

Alkylation Using EPZ10

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EPZ10, a supported reagent catalyst, offers an environmentally benign and a commercially viable alternative to the conventional Friedel-Crafts catalyst, anhydrous AlCl_3 . Aluminium chloride is mainly associated with unacceptable levels of waste and by-products. With EPZ10, the aqueous effluent from quenching is eliminated and acidic gaseous emissions are limited to those produced from the reaction mixture itself. It can be filtered off from the process, and may be reused, depending on the reaction type and temperature. It is also reported to give higher yields as compared to the corresponding reactions using AlCl_3 . In this article, synthesis of three alkylbenzenes using EPZ10 as the catalyst is discussed.

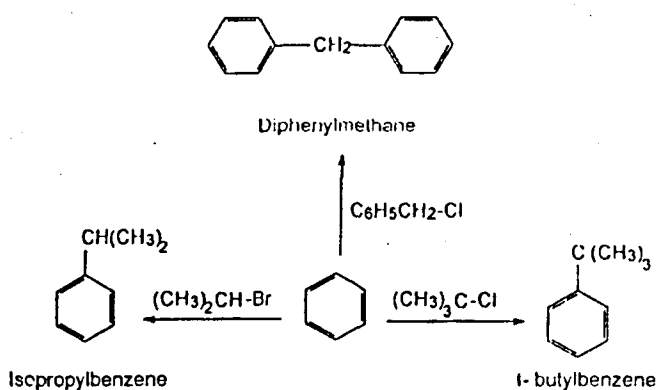
Friedel-Crafts reaction is the most versatile and frequently used tool of organic chemistry. It is commonly considered as a process of uniting two or more organic molecules through the formation of carbon to carbon bonds under the influence of a strongly acidic metal halide¹ such as aluminium chloride, boron trifluoride, ferric chloride or zinc chloride, used as catalysts. The most important catalyst of Friedel-Crafts reaction is the Lewis acid, AlCl_3 . This catalyst, however, is associated with serious problems. Aluminium chloride is a corrosive irritant that decomposes in presence of water. It cannot be reused. Most importantly, aluminium residues often remain in the reaction products, and large volumes of acidic gaseous emissions are also created.

The new supported reagent catalyst, EPZ10, is a solid acid with both Bronsted and mainly Lewis acid characteristics². It promotes Friedel-Crafts alkylation reactions with a range of alkylating agents including alkyl halides and olefins³. It can be used in place of conventional anhydrous AlCl_3 in Friedel-Crafts reactions. EPZ10 acts as a true catalyst, usually offering a ten-fold reduction in catalyst quantity compared to that of AlCl_3 . The use of a solvent-free system is possible with EPZ10 catalyst, which results in reduced raw material cost. EPZ10 leads

to improved reaction selectivity and thus maximizes the yield of the product. The elimination of by-products results in the reduction of purification cost. The catalyst can be filtered-off after the reaction without the need for a quench, resulting in faster separation between the catalyst and the final product. The catalyst can be reused several times depending upon the reaction conditions.

In the present study, synthesis of alkylbenzenes, such as diphenylmethane, t-butylbenzene and isopropylbenzene (cumene), by Friedel-Crafts reaction, using EPZ10 as the catalyst in place of anhydrous aluminium chloride, is discussed.

Synthesis of alkylbenzenes



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EXPERIMENTAL

Synthesis of alkylbenzenes was carried out by reacting dry benzene and alkylating agents in presence of activated EPZ10. The catalyst EPZ10 was imported from the Contract Catalysts, a Division of Contract Chemicals (Knowsley) Ltd., Prescot, Merseyside, U.K. Benzyl chloride, t-butyl chloride and isopropyl bromide were used as alkylating agents for the synthesis of diphenylmethane, t-butylbenzene and isopropylbenzene, respectively.

Synthesis of alkyl halides⁴:

Tertiary butyl chloride was prepared by mixing t-butyl alcohol (25 g, 0.34 mol.) and hydrochloric acid (85 ml) in a separating funnel. The upper layer of t-butyl chloride was washed with 2% sodium bicarbonate solution and water. The product thus obtained was dried with anhydrous CaCl_2 and further purified by distillation. The fraction boiling between 49-51° was collected. This resulted in 84.4% yield of t-butyl chloride.

