J. Chem. Research (S), 1999, 568–569†

Friedel–Crafts Acylation Reaction using Polymer Supported Aluminium Chloride†

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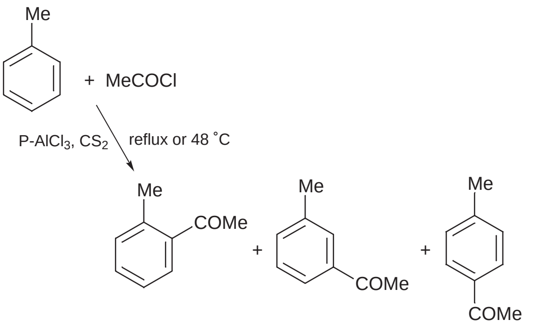
Friedel–Crafts reactions using polymer supported $AlCl_3$ are reported and the effect of crosslinking level on *ortho*:*para* ratio is studied.

Polymer supported reagents offer several advantages in organic synthesis.[1–3] The complex of polystyrene and aluminium chloride provides a stable acidic material which has been reported in the literature for etherification,[4] acetal formation[5] and esterification[6] but is inactive for the Friedel–Crafts reaction.[7] This polymer supported reagent, P-$AlCl_3$, which is a tightly bound complex between anhydrous aluminium chloride and polystyrene–divinylbenzene copolymer beads, has been described as a polymer protected dehydrating agent from which $AlCl_3$ can be released by placing the polymer supported reagent in the appropriate swelling solvents.

As a part of a general programme to investigate the reaction of polymer supported reagents.[8–10] we report here the Friedel–Crafts acylation reaction using P-$AlCl_3$ and the effect of crosslinking on the *ortho*:*para* ratio of product.

The Friedel–Crafts reaction (Scheme 1) was carried out using P-$AlCl_3$ as the catalyst and the results of acylation are given in Table 1.

It has been observed that a stoichiometric amount of P-$AlCl^3$ is required for the reaction. To find out whether the reaction takes place in the solid matrix of P-$AlCl_3$ or whether aluminium chloride simply released in CS_2 is responsible for the Friedel–Crafts reaction, P-$AlCl_3$ was refluxed in CS_2 for 7 h and then filtered off and the filtrate analysed for its aluminium content, which showed negligible release of $AlCl_3$. The filtrate was found to be inactive for the Friedel–Crafts acylation reaction. These observations indicate that the reaction takes place in the solid matrix of P-$AlCl_3$.



Scheme 1

To establish the activity of the polymer supported $AlCl_3$ a control experiment was carried out by using polystyrene–divinylbenzene alone under the same experimental conditions, for which no acylation reaction of toluene was observed. Further, no band corresponding to $>C=O$ stretching in the IR spectrum of P-$AlCl_3$ was observed after the acylation reaction in either the presence or absence of substrate, indicating that polystyrene itself does not undergo acylation under the experimental conditions used. Attack of an acylium ion on polystyrene would be a heterogeneous reaction and would not be favored at the low temperature (48 °C) used here. In addition to this, acylation is not favored with P-$AlCl_3$ as a π complex is formed between polystyrene and $AlCl_3$.

Table 1 Acylation of toluene[a]

			Relative yield (%)			
Entry	Solvent	Catalyst	*o*	*m*	*p*	Overall yield (%)
1	CS_2	$AlCl_3$	7.12	4	89	81
2	CS_2	P-$AlCl_3$ (2.0%)	29.7	—	70.3	68
3	CS_2	P-$AlCl_3$ (3.8%)	32.29	—	62.35	69
4	CS_2	P-$AlCl_3$ (20%)	61.82	—	38.18	73
5	$PhCH_3$	$AlCl_3$	3.0	—	97	85
6	$PhCH_3$	P-$AlCl_3$ (2.0%)	4.7	—	95.4	73
7	$PhCH_3$	P-$AlCl_3$ (3.8%)	6.0	—	94	72
8	$PhCH_3$	P-$AlCl_3$ (20%)	72	—	23	76
9	CH_2Cl_2	P-$AlCl_3$ (20%)	—	—	—	0
10	$ClCH_2CH_2Cl$	P-$AlCl_3$ (20%)	—	—	—	0

[a]Reactions carried out for 9 h at 48 °C.

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†This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1999, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

It has also been observed that *ortho*:*para* ratio depends on the level of crosslinking in the polystyrene. An increasing percentage of crosslinking in the polystyrene results in a higher percentage of *ortho* product in acylation reactions in contrast to aluminium chloride alone which preferably leads to a higher percentage of *para* product. The overall conclusion is that the ultimate orientation of the electrophile is governed by crosslinking levels in the polystyrene and specific solvation effect, as indicated in Table 1. The fact that *ortho* substitution occurs predominantly may be due to formation of a complex of P-$AlCl_3$ with toluene in which acetyl chloride is oriented in such a way that at higher crosslinking levels the electrophile is steered towards the adjacent *ortho* position.

