Bromine/Bentonite Earth System, Promoter of Phenylmethanes from Toluene

Manuel Salmón,*[a] Enrique Angeles,[b] René Miranda[b]

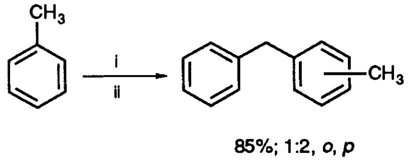
[a] *Instituto de Quimíca, Universidad Nacional Autónoma de México Circuito Exterior, Ciudad Universitaria, Coyoacán 04510 México, D.F.*

[b] *Facultad de Estudios Superiores, Cuautitlán, UNAM Cuautitlán, Izcalli, Estado de México, México*

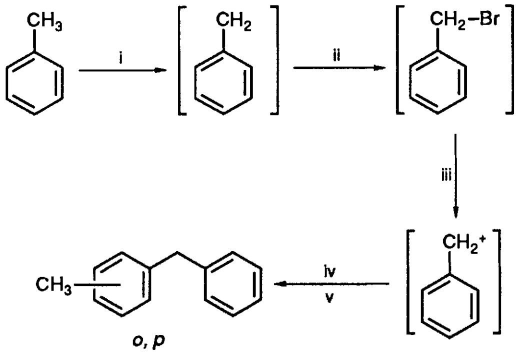
The condensation of toluene to produce *o*- and *p*-methylphenylmethanes by use of bromine with a bentonitic earth catalyst has been investigated and a mechanism is proposed based on the isolated intermediates and other related reactions.

Ortho- and *para*-phenylmethanes have important applications as insulating oil in high-voltage electrical devices,[1] as possible fuels for aircraft engines[2] and in particular, the *ortho* isomer, in the synthesis of anthraquinones.[3]

The preparation of phenylmethanes has been carried out mainly through Friedel–Crafts reactions between benzylhalides and toluene,[4] by reduction of diphenylketones,[5] or with a Grignard reaction between an arylmagnesium halide with benzaldehyde and further reduction of the resultant benzydrol.[6]



Scheme 1. i, Br_2/Clay; ii, Heat, dark, CS_2.



Scheme 2. i, Br_2/Clay; ii, Br_2/Clay; iii, Clay; iv, Toluene; v, Clay.

In this communication we report a simple new synthesis of phenylmethanes through a heterogeneous reaction catalysed by a commercial bentonitic earth.† The reaction was carried out by dropping bromine (0.021 mol) onto a dry solution of toluene (0.01 mole) in CS_2 (20 ml) with the bentonite (0.050 g) in suspension. The procedure was performed in the dark with stirring and refluxed for 4 h. The conversion was monitored by GLC.

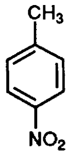
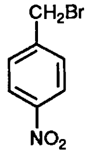
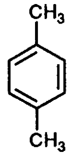
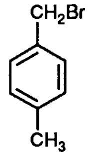
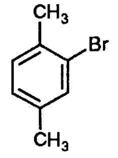
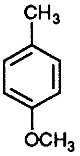
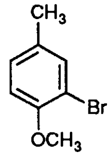
The suspension was allowed to stand at room temperature, filtered over celite to remove the bentonite, and the filtrate concentrated under reduced pressure. The residue was analysed by GCMS and purified by column chromatography using SiO_2 and hexane as eluent. The *ortho* and *para* phenylmethane isomers were obtained in 85% yield in a ratio of 1 : 2 and characterized by spectroscopic analysis.

If we compare the above reaction with common bromination methods, toluene will produce benzylbromide as a final product with bromine or *N*-bromosuccinimide under irradiation.[7] Furthermore, in order to form phenylmethanes, benzylhalides must be condensed with the selected substituted benzene using Lewis acids[4] or supported metal ions on a clay as the catalyst.[8]

In the present instance we have successfully employed a montmorillonite type clay to synthesize phenylmethanes in one step under milder conditions than those required in homogeneous reactions. Thus, the very simple one-pot synthesis of phenylmethanes represented in Scheme 1, should allow more than one reaction pathway.

Therefore, we propose a mechanism that includes as a first species the formation of benzylbromide. In fact, this compound was isolated when the reaction was performed at lower temperature (25 °C) and must necessarily be formed *via* a free radical reaction. The hydrogen abstraction by atomic bromine through free radicals to lead to the specific bromination of toluene, was confirmed when hydroquinone was added to the reaction. Total inhibition of the expected products resulted.

Table 1.

Substituted toluene	Product (yield %)
	 80%
	 +  30% 50%
	 75%

Catalyst bromine–bentonite; reflux 4 h.

The second step to produce the aromatic substitution involves a benzylic carbocation species formed by a heterolytic scission promoted by the clay, followed by the electrophilic substitution of toluene to give the *o*- and *p*-phenylmethane isomers. These compounds were also isolated when commercial bromo or chloro benzyltoluene were used as reactants and treated with the bentonite in the presence of toluene, affording the same yield and proportion of phenylmethanes.

