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Synthesis and Application of New Oxidant bis(banzyltriphenylphosphonium) peroxodisulfate on Oxidation of Benzylhalides to Corresponding Benzylaldehyde Compounds

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Abstract- Put the peroxodisulfate ion ($S_2O_8^{2-}$) in the phase transfer catalyst banzyltriphenylphosphonium can make a catalyst with mild oxidation property, and used it for oxidation of Benzylhalides to corresponding Benzylaldehyde Compounds. For making catalyst used xylene and water as solvent, and it was an easy process with high yield. Oxidation used in reflux condition with acetonitrile as solvent. The advantages of this oxidation: high yield and short time.

Keywords: Benzaldehyde; Oxidation; Catalysis; BBTPPPDS; Benzylhalide.

Introduction:

Aromatic aldehydes are one of the most important aromatic compounds. Scientists have been interested to find selective methods for making these compound. Selective oxidation of toluene with air to synthesize benzaldehyde and benzyl alcohol by the chlorination of toluene followed by hydrolysis, a seriously polluting process.[1] Some researcher tried the selective aerobic oxidation of toluene catalyzed by the transition metal salts, but these technologies are compaied by drawback such as low selectivity and use of large amounts of solvents and bromides. [2-7] A procedure for the preparation of o-tolualdehyde from o-toluanilide by the Sonn-Müller method has been published in Organic Syntheses. [8] In addition to the alternative methods of preparation listed there, o-tolualdehyde has been prepared from o-xylyl bromide[10] or chloride and hexamethylenetetramine; by the Stephen reduction of o-tolunitrile,[11] by the reduction of the latter with lithium triethoxyaluminohydride [12] or sodium triethoxyaluminohydride, [13] by the condensation of crotonaldehyde with barium or calcium oxide at 300°,[14] by the oxidation of o-methylbenzyl alcohol with N-chlorosuccinimide, [15] by the reaction of ethyl orthoformate with o-tolylmagnesium bromide.[16] Many of the current pathway to produce these products are environmentally hazardous.

The oxidation of benzylic halides to their corresponding aldehyde compounds by the readily available peroxydisulfate ion, $S_2O_8^{2-}$is an excellent and versatile oxidant for a variety of organic and inorganic compounds.[17-18] peroxodisulfate radical anion SO_4^-, is one of the best and strong one-electron oxidant in organic synthesis.[19]

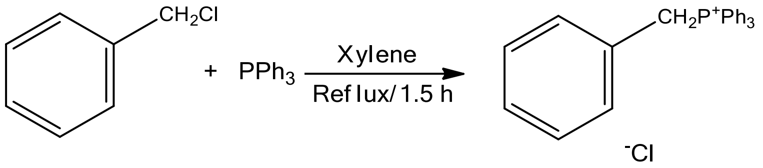
In this article, we have reported the synthesis and application of bis(banzyltriphenylphosphonium) peroxodisulfate (BBTPPPDS) that use of cheap, efficient, simple convenient and selective method for the oxidation of benzylic halides to their corresponding aldehyde compounds with (BBTPPPDS) in reflux condition and in the absence of metal catalysts.

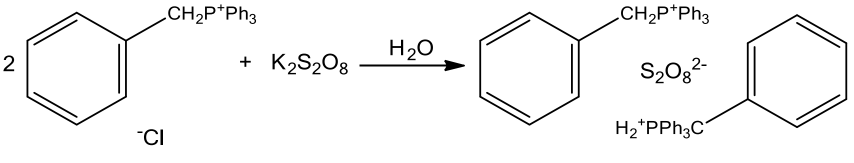
Experimental:

1-Syn.Catalyst:

26.2g (0.1mol) of Triphenylphosphine was dissolved in 80ml of Xylene in a round-bottomflask. 12.6g (0.1mol) of Benzylchloride is added. The flask is attached to a reflux condenser, The mixture is stirred and heated (138℃) under reflux for 90 mins. The product is filtered then washed with Petroleum ether (3×100ml). For drying, Used oven with 50℃ for 2 hours. The yield of Triphenylphosphoniumbanzylchloride is more than 99% (38.8g).

7.7g (0.02mol) of Triphenylphosphoniumbanzylchloride was dissolved in at least distilled water in a 100ml beaker, then used a bit CH_2Cl_2 as auxiliary solvent. In another 100ml beaker solved 2.7g (0.01mol) of Potassium persulfate in at least distilled water ,then added second beaker to first container slowly. The mixtuer is stirred for 30 minsthenfiltered and drying by oven for 2 hours in 90℃. The yield of Bis(banzyltriphenylphosphonium) peroxodisulfate (BBTPPPDS) is more then 99% (8.9g).IR (KBr) cm^{-1}:3082 & 3060 C-H (arom., stretch), 2928 & 2880 C-H (aliph., stretch), 1601-1405 C=C (arom,. Stretch), 1111 C-P (starch).

