Pergamon

Tetrahedron Letters, Vol. 36, No. 18, pp. 3133-3136, 1995
Elsevier Science Ltd
Printed in Great Britain
0040-4039/95 $9.50+0.00

0040-4039(95)00472-6

Ultrasound-promoted Benzylation of Arenes in the Presence of Zinc Chloride Mixed with a K10 Clay

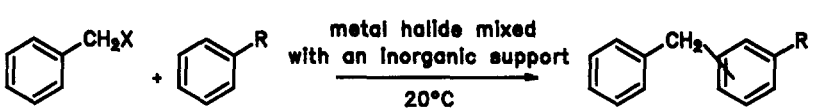
Jean Jacques Vanden Eynde,* Annie Mayence, and Yves Van Haverbeke

University of Mons-Hainaut, Organic Chemistry Laboratory
20, Place du Parc, B-7000 Mons (Belgium)

Abstract: Using K10 clay-supported zinc chloride, Friedel-Crafts benzylations proceed readily at room temperature. Significant improvements of the rates can be obtained when the reaction mixtures are sonicated.

Because of environmental problems, there is a growing interest in the study of heterogeneous reactions that involve solid reagents supported on high surface area inorganic materials. [1, 2] Among the advantages of such systems, mention should be made of an enhanced reactivity and an isolation step that is often reduced to a mere filtration.

Several metal halides on montmorillonite K10 have been recently employed to catalyze Friedel-Crafts reactions. [3-8] The method is tempting but preparation of the catalyst requires either an exchange [3] of the interstitial cations in the clay or a pre-treatment at high temperature. [4] In order to improve that novel procedure, we tested the possibility of using a simple mixture of a metal halide and a clay to synthesize diarylmethanes from technical grade reagents and without any prevention from moisture.



The reactions were monitored by ^{1}H NMR (Varian EM 360-L) by measuring the variations of the integrated intensities of the peaks due to the -CH_2- groups in the benzyl halide (δ = 4.0 ppm) and the diarylmethane (δ = 3.7 ppm). Our results concerning the preparation of diphenylmethane from benzyl chloride and benzene are gathered in the Table.

Table. Preparation of Diphenylmethane from Benzyl Chloride and Benzene in the Presence of a Solid Catalyst[a]

Magnetic stirring

Entry	Catalyst	Yield (%) after 5 min	15 min	30 min	60 min
1[b]	$ZnCl_2$				<5
2[c]	montmorillonite K10				5
3	$ZnCl_2$/montmorillonite K10	40	75	>95	
4	$ZnCl_2$/montmorillonite K10/H^+	20	45	70	>95
5	$CdCl_2$/montmorillonite K10				10
6	$CuCl_2$/montmorillonite K10				5
7	$AlCl_3$/montmorillonite K10	5	20	30	35
8	$ZnCl_2$/bentonite K10	20	40	65	>95
9	$ZnCl_2$/bentonite K10/H^+	25	55	75	>95
10	$ZnCl_2$/montmorillonite KSF				<5
11	$ZnCl_2$/montmorillonite KSF/H^+	<5	25	30	55
12	$ZnCl_2$/alumina				<5

Ultrasonic irradiation

Entry	Catalyst	Yield (%) after 1 min	2.5 min	5 min	7.5 min	10 min
13	$ZnCl_2$/montmorillonite K10	35	55	90	>95	
14	$ZnCl_2$/bentonite K10	20	40	85	>95	
15	$ZnCl_2$/montmorillonite KSF					<5
16	$ZnCl_2$/alumina					<5
17[d]	$ZnCl_2$/montmorillonite K10	15	25	45	55	60
18[e]	$ZnCl_2$/montmorillonite K10	15	30	60	75	85

[a]: In a typical experiment, a suspension of the solid catalyst (2.0 g; 1.1 mmol of metal halide/g of support) in benzene (18 mL; 200 mmoles) and benzyl chloride (1.15 mL; 10 mmol) was stirred or irradiated[14] with sonic waves (VCR-375; 20 KHz; Sonics and Materials, Inc., Danbury, CT, USA) at room temperature. [b]: 2.0 g of $ZnCl_2$. [c]: 2.0 g of the clay. [d]:0.5 mmol of $ZnCl_2$/g of support. [e]: 3.0 mmol of $ZnCl_2$/g of support.

We observed that zinc chloride mixed with montmorillonite K10 constituted an excellent association (entries 3 and 13), provided that the catalyst was dried at 100°C before use since its activity decreased when exposed to air for a few hours. Pre-treatment of the clay with hydrochloric acid [9] was not necessary and even slightly unfavorable (entry 4).