In a study performed with bromine and alumina or silica as catalysts, benzylbromide was exlusively isolated in 80—85% yield from the reaction. Based on the above observations, a mechanistic sequence of reactions can be summarized, Scheme 2. It is also worth mentioning that nuclear substitutions have been observed to markedly affect the reactivity of the benzylic hydrogens of alkyl benzenes toward attack by certain free radicals.[9] Electron-releasing and -withdrawing groups were reported to increase and decrease, respectively, the rate of benzylhalide formation in substituted toluenes toward attack by atomic bromine.[9]

Examination of our data shows that nuclear substituents have a definite effect on the reactivity of benzylic hydrogens, with the clay–bromine system. Table 1 shows the qualitative results obtained with *para*-substituted toluenes which are in disagreement with those reported by other researchers.[7,9] Strong electron-withdrawing groups tend to stabilize benzylradicals yielding exclusively the corresponding benzylbromide. However, on substituted and weak electron-releasing groups the clay evidenced a dual catalytic effect as inductor of free radicals and as a catalyst of electrophilic aromatic

---

† The bentonite earth used in this work was shown by *X*-ray diffraction to have the following composition: SiO_2, 75.43, Al_2O_3, 9.33, MgO, 0.43; Fe_2O_3, 1.26; CaO, 4.04; K_2O, 0.40; TiO_2, 0.43; HÔH 110°, 9.46. The material was obtained from *Tonsil Mexicana* and has an specific surface area of 307 m^2 g^{-1} (BET N_2 with a pore volume of 0.4789 cm^3 g^{-1}) and a total acidity by NH_3 Thermodesorption of 0.099 meq/g. Particle size, 325 mesh.

substitution. Strong electron-releasing groups, however, yield only bromination on the aromatic ring.

The present study shows the difference in the effect of nuclear substituents of toluene on the reactivity of benzylic and aromatic substitutions with the bromine–bentonite systems in the dark.

The formation of the phenylmethanes is to our knowledge the first reported example of two catalysed reactions within one system. One involving free radicals and the other a Friedel–Crafts type alkylation with a predominant *ortho–para* directing effect. No *meta* isomer was formed.

Received, 5th December 1989; Com. 9/05178C

References

1 N. Berger and P. Jay, *IEEE Trans. Electr. Insul.*, 1986, **EJ-21**, 59; W. Edler and S. Friedewald, *Eur. Pat. Appl.*, 170054, 1986; *Chem. Abstr.*, 1986, **104**, 1712584.

2 J. H. Lamneck Jr. and P. H. Wise, *Natl. Advis. Comm. Aeronaut. Tech. Notes*, 1950, **17**, 2230.

3 Nippon Shokubai Kagaku Kygo, Co. Ltd., *Jpn. Kokai, Tokkio Koho*, 1983, J.P. 58, 201, 742; *Chem. Abstr.*, 1984, **100**, 174479m J. Markert, and H. Hagen. *Ger. Offen.*, 1984, D E 3, **241**, 449; *Chem. Abstr.*, 1984, **101**, 191403v.

4 H. C. Brown and M. Grayson, *J. Am. Chem. Soc.*, 1953, **75**, 6285; G. A. Olah, S. J. Kuhn, and S. H. Flood, *J. Am. Chem. Soc.*, 1962, **84**, 1688; G. A. Olah and J. A. Olah, *J. Org. Chem.*, 1967, **32**, 1612; F. P. DeHaan, W. D. Covey, R. L. Ezelle, J. E. Margetan, S. A. Pace, M. J. Sollenberger, and D. S. Wolf, *J. Org. Chem.*, 1984, **49**, 3954; F. P. DeHaan, W. H. Chan, W. D. Chen, D. M. Ferrara, C. L. Giggy, and M. J. Pinkerton, *J. Org. Chem.*, 1989, **54**, 1206.

5 J. Blackwell and W. J. Hickinbottom, *J. Chem. Soc.*, 1961, 1405.

6 J. H. Lamneck Jr. and P. H. Wise, *J. Am. Chem. Soc.*, 1954, **76**, 1104; F. A. Vingiello, S. G. Quo, and J. Sheridan, *J. Org. Chem.*, 1961, **26**, 3202.

7 C. Walling, 'Free Radicals in Solution,' Wiley, New York, 1957, pp. 361–365; K. B. Wiberg and H. H. Slaugh, *J. Am. Chem. Soc.*, 1958, **80**, 3033; G. A. Russel, C. DeBoer, and K. M. Desmond, *ibid.*, 1963, **85**, 365; R. E. Pearson and J. C. Martin, *ibid.*, 1963, **85**, 354.

8 J. H. Clark, A. P. Kybertt, D. J. Macquarrie, S. J. Barlow, and P. Landon, *J. Chem. Soc., Chem. Commun.*, 1989, 1353.

9 G. A. Russell, *J. Org. Chem.*, 1958, **23**, 1407; C. Walling and B. Miller, *J. Am. Chem. Soc.*, 1957, **79**, 4181; C. Walling and B. B. Jacknow, *J. Am. Chem. Soc.*, 1960, **82**, 6113; M. M. Martin and G. J. Gleicher, *J. Org. Chem.*, 1963, **28**, 3266; T. P. Low and K. W. Lee, *J. Chem. Soc. (B)*, 1970, 536.