SHORT PAPER

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Baeyer condensation in chloroaluminate ionic liquid[†‡]

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1-*n*-butylpyridinium chloroaluminate serves the dual purpose of a reaction medium and a Lewis acid catalyst for condensation of substituted benzaldehydes with *N, N*-dimethylaniline to obtain triarylmethanes (leuco bases) in good yields with significant reduction in reaction time and simplification of the workup process.

Keywords: ionic liquid, Baeyer condensation, triarylmethanes

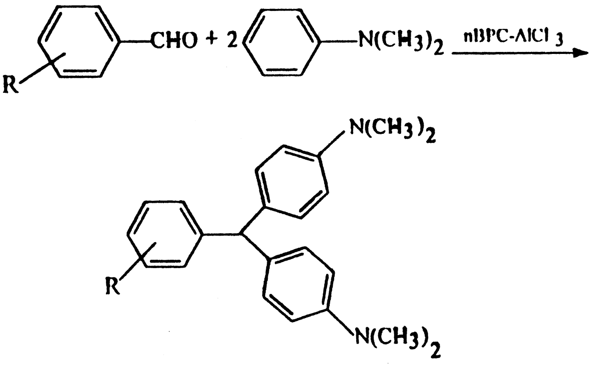
Triarylmethanes find widespread application as intermediates for the preparation of commercially important triarylmethane dyestuffs. These dyes are used for the preparation of printing inks, for dyeing of polyacrylonitrile fibres and for colouration of other substrates such as ceramics, leather, fur, drugs and cosmetics. They are also used for the preparation of heat-, light- and pressure sensitive recording materials for high speed photoduplicating and photo imaging devices. In addition to these, triarylmethanes have a host of other applications.[1, 2.]

The Baeyer condensation of various substituted benzaldehydes with *N, N*-dimethylaniline catalyzed by $ZnCl_2$[3], *p*-toluenesulfonic acid[4], hydrochloric acid[5], sulfuric acid[6] and Montmorrilonite K-10 clay[7,8] have already been reported. These methods, however, suffer from some drawbacks such as extended reaction times, use of corrosive acids, tedious workup procedures and the need for using a volatile organic solvent as a reaction medium. Another method for synthesis of triarylmethanes under high pressure catalysed by benzoic acid, 2-chlorobenzoic acid[9] has been reported.

Ionic liquids provide an attractive alternative to conventional organic solvents for cleaner synthesis of reaction products.[10] They have gained immense popularity due to their low vapour pressure which makes them suitable for high vaccuum systems and they function as good solvents for a wide range of organic, inorganic and organometallic substances. Chloroaluminate ionic liquids have been used for carrying out reactions such as Friedel Craft's alkylation[11] and acylation,[12] Diels Alder reaction,[13] Fries rearrangement,[14] hydrogenation[15] and olefin dimerisation.[16]

We have already reported the utility of chloroaluminate ionic liquid for carrying out benzoylation,[17] Fischer indole synthesis[18] and Pechman condensation reactions[19].

We therefore envisioned the use of 1-*n*-butylpyridinium chloroaluminate (*n*BPC-$AlCl_3$) ionic liquid for carrying out Baeyer condensations. The reactions were performed using the acidic melt with X=0. 67,[16] where X is the mole fraction of $AlCl_3$ present. Aldehydes with electron withdrawing groups undergo rapid condensation with *N, N*-dimethylaniline, giving good yields of the corresponding triarylmethanes at ambient temperature. Benzaldehydes and aldehydes with electron withdrawing groups were found to undergo conversion in to triarylmethanes at a moderate temperature of 90°C. The observed reaction times are considerably less and this is a remarkable achievement as compared to some of the reports mentioned earlier, *e.g.*, the reaction of 4 – nitrobenzaldehyde and *N, N*-dimethylaniline with $ZnCl_2$[3] required 4 h, when heated on a water bath. The reaction times for the various substrates with K – 10 Montmorillonite[7] are given in the Table 1.



Scheme 1

Table1 Baeyer condensation using chloroaluminate ionic liquid

Entry. no.	R	Time /min	Yield[a] /%	Yield (time/h)[d] /%	M.p./°C Found	M.p./°C Reported[6,7]
1	2-NO_2	40	87[b]	96 (5)	157–158	159–160
2	3-NO_2	40	86[b]	90 (4)	151–152	152–153
3	4-NO_2	40	84[b]	92 (4)	181–182	184–185
4	2-Cl	40	78[b]	-	142–144[e]	–
5	4-Cl	40	68[b]	89 (8)	95–97	97–98
6	H	40	82[c]	84 (10)	94–95	95–96
7	4-CH_3	150	80[c]	81 (18)	100–101	99–100
8	3-OCH_3	180	86[c]	-	122–123	124
9	4-OCH_3	180	72[c]	77 (20)	103–105	102–103
10	4-$N(CH_3)_2$	240	62[c]	73 (24)	174–175	173–175

[a] Pure isolated yields based on aldehydes.
[b] Reaction carried out at ambient temperature.
[c] Reaction carried out in a preheated oil bath at 90°C.
[d] Yields (time/ h) obtained with K-10 Montmorillonite[7] at 100°C.
All products gave satisfactory spectral data.
Melting points were taken in an Oswal Precision melting point apparatus.
[e] Tentative structural assignment – the absence of analytical data.

Experimental

Melting points were uncorrected and taken in an Oswal precision melting point apparatus. The ionic liquid was prepared as per the procedure mentioned in ref. 16. The products were characterized by comparision of their melting points,[6,7] IR and ^1H NMR with the literature data.

General procedure: To a mixture of an aldehyde (2.5mmol) and *N, N*-dimethylaniline 0.91 g (7.5 mmol), 1ml of 1-*n*-butylpyridinium chloroaluminate (X=0.67; 3 mmol) was added.The reaction mixture was stirred at the specified temperature and time. Subsequently, the reaction mixture was quenched by adding ice cold water and the solid

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[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*
[‡] This work is dedicated to late Dr B. M. Khadilkar.

product so obtained was filtered and washed with water. Purification of the product was carried out by recrystallisation from ethanol.

In conclusion, we have developed a simple and effective method for the synthesis of commercially important triarylmethane dye intermediates in 1-*n*-butylpyridinium chloroaluminate ionic liquid. There is a substantial decrease in reaction time and the workup process is less cumbersome than some of the other methods.

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