Mixtures of montmorillonite K10 with other metal halides, including a powerful Friedel-Crafts reactions promoter such aluminium chloride, were less effective (entries 5-7). This parallels the findings [4] of Clark, but cannot be clearly explained.

We also found that bentonite K10 and acidified bentonite K10 were good supports (entries 8 and 9) but use of montmorillonite KSF, especially when not acidified, or alumina gave rise to disappointing results (entries 10-12).

Since ultrasound accelerates many heterogeneous reactions [10, 11] in organic syntheses, including [12, 13] Friedel-Crafts alkylations, we reasoned that application of sonic waves could be beneficial in our experiments. As it can be seen from the results mentionned in the Table (entries 3 and 13; 8 and 14), ultrasound effectively promoted the benzylation of arenes in the presence of zinc chloride supported on a K10 clay. This can be attributed to an extremely effective mixing resulting in greatly intime contacts between the reactive species and, hence, in increased alkylation rates.

However, even under irradiation by sonic waves, we noticed that montmorillonite KSF as well as alumina remained bad supports (entries 15 and 16), that yields remained dependent [4] on the metal halide loading (entries 13, 17, and 18), and that the expected [3] regioselectivity for the benzylation of chlorobenzene with benzyl chloride was maintained as (4-chlorophenyl)-phenylmethane was obtained in higher yield than the 2-chlorophenyl isomer.

To the best of our knowledge, this is the first report on the use of ultrasonic waves to promote Fridel-Crafts alkylations in the presence of a metal halide supported on a clay. Although more information is required to evaluate the scope of the procedure, the results define simple reaction conditions for the efficient benzylation of arenes. In addition, the catalyst can be readily prepared, it is separated from the product(s) by a mere filtration, and in our hands, it could be reused several times without any loss of its activity.

ACKNOWLEDGEMENT

This work was financially supported by the Province de Hainaut.

REFERENCES AND NOTE

1. Clark, J.H.; Kybett, A.P.; Macquarrie, D.J. *Supported Reagents Preparation, Analysis and Applications*, VCH Publishers, Inc.: New York. **1992.**
2. Balogh, M.; Laszlo, P. *Organic Chemistry Using Clays*, Springer-Verlag: New York. **1993.**
3. Laszlo, P.; Mathy, A. *Helv. Chim. Act*, **1987**, *70*, 577-586.
4. Clark, J.H.; Kybett, A.P.; Macquarrie, D.J.; Barlow, S.J; London, P. *J. Chem. Soc., Chem. Commun.*, **1989**, 1353-1354.
5. Barlow, S.J.; Clark, J.H.; Darby, M.R.; Kybett, A.P.; London, P.; Martin, K. *J. Chem. Res. (S)*, **1991**, 74-75.
6. Sieskind, O.; Albrecht, P. *Tetrahedron Lett.*, **1993**, *34*, 1197-1200.
7. Barlow, S.J.; Bastoch, T.W.; Clark, J.H.; Culens, S.R. *Tetrahedron Lett.*, **1993**, *34*, 3339-3342.
8. Cornelis, A.; Laszlo, P.; Wang, S. *Tetrahedron Lett.*, **1993**, *34*, 3849-3852.
9. Chouday, B.M.; Valli, V.L.K.; Durga Prasad, A. *Synth. Commun.* **1991**, *21*, 2007-2013.
10. Lindley, J.; Mason, T.J. *Chem. Soc. Rev.* **1987**, *16*, 275-311.
11. Einhorn, C.; Einhorn, J.; Luche, J.L. *Synthesis* **1989**, 787-813.
12. Ando, T.; Sumi, S.; Kawate, T.; Ichihara, J.; Hanafusa, T. *J. Chem. Soc., Chem. Commun.*, **1984**, 439-440.
13. Boudjouk, P.; Ohrbrom, W.H.; Woell, J.B. *Synth. Commun.*, **1986**, *16*, 401-410.
14. Using the same power settings as in the reactions under study, we observed the formation of 89 mg (0.07 mequiv.) of iodine when a 1M KI aqueous solution saturated with carbon tetrachloride and maintained at 20 °C was sonicated for 10 minutes (Weissler reaction [15]).
15. Weissler, A. *J. Chem. Ed.*, **1948**, 28-30.

(*Received in France* 6 *December* 1994; *accepted* 10 *March* 1995)