

BiCl₃ catalyzed reaction of aromatic aldehydes with 5,5-dimethyl-1, 3-cyclohexandione in ionic liquids

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ABSTRACT

The reaction of aromatic aldehydes **1** with 5, 5-dimethyl-1, 3-cyclohexandione **2** was investigated in this paper by using [bmim][BF₄] as the reaction medium. It was found that when the reaction was carried out in the presence of catalytic amount of BiCl₃, xanthenediones **3** was obtained in high yields.

Key words: BiCl₃, ionic liquids, xanthenedione.

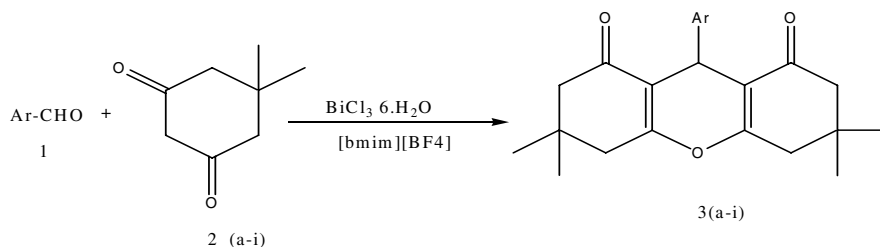
INTRODUCTION

The ionic liquids with low melting point (<100°C) salts represent a new class of non-molecular, ionic solvents. Especially those based on the 1-N-alkyl-3-methylimidazolium cations, have shown great promise as an attractive alternative to conventional solvents for catalytic reactions¹. On the other hand, BiCl₃ was considered to be an environmentally benign Lewis acid and has been used successfully in several kinds of organic reactions². Recently we have focused our interests on using a combination of BiCl₃ and ionic liquids as novel green catalysis system in carbon-carbon forming reactions. As a continuation of our research, we described here the interesting results of the reaction between aromatic aldehydes **1** and 5, 5-dimethyl-1,3-cyclohexandione **2** in ionic liquid, 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF₄]) by using BiCl₃ (Scheme 1). Through these reactions, a group of synthetically and biologically important compounds, namely xanthenediones **3** were obtained in high yields under mild reaction conditions. It is well known that xanthenedione derivatives constitute a structural

unit in a number of natural products³ and have been used as versatile synthons due to the inherent reactivity of the inbuilt pyran ring⁴. Conventional synthesis of xanthenediones usually involves acid or base catalyzed condensation of appropriate active methylene carbonyl compounds with aldehydes⁵. Recently, several reports have been put forward in which xanthenedione derivatives were obtained through condensation of aldehyde and 5, 5-dimethyl-1, 3-cyclohexanedione under various conditions⁶. In this we are reporting economically and eco-friendly procedure in high yields.

EXPERIMENTAL

In a general procedure, **1** (0.50 mmol) and **2** (1.00 mmol) were added to 1 mL [bmim][BF₄] containing 0.10 mmol BiCl₃ in a 10 mL round-bottomed flask. Then the mixture was stirred at 60°C for a certain period of time to complete the reaction (monitored by TLC). At completion, water was added to the reaction mixture and the solid was collected by suction and subsequently rinsed with cold ethanol to give product **3** with high purity. The results were shown in Table 1.



Scheme 1: Aromatic Aldehydes with 5, 5-Dimethyl-1, 3-cyclohexandione in Ionic Liquids

Table 1: Preparation of 3 catalyzed by BiCl₃ in [bmim][BF₄] at 60°C

Product	Ar	Reaction time (h)	Isolated yield (%)	M. p. (lit.) (°C)
3a	<i>m</i> -NO ₂ C ₆ H ₄	6	90	145 – 148
3b	C ₆ H ₅	6	92	203 - 205 (198 - 200) ^{7b}
3c	<i>p</i> -CH ₃ C ₆ H ₄	6	93	205 - 207 (218 - 220) ^{7b}
3d	<i>p</i> -NO ₂ C ₆ H ₄	6	95	226 - 228 (222 - 224) ^{7b}
3e	<i>p</i> -ClC ₆ H ₄	7	93	230 - 233 (230 - 231) ^{7b}
3f	<i>p</i> -BrC ₆ H ₄	6	91	236- 238
3g	<i>p</i> -FC ₆ H ₄	5	95	225 - 228 (225 - 227) ^{7c}
3h	<i>o</i> -ClC ₆ H ₄	6	87	224 - 226 (228 - 229) ^{7c}
3i	<i>o</i> -BrC ₆ H ₄	6	85	220 – 222

^aAll reactions were conducted at 60 °C using BiCl₃ in ionic liquid.

^bAll products characterized by m.p and spectral data comparison with authentic samples.

^cYields refers to isolated pure products and melting points are uncorrected.

All the products in Table 1.were fully characterized by 1H NMR, IR, MS and by comparison with authentic samples.

CONCLUSION

In conclusion, we have provided a novel green procedure for the preparation of xanthenediones and their ring-opening derivatives. The main advantages of this method include high

yields, simple experimental procedure, ease of recovering and reusing of the catalyst and the reaction media, as well as green and environmentally benign properties.

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REFERENCES

- J. Dupont, R. F. de Souza, P. A. Z. Suarez, *Chem. Rev.*, **102**: 3667 (2002).
 - D. B. Zhao, M. Wu, Y. Kou, E. Z. Min, *Catal. Today*, **74**: 157 (2002)
- T. Ollevier and T. Ba , *Tetrahedron lett.*, **44**: 9003 (2003).
 - H. Suzuki , T. Lkegami and Y. Matano, *Synthesis*, 2491(1997).

- (c) H. Suzuki and Y. Matano., *Organobismuth Chemistry* (Edited by Elsevier Amsterdam) (2001).
- (d). N.N. Leonard, L.C. Wieland and R. Mohan., *Tetrahedron.*, **58**: 8373 (2002).
3. (a) S. Hatakeyama, N. Ochi *et al.*, *J. Chem. Soc., Chem. Commun.*, 1202, (1988) and references cited therein.
(b) G. M. Cingolant, M. Pigni, *J. Med. Chem.*, **12**: 531 (1988).
4. C. N. O' Callaghan, T. B. H. Mc Murry, *J. Chem. Res. (S)*, 214 (1995) and *(M)*, 1448 (1995) and references cited therein.
5. J. Kuthan, P. Sebek *et al.*, *Advances in Heterocyclic Chemistry*, Academic Press, Inc.: New York, , 62, 19,(1995).
6. (a) K. Singh, J. Singh *et al.*, *Tetrahedron.*, , **52**: 14273 (1996).
(b) S. J. Tu, Y. Gao *et al.*, *Chin. J. Org. Chem.*, **21**: 1164 (2001).
(c) D. Q. Shi, Q. Y. Zhuang *et al.*, *Chin. J. Org. Chem*, **23**: 694 (2003).
(d) D. Q. Shi, Y. C. Wang *et al.*, *Synth. Commun.*, , **30**: 713 (2000).
(e) K. Nagarajan, S. J. Shenoy, *Indian J. Chem.*, **31B**: 73 (1992).