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Synthesis of Alkylbenzenes by Friedel-Crafts Reactions catalysed by K10-Montmorillonite

Odette SIESKIND and Pierre ALBRECHT*

Faculté de Chimie, Université Louis Pasteur, 1 rue Blaise Pascal
67000 Strasbourg, France.

Key words : Friedel-Crafts alkylation, K10-montmorillonite, acyclic alcohols, cholestanol, cholesterol.

Abstract : Monoalkylation of benzene with primary, secondary and tertiary alcohols took place in high yields when K10-montmorillonite was used as acidic catalyst. Unexpected formation of 1-phenylalkylbenzenes occurred, beside other isomers with primary alcohols. Monoalkylation with cholestanol and cholesterol was regiospecific and located at C-3. Clay-catalysed alkylbenzene formation may also be of geochemical interest.

Many organic syntheses needing protic or Lewis acid media to produce carbocations[1,2] as intermediates are often carried out more easily and quickly using solid acid catalysts such as K10-montmorillonite.[3] This clay has a high specific area (270 m^2/g). Its Brönsted acid sites are strong enough to catalyse backbone reactions in steroids.[4,5] Its Lewis acidity, at least as efficient as $AlCl_3$, also promotes Friedel-Crafts reactions.[6]

We report here some Friedel-Crafts alkylations catalysed by K10-montmorillonite, which are particularly attractive because of their high yields and possible geochemical implications.

Octan-1-ol, the three isomeric alcohols hexadecan-1-ol, hexadecan-2-ol and 2-methylpentadecan-2-ol, as well as 2-methylhexadecan-2ol, cholestanol and cholesterol were used as alkylating agents for benzene, the latter being both reagent and solvent. All reactions were carried out under anhydrous conditions. The reaction vessel was equipped with a Dean Stark apparatus. K10-montmorillonite (Fluka) was activated at 120°C overnight before use. Typically, the K10 catalyst (2g) was added to a solution of the alcohol (200 mg) in benzene (250 ml). The stirred mixture was then heated at the reflux temperature of the solvent. Reaction products were separated from the catalyst by filtering over celite, followed by vacuum drying. The alkylbenzenes were recovered after TLC (silica gel, hexane) and analysed by GC, GC-MS and NMR. Reaction times, yields, K10/alcohol ratios, as well as alkylbenzene distributions are given in Table1.

The two tertiary alcohols, 2-methylpentadecan-2-ol and 2-methylhexadecan-2-ol, gave only one alkylation product, i.e. 2-methyl-2-phenylpentadecane and 2-methyl- 2-phenylhexadecane respectively, for obvious carbocation stability reasons. Yields were nearly quantitative for reaction times of only a few minutes.

Friedel-Crafts reactions with primary alcohols needed longer reaction times (16-24 hrs) and gave each a mixture of isomeric alkylbenzenes, explained by carbocation migration along the alkyl chain. So, octan-1-ol,

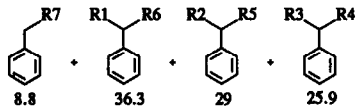
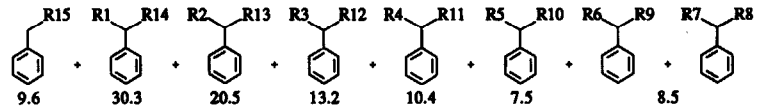
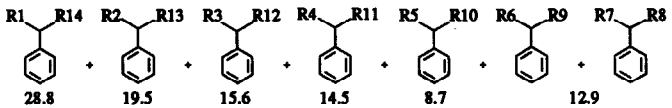
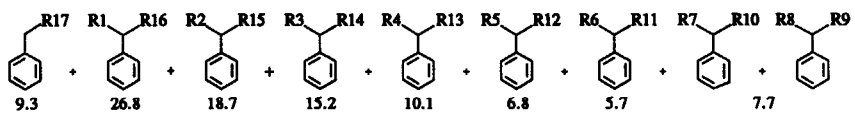
Alkylating Agent	K10/ alcohol (w/w)	Yield %	Time	Alkylbenzenes Relative amounts (%)
Octan-1-ol	10	38	16 hrs	
Hexadecan-1-ol	10 50	42 >90	20 hrs 7 hrs	
Hexadecan-2-ol	10 50	60 >90	3 hrs 1 hrs	
2-Methylpentadecan-2-ol	10	>95	5 min	2-Methyl-2-phenylpentadecane
2-Methylhexadecan-2-ol	10	>95	5 min	2-Methyl-2-phenylhexadecane
Octadecan-1-ol	10 50	40 >90	24 hrs 8 hrs	
Cholestanol	10	40	1 hr	3β-Phenylcholestane
Cholesterol	5	50	30 min	3β-Phenylcholest-5-ene (85%) + 3β-Phenylcholest-4-ene (15%)

