Synthesis of 1-Arylalk-2-enes and 1-Arylalkanes *via* Friedel–Crafts Alkylation with Allylic Alcohols Catalysed by an Acidic Clay

Keith Smith* and Guy M. Pollaud

Moderately activated benzenoid compounds undergo alkylation with allylic alcohols in the presence of acidic K10 clay to give almost exclusively 1-arylalk-2-enes by attack at the terminal position of the intermediate allyl cation; catalytic hydrogenation yields the corresponding 1-arylalkanes.

1-Arylalkanes are important materials [1] which are more viscous and more easily biodegradable than analogous 2- or 3-arylalkanes. Unfortunately, they are not usually available *via* direct Friedel–Crafts alkylation of aromatic substrates [2] on account of the tendency of the primary carbocation intermediates to rearrange. Consequently, when they are needed in pure form they are generally prepared by Friedel–Crafts acylation followed by reduction of the ketone so produced to the hydrocarbon level. However, such procedures are too costly and too unfriendly towards the environment to be used for production of the bulk requirements of the detergents or lubricants industries, which therefore continue to use mixtures consisting mainly of 2-arylalkanes.

In recent years there have been many advances in the use of solid acid catalysts to control organic reactions. [3–6] In accord with our own continuing interest in the use of solids for controlled organic synthesis [5,7,8] we decided to investigate the possibility of using a solid acid to catalyse production of 1-arylalkanes *via* Friedel–Crafts alkylation and now report a novel, catalysed alkylation of aromatic substrates with allylic alcohols which, in favourable cases, produces 1-arylalkenes selectively and in high yield. Such products are readily hydrogenated to give 1-arylalkanes.

Friedel–Crafts alkylations using alkenes as reagents are selectively catalysed using an H-mordenite zeolite, but the major products are the corresponding 2-arylalkanes. [9] We were not able to find a way of diverting the reaction to produce 1-arylalkanes. Attempted use of 1-halogenoalkanes as alkylating agents also led to only limited success, 32% of a 1-arylalkane being obtained with a 1-chloroalkane over a dealuminated HY zeolite. Higher proportions of 1-arylalkanes than this have been claimed with conventional catalysts. [10] We therefore turned our attention to allylic derivatives of types **1** and **2** in the hope that these would generate the stabilized allylic cation **3** and that this would react preferentially at its terminal position with aromatic substrates. Little work has been carried out using solid acid catalysts and allylic reagents of this type, but in homogeneous reactions protonic acids tend to catalyse reactions at the double bond while Lewis acids tend to catalyse allylic substitution. [2b]

R–CH=CH–CH$_2$X   R–C(X)H–CH=CH$_2$

     1 (*E*)   **2**

+

R–CH–CH–CH$_2$ MeCH=CHCH$_2$Ar

     3   **4** (*E*)
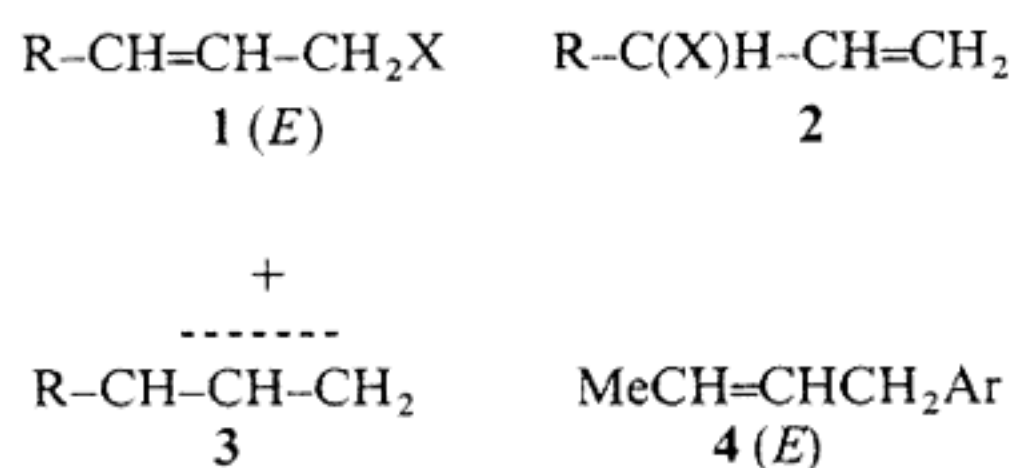
In the presence of H-mordenite allylic chlorides **1** and **2** (R = Me, X = Cl) reacted with refluxing toluene to give
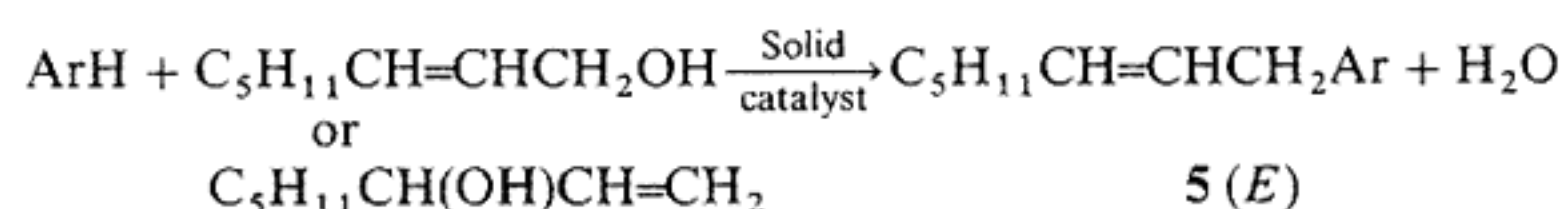
Table 1 Efficiency of different catalysts[a] for reaction Scheme 1 (ArH = toluene)