Synthesis of isopropyl bromide was carried out by mixing isopropyl alcohol (20 g, 0.34 mol.) and constant boiling point hydrobromic acid (230 g, 155 ml). The reaction mixture was distilled slowly until about half of the liquid was passed over. The distillate was allowed to stand for few minutes. The lower layer of isopropyl bromide was separated and washed successively with 1:1 hydrochloric acid, 5% sodium bicarbonate solution and water. It was then dried and distilled. The fraction at 59° was collected so as to get 75.55% yield of isopropyl bromide.

Activation of EPZ10:

EPZ10 requires activation prior to use. Activation is achieved by removing loosely bound water associated with the clay support through azeotropic drying overnight. It can also be activated thermally by heating in air at 275° overnight. The method used for activation can influence the performance of the catalyst in certain reactions. EPZ10 (1 g) was added to dry benzene (15-20 ml) the mixture was refluxed overnight by using Dean Stark apparatus. This reaction mixture was then immediately used for further reaction. EPZ10 was also activated thermally by heating it at 275° overnight. After activation, the catalyst was immediately suspended into dry benzene. However, thermal activation is reported to produce active sites in the catalyst that are highly moisture sensitive.

Synthesis of alkylbenzenes⁵:

A mixture of dry benzene (8 g, 0.1 mol.) and

activated EPZ10 (1 g) was stirred in a round bottom flask equipped with a reflux condenser, dropping funnel and a guard tube. Alkyl halide was added to this mixture and the mixture was refluxed. The reaction conditions maintained during the synthesis of diphenylmethane, t-butylbenzene and isopropylbenzene are mentioned in Table 1. When the evolution of hydrogen chloride gas was ceased, the reaction mixture was cooled to room temperature. The catalyst was then separated from it by filtration. The filtrate was dried and benzene was recovered so as to get alkylbenzene. Alkylbenzenes were distilled and checked for their purity.

TABLE 1: REACTION CONDITIONS FOR ALKYLATION OF BENZENE

Alkylating Agent	Quantity g (mol.)	Reaction Temperature (°)	Reaction Time (h)
Benzyl chloride	2.25 (0.02)	R.T.	4
t-Butyl chloride	1.85 (0.02)	Reflux	6
Isopropyl bromide	2.45 (0.02)	Reflux	6

The purity of the synthesised compounds was confirmed by determining their boiling points, R_f values and by recording infrared (IR) and nuclear magnetic resonance (NMR) spectra. The boiling points were recorded by using open glass capillaries. IR absorption spectra for the neat liquids were recorded on a JASCO FT/IR-410 spectrophotometer. NMR spectra were recorded on an EM-390/90 MHz NMR spectrophotometer.

RESULTS AND DISCUSSION

The overall per cent yields of the synthesised alkylbenzenes were calculated based on the respective alkyl halides used for their synthesis. Two separate sets of alkylations were carried out using EPZ10 activated by azeotropic drying and EPZ10 activated thermally. Table 2 gives the comparative data for the percent yield of the alkylbenzenes obtained in these two sets and also the per cent yield reported in the literature by using conventional Friedel-Crafts catalyst, anhydrous aluminium chloride.

Azeotropic drying method for activation of EPZ10 was found to give higher yield of alkylbenzenes as compared to that with thermally activated EPZ10, and Friedel-

TABLE 2: COMPARATIVE DATA FOR ALKYL BENZENES

Alkylbenzene	Percent yields of alkylbenzenes		
	Azeotropically Dried EPZ10	Over Dried EPZ10	Anhydrous AlCl ₃
Diphenylmethane	89.1	74.3	50.0 ⁵
t-Butylbenzene	83.4	64.2	62.0 ⁵ , 77.0 ⁶
Isopropylbenzene	98.3	51.7	29.0 ⁷

Comparative data for per cent yields of alkylbenzenes prepared using EPZ10 activated by 2 different methods and the conventional catalyst.