Experimental

IR spectra were recorded on a Perkin-Elmer 257 spectrophotometer. GC analysis was performed on chromosorb W AW DMCS, using a 10 ft 1/8 in diameter 20% SE-30 column, GC–MS analysis was performed on a Schimadzu instrument using a DB-5, 50 m, 0.221D column. NMR were taken on a 500 MHZ Bruker spectrometer. Toluene, CS_2 and acetyl chloride were of reagent grade.

Preparation of P-$AlCl_3$.—Polystyrene–divinylbenzene (3.8% or 20%) copolymer beads forming the water stable aluminium chloride complex (P-$AlCl_3$) were prepared by addition of 2.0 g of $AlCl_3$ to 7.75 g of polystyrene–divinylbenzene copolymer beads (3.8 or 20%) in carbon disulfide (112 ml). The mixture was stirred at reflux for 40 min and cold water then cautiously added to hydrolyze the excess aluminium chloride. The mixture was stirred until the deep orange color disappeared and the polymer became light yellow. The polymer beads were then filtered off and washed with 250 ml of water and 37 ml of acetone. After washing the polymer was dried for 18 h in a vacuum oven. Complex formation was demonstrated by the increased color of the polymer prepared using higher concentrations of aluminium chloride and by a new band at 1637 cm^{-1} in the IR spectrum of the polymer. The aluminium content of P-$AlCl_3$ was found to be 2.4, 2.6 and 3.8% for 2, 3.8 and 20% crosslinked polystyrene–divinylbenzene, respectively, while the chlorine content was 9.3, 10.2 and 14.7% for 2, 3.8 and 20% crosslinked polystyrene–divinylbenzene respectively.[11]

General Experimental Procedure.—To a well stirred mixture of P-$AlCl_3$ (0.3 mmol) and dry toluene (0.3 mmol) in CS_2 (10 ml) (or solvent indicated in the entries of Table 1) was added acetyl chloride (0.32 mmol) at room temperature. The mixture was then heated to reflux for 9 h. The reaction was followed by TLC. P-$AlCl_3$ was filtered off and the filtrate treated with 1:1 HCl and extracted with chloroform. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in a rotary evaporator. Products were analyzed by GC–MS and NMR.

Recycling of P-$AlCl_3$.—P-$AlCl_3$ can be reactivated without appreciable loss in its $AlCl_3$ content by leaving the polymer overnight in 1 M HCl. The Al and Cl content of P-$AlCl_3$ remains almost unchanged after recycling; P-$AlCl_3$ could be reused three times with the same results.

We thank Mr Suhas Patole (Toshniwal Brothers, Mumbai), Mr Milind Narvekar (Wool Research, Mumbai) for GC–MS analysis and Mr P. G. Deshmukh (Pratap Organics, Mumbai) for GC analysis. One of us (K.J.P.) thanks the Department of Atomic Energy, Mumbai for J.R.F.

Received, 17th November 1998, Accepted, 9th June 1999
Paper 8/08986H

References

1 (*a*) *Polymer Supported Reactions in Organic Synthesis*, ed. P. Hodge and D. C. Sherrington, Wiley, London, 1980; (*b*) A. Akelah and D. C. Sherrington, *Chem. Rev.*, 1981; (*c*) *Functionalized Polymers and Their Applications,* ed. A. Akela and A. Moet, Chapman and Hall, London, 1990.
2 A. Mckillop and D. W. Young, *Synthesis,* 1979, 401.
3 A. Mckillop and D. W. Young, *Synthesis,* 1979, 481.
4 D. C. Neckers, D. A. Kooistra and G. W. Green, *J. Am. Chem. Soc.*, 1972, **94**, 9284.
5 E. C. Blossey, L. M. Turner and D. C. Neckers, *J. Org. Chem.*, 1975, **140**, 959.
6 E. C. Blossey, L. M. Turner and D. C. Neckers, *Tetrahedron Lett*., 1973, **24**, 1823.
7 *Polymers as Aids in Organic Chemistry,* ed. N. K. Mathur, C. K. Narang and R. E. Williams, Academic Press, New York, 1980.
8 J. G. Deshmukh, M. H. Jagdale, R. B. Mane, M. M. Salunkhe and P. P. Wadgaonkar, *Eur. Polym. J.,* 1987, **23**, 577.
9 A. S. Kanade, G. S. Gokavi and M. M. Salunkhe, *Eur. Polym. J.,* 1993, **29**, 565.
10 M. M. Salunkhe, M. T. Thoat, R. B. Mane, A. R. Sande and P. P. Wadgaonkar, *Bull. Chim. Belg.,* 1994, **103**, 691.
11 100 mg of P-$AlCl_3$ was fused with Na metal, extracted with 10 ml of water and filtered, the filtrate then being diluted to 25 ml. The aluminium and chlorine content of this solution was determined by the Mohr titration method. For the procedure refer to: *A Textbook of Macro and Semimicro Qualitative Analysis*, A. I. Vogel, 5th edn., pp. 349–350, Longman, UK, 1989.