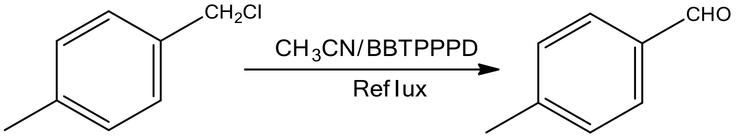




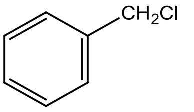
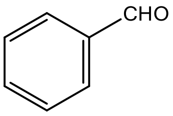
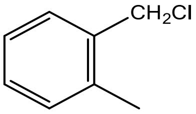
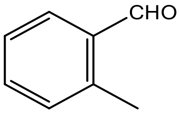
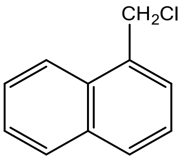
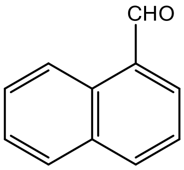
BBTPPPDS

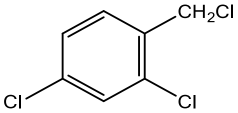
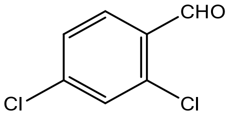
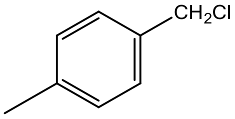
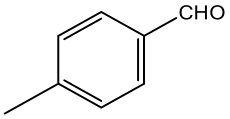
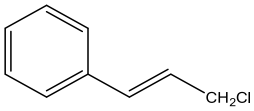
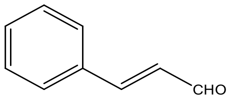
2-Syn.Benzaldehyde:

A dry 200ml round-bottom flask equipped with a stirring bar. 2.47g (0.02mol) of Bezylchoride, 40ml of Acetonitrile and 8.9g (0.01mol) of BBTPPPDS are added, the mixture is refluxed 5 min. The crude product was purified by TLC (n-Hexane:ethylacetate, 7:1) to yield more than 99%.



Result and Discussion

Num	Reaction	Product	Time)min(	b.p (^OC)	m.p (^OC)	b.p&m.p(^OC)^a	Yeild (%)
١			٥	١٧٣	-	178 - 179	٩٥
٢			٣	١٨٨ - ١٩٣	-	199 - 200	٩٥
٣			٦	١٤٧ - ١٥٩	-	160 - 161	٨٠

٤			٤	-	٥٣-٥٧	64-69^b	٩٠
٥			٥	١٧٥ - ١٨٠	-	204 – 205	٩٠
٦			١١	٢٣٠ - ٢٣٨	-	248	٧٥

BBTPPPDS was an easily prepared reagent, which was used recently for the oxidation of Benzylic halides. The oxidative formation of Benzaldehydewith this reagent was investigated in CH3CN. As shown in Table 1, a series of appropriate arenas were reacted with 2M equivalents of the reagent to afford the corresponding carbonyl group in excellent yields Use of an efficient, cheap, simple and selective method for the oxidation of Benzylic halides to their corresponding Benzaldehydewith (BBTPPPDS) under reflux conditions and in the absence of metal catalysts. The procedure developed for oxidation of Benzylic halides consists of simply addition of BTPPBPDS in small portions to a refluxing solution. The experimental results showed that acetonitrile was the best choice for our procedur, and no product in CH2Cl2. The results obtained are summarized in Table 1. Because of the stability and solubility of BBTPPPDS, reactions could be performed at reflux condition and the separation of the products was facile. In addition, this oxidant and the oxidation conditions could be used for the synthesis of highly functionalized molecules. This reagent has certain advantages over similar oxidizing agents in terms of amounts of oxidantand solvent required, and especially in the short reaction times required and in higher product yields.

1. IR (KBr) cm^{-1}:3071 & 3002 C-H (arom.,stretch), 2724 & 2834 C-H (alde.,stretch), 1688 C=O (stretch).

2. IR (KBr) cm^{-1}:3057 & 3009 C-H (arom.,stretch), 2745 C-H (alde.,stretch), 1696 C=O (stretch).

3. IR (KBr) cm^{-1}: 3065 & 3026 C-H (arom.,stretch), 2745 C-H (alde.,stretch), 1675 C=O (stretch), 1626 C=C (arom., stretch).

4. IR (KBr) cm^{-1}: 3026 C-H (arom.,stretch), 2829 C-H (alde.,stretch), 1692 C=O (stretch), 1611 C=C (arom., stretch).

5. IR (KBr) cm^{-1}: 3059 C-H (arom.,stretch), 2853 C-H (alde.,stretch), 1720 C=O (stretch), 1588 C=C (arom., stretch).

6. IR (KBr) cm^{-1}: 3062 & 3028 C-H (arom.,stretch), 2837 C-H (alde.,stretch), 1692 C=O (stretch), 1602 C=C (arom., stretch).

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