Crafts reaction using anhydrous AlCl₃. Table 3 indicates the boiling points, R_f values and characteristic peak positions in IR and NMR spectra for all the three alkylbenzenes. These characteristics were found to match with the values reported in the literature⁸⁻¹⁰.

Thus, EPZ10 can be a viable alternative to the conventional anhydrous AlCl₃ catalyst in Friedel-Crafts chemistry. It is environmentally benign and is reusable, hence it can be used safely and economically in industries for alkylation on a large scale.

TABLE 3: PHYSICAL CHARACTERISTICS OF ALKYL BENZENES

Alkylbenzene	Boiling Point	R _f values	IR Wavenumbers (cm ⁻¹)	NMR δ (ppm)
Diphenylmethane	264-265	0.61	3060, 3025 (C-H, Ar str) 2910, 2842 (C-H str for -CH ₂) 1596, 1492 (C-C, Ar str) 1450, 1386 (C-H b for -CH ₂) 732, 698 (C-H, Ar b)	δ=6.8 - 7.2 (Ar, m, 10 H) δ=3.7 (s, 2 H)
t-Butylbenzene	168-169	0.54	3085, 3056, 3029 (C-H, Ar str) 2962, 2906, 2867 (C-H str, alkyl - CH ₃) 1600, 1509 (C-C, Ar str) 1394, 1363 (C-H b, alkyl - CH ₃) 698 (C-H, Ar b)	δ=6.9 - 7.3 (Ar, m, 5 H) δ=1.2 (s, 9 H)
Isopropylbenzene	152-153	0.65	3062, 3027 (C-H, Ar str) 2962 (C-H str, alkyl - CH ₃) 1602, 1492, 1452 (C-C, Ar str) 1382, 1363, 1180 (C-H b alkyl - CH ₃) 759, 698 (C-H, Ar b)	δ=7.0 - 7.3 (Ar, m, 5 H) δ=1.1 - 1.35 (d, 6H) δ=2.7 - 3.1 (m, 1 H)

str = stretching, b=bending, Ar = aromatic protons, m=multiplet, s=singlet, d=doublet

ACKNOWLEDGEMENTS

Authors thank Contract Catalysts, a Division of Contract Chemicals (Knowsley) Ltd., Prescot, Merseyside, U.K. for providing the catalyst.

REFERENCES

- 1) Olah, G.A., Eds., In; Friedel-Crafts Chemistry, John Wiley and Sons, Inc., New York, 1973, 28.
- 2) Mukaiyama, T., Ohno, T., Nishimura, T., Han, S. and Kobayashi, S., *Chem. Lett.*, 1991, 1059.
- 3) Clark, J.H. and Macquarrie, D.E., *J. Chem. Soc. Rev.*, 1996, 303.
- 4) Furniss, B.S., Hannaford, A.J., Smith, P.G. and Tatchell, A.R., Eds., In; Textbook of Practical Organic Chemistry, 5th Edn., ELBS, Longman Publisher, Singapore, 1989, 556.
- 5) Furniss, B. S., Hannaford, A.J., Smith, P.G. and Tatchell, A.R., Eds., In; Textbook of Practical Organic Chemistry, 5th Edn., ELBS, Longman Publisher, Singapore, 1989, 832.
- 6) Nield, P.G., *J. Chem. Soc.*, 1964, II, 2278.
- 7) Ipatieff, V.N., Pines, H. and Schmerling, L., *J. Org. Chem.*, 1940, 5, 259.
- 8) Pouchert, C.J., Eds., In; The Aldrich Library of IR spectra, Part II, Aldrich Chemical Company, Inc., U.S.A., 1975, 499.
- 9) Pouchert, C.J. and Campebell, J.R., Eds., In; The Aldrich Library of NMR Spectra, Vol. 4, Aldrich Chemical Company, Inc., U.S.A., 1974, 4.
- 10) Budavar, S., O' Neil, M.J. and Smith, A., Eds., In; The Merck Index, 11th Edn., Merck and Co, Inc., U.S.A., 1989, 445.