Table 1 : Friedel-Crafts Alkylations catalysed by K10-Montmorillonite : alcohols, reaction conditions and alkylation products.
Dilution : 200 mg alcohol/250 ml benzene. Temperature : room temperature for cholesterol, 80°C elsewhere. Rn designates an alkyl radical C_nH_{2n+1}.

hexadecan-1-ol and octadecan-1-ol gave respectively 4, 8 and 9 isomeric alkylbenzenes. The major compound was always the 2-phenylalkane (about 30%). Noteworthy in these experiments was the formation of 1-phenylalkanes (about 10% for all primary alcohols).This indicated a trapping of the primary carbocation by substitution with a benzene ring, prior to migration of the carbocation along the alkyl chain.

Linear alkylbenzenes were not formed with a secondary alcohol, as seen in the case of hexadecan-2-ol, evolution of the initial secondary carbocation toward the primary site at C-1 being very improbable. Otherwise the alkylbenzenes observed here were identical to those produced with hexadecan-1-ol, as a result of migration of the initial carbocation along the alkylchain to other secondary positions.

Increasing the K10/alcohol ratio from 10 to 50 (w/w) shortened the reaction time by a factor three, and allowed the reaction yields to be practically quantitative for all acyclic alcohols. Such high yields are unusual in Friedel-Crafts reactions.[7]

Neither dialkylbenzenes, nor dialkylethers, or cracking products were observed, in contrast to RIGBY *et al.*.[8], who used bentonite from Wyoming as catalyst, heptan-1-ol as alkylating agent, and worked at 270°C. Furthermore, these authors did not report the occurrence of 1-phenylheptane among the reaction products of heptan-1-ol. WILLIAMS *et al.*[9] repeated the high temperature experiment using pentadecan-1-ol as alkylating agent. They observed mainly cracking products, and some 1-phenylpentadecane among the branched alkylbenzenes formed. In contrast to our results, the amount of 1-phenylpentadecane was quite small, compared to the other reaction compounds, leading the authors to the conclusion that clay catalysis was not operative in the formation of linear alkylbenzenes.

Although cholestanol and cholesterol are secondary alcohols, arylation with benzene remained at C-3, probably by trapping of the secondary carbocation. Indeed, cholestanol gave only 3β-phenylcholestane (yield : 40 %), whereas cholesterol produced two phenylated compounds resulting from isomerisation of the C-5 double bond (total yield: 50 %). The major compound was 3β-phenylcholest-5-ene (85 %) as seen from NMR studies (^{1}H, ^{13}C NMR; ^{1}H-^{1}H COSY and NOESY ; ^{1}H-^{13}C one bond and long range correlation experiments). The minor compound (15 %) isolated by reversed phase HPLC, was probably its Δ^4-isomer as deduced from mass spectral data (mass fragment base peak at m/z = 157 resulting from double β-cleavage of ring B). To limit double bond migration, Friedel-Crafts reactions with cholesterol were realised at room temperature using smaller amounts of catalyst (K10/sterol = 5) and shorter reaction times (30 min). Under similar conditions cholestanol remained unchanged. Greater amounts of catalyst did not increase the yields, due to competing reactions. In the case of cholesterol, backbone reactions took place at the same time, leading to complex mixtures of D-ring homologated compounds.

Although synthesis of phenylcholestane and phenylcholestene, from cholestanol and cholesterol methyl ether respectively, had been observed a long time ago in the presence of Japanese clay [9,10] the lack of adequate separation and analytical techniques prevented conclusive identification of the reaction products.

