydes to Homoallylic Alcohols in Aqueous Solvent[J]. J Chem Soc (Chem Commun), 1987:708.
- [5] Miyoshi N, Fukuma T, Wada M. The Cross-Coupling Reaction of Aldehydes with α -Diketones by the Use of Bismuth Trichloride and Metallic Zn[J]. Chem Lett, 1995: 999.
- [6] Tanaka H, Taniguchi M, Kameyama Y. A Facile Access to 3-Hydroxycephems from Penicillin G through Bi/Sn or Ti/Sn Redox-Promoted Cyclization of 4-(Phenylsulfonylthio)azetidinones[J]. Chem Lett, 1990:1867.
- [7] Sun P P, Xiao Y P, Shi B C. Bismuth Mediated Organic Reaction: A Convenient Method for the Synthesis of Allylic (Benzylic) Selenides and α -Organylselenocarbonyl Compounds in Aqueous Media[J]. Chin Chem Lett, 2000, 11: 1037.
- [8] Demuth M, Mikhail G. New Developments in the Field of Photochemical Syntheses[J]. Synthesis, 1989: 145.
- [9] Labadie J W, Tuetting D, Stille J K. Synthetic Utility of the Palladium-Catalyzed Coupling Reaction of Acid Chlorides with Organotin[J]. J Org Chem, 1983, 48:4634.
- [10] Kasatkin A N, Kulak A N, Tolstikov G A. Acyldemetallation of Titanium(III) π -Allylic Complexes[J]. J Organomet Chem, 1988, 346: 23.
- [11] Larock R C, Lu Y. Synthesis and Acylation of Allylic Mercuric Iodides: A Convenient Synthesis of Allylic Ketones[J]. J Org Chem, 1993, 58: 2846.

金属铋作用下的有机反应： β, γ -不饱和酮的合成

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[摘要] 在 BiCl_3/Al 体系作用下, 在 THF 中, 烯丙基溴与酰氯反应得到 β, γ -不饱和酮, 产率中等。该方法具有条件温和, 操作简便等优点。

[关键词] 铋, β, γ -不饱和酮, 合成

[中图分类号] O621.3, **[文献标识码]** B, **[文章编号]** 1672-1292(2002)04-0013-03

[责任编辑: 孙德泉]