RIGBY *et al.* [9] obtained only degradation products of cholesterol when heating it with toluene and Wyoming bentonite in sealed vials at 270°C over a period of 4 weeks. Too drastic experimental conditions and perhaps the nature of their clay [12] would explain their results.

Noteworthy is the fact that alkylation of benzene with cholesteryl acetate at room temperature gave a complex mixture of unidentified products when $AlCl_3$ was the catalyst, as shown by STEFANOVIC *et al.*[13]. They also observed the fixation of two phenyl rings on 3β-acetoxy-5-androstene-17-one to give 3β, 6α-diphenyl-5α-androsta-17-one (12%).

The high yields with acyclic alcohols, and the regioselectivity of benzene substitution at C-3 in steroids confer a synthetic interest on the above reactions. But these results have also geochemical implications. Indeed, they simulate a possible diagenetic pathway occurring in the subsurface and leading to alkylbenzenes, which are widespread molecular markers of petroleum, sediments and coals. Some of the phenylalkanes observed in shales and coal pyrolysates[14-16] may indeed have been formed by reaction between alcohols and aromatic entities during early maturation. Furthermore it has become evident from chemical degradation studies of petroleum asphaltenes, kerogens and coals that Friedel-Crafts reactions could also play a role in the formation of carbon-carbon bonds between alkyl residues and aromatic moieties, thus contributing to the build-up of the macromolecular network of these complex materials.[17,18] It is interesting to note in this respect that in the latter the steroid skeletons are attached to aromatic subunits at C-3 exclusively.

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References

1. Olah, G.A. *Angew. Chem., Intern. Ed.* **1973**, *12*, 173-224.
2. Olah, G.A. *Friedel-Crafts Chemistry*; Wiley Interscience: New York 1973.
3. Laszlo, P. *Science* **1987**, *235*, 1473-1477, and references therein.
4. Sieskind, O.; Albrecht, P. *Tetrahedron Lett.* **1985**, *26*, 2135-2136.
5. Sieskind, O.; Albrecht, P. *Chem.* Soc., *Chem. Commun.* **1981**, 133-135.
6. Laszlo, P.; Mathy, A. *Helv. Chim. Acta* **1987**, *70*, 577-586.
7. Schriesheim, A. Alkylation of Aromatics with Alcohols and Ethers. In *Friedel-Crafts and related Reactions, vol. II, Part 1;* Olah, G.A. Ed.; John Wiley and Sons, Inc.: New york 1964; 478-595.
8. Rigby, D.; Gilbert, T.D.; Johns, J.W. *Org. Geochem.***1986**, *9*, 255-267.
9. Williams, J.A.; Dolcater, D.L.; Torkelson, B.E.; Winters, J.C. *Org. Geochem.* **1988**, *13*, 47-59.
10. Kawasaki, C.; Yamamura, J. *J. Pharm. Soc. Japan* **1937**, *57*, 713-718.
11. Kawasaki, C.; Yamamura, J. *J. Pharm. Soc. Japan* **1938**, *58*, 606-608.
12. Thomas, J.M. *Am. Sci.* **1992**, *266*, 112-118.
13. Stefanovic, M.; Dermanovic, M.; Solaja, B.; Dermanovic, V; Prewo, R. *J. Serb. Chem. Soc.* **1987**, 549-551.
14 Gallegos, E.J. *J. Chrom. Sci.* **1981**, *19*, 177-182.
15. Connan, J. *Bull. Centres Rech. Explor. Elf-Aquitaine* **1992**, *16*, 33-53.
16. Hussler G.: *Marqueurs géochimiques en séries carbonatées.* Université Louis Pasteur,Strasbourg, France,1985.
17. Trifilieff, S.; Sieskind, O.; Albrecht, P.; Biological Markers in Petroleum Asphaltenes: possible Mode of Incorporation. In *Biomarkers in Sediments and Petroleum;* Moldowan, J.M.; Albrecht, P.; Philp, R.P. Eds.; Prentice Hall, Englewood Cliffs, New Jersey, 1992; pp 350-359.
18. Blanc, P.: *Structure moléculaire de charbons : évolution en fonction du rang et du type.* Université Louis Pasteur, Strasbourg, France, 1989.

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