Catalyst	Reagent	Octenol converted (%)[b]	Yield of 5 (%)[c,d]
None	2	9	0
MeSO$_3$H	2	2	0
Amberlyst-15	2	54	0
Silica	2	17	0
Synclyst (silica–alumina)	2	97	62
K10	2	100	79
K10	1	100	89
H-ZSM-5	2	48	0
H-Mordenite	2	100	61
H-Mordenite	1	100	69
H–X (SiO$_2$:Al$_2$O$_3$ = 2.5)	2	35	0
H–Y (SiO$_2$:Al$_2$O$_3$ = 5)	2	100	71
H–Y (SiO$_2$:Al$_2$O$_3$ = 5)	1	100	83
H–Y (SiO$_2$:Al$_2$O$_3$ = 40)	2	100	33

[a] Under standard conditions using catalyst (96 mg) in toluene (7.5 cm^3) at reflux and addition of octenol (320 mg, 2.5 mmol) in toluene (5 cm^3) over a few min with stirring, followed by a further 5 min at reflux (see text). [b] Determined from amount of octenol remaining (by GC). [c] Determined by GC using an added standard. [d] Products were characterized, following isolation by spinning band distillation of larger scale reaction mixtures, by NMR and mass spectrometry and by conversion into arylalkanes by catalytic hydrogenation.

reasonable yields of the terminally substituted product, **4**. There was little evidence of further alkylation or of addition of hydrogen chloride to the double bond [11] under the conditions used. Nevertheless, hydrogen chloride is not a favourable by-product since it is corrosive, can damage the structure of the solid catalyst and can act as a competitive catalyst in its own right, leading perhaps to a different selection of products. Therefore, allylic alcohols were studied more extensively and **1** and **2** (R = pentyl, X = OH) were chosen as the test reagents (Scheme 1).

$$ArH + C_5H_{11}CH{=}CHCH_2OH \xrightarrow[\text{catalyst}]{\text{Solid}} C_5H_{11}CH{=}CHCH_2Ar + H_2O$$

or

$$C_5H_{11}CH(OH)CH{=}CH_2 \qquad\qquad \mathbf{5}\ (E)$$

Scheme 1

The efficiency of a number of different catalysts was tested under a standard set of reaction conditions (refluxing toluene solvent; 5 min reaction; mass ratio octenol : catalyst 1 : 0.3). The results are shown in Table 1.

Several important features emerge from Table 1. (*i*) There is little or no reaction under these conditions in the absence of a catalyst or with a soluble acid (MeSO$_3$H) catalyst. (*ii*) Several catalysts, notably silica, Amberlyst-15, H-ZSM-5 and H-X,

Table 2 Syntheses of products 5 according to Scheme 1 with K10 as catalyst (ratio alcohol:catalyst = 1:2; reaction time 5 min for each case)

Ar	Reaction $T/°C$	Yield of 5 (%)[a]	Ratio $o:m:p$[b]
Ph	80	80	—
MeC_6H_4	111	94	46:5:49
EtC_6H_4	111	80[c]	42:4:54
$Pr^iC_6H_4$	111	70[c]	36:0:64
$Bu^tC_6H_4$	111	83[c]	24:0:76
FC_6H_4	85	43	16:0:84
$MeOC_6H_4$	111	92[c,d]	55:0:45

[a] Isolated yield. [b] Determined by GC. [c] The K10 was not dried prior to use in these cases. [d] Product contains ca. 12% of 3-aryloct-1-ene as an impurity.

bring about decomposition of the octenol without causing alkylation. (*iii*) The most acidic catalyst tried, H-Y with a silica:alumina ratio of 40, effectively catalyses the reaction but also catalyses further reaction of the product 5, leading to a lowering of the yield of 5. (*iv*) Fairly strongly Brønsted acidic large-port zeolites and the acidic clay K10 are the most effective catalysts for the reaction. (*v*) The primary octenol produces somewhat higher yields than the secondary octenol, but both are effective reagents. Therefore, it is possible to use a mixture of the two.

In view of these findings, K10 was chosen for further investigation. The amount of catalyst could be reduced to a mass ratio of octenol:catalyst of ca. 1:0.05 by use of a longer reaction time (1 h), but the yield of 5 was a little lower. Drying of the K10 prior to use produced somewhat better yields. Zinc chloride supported on K10[12] was not as active as K10 alone. Therefore, K10 in high ratio was applied to a range of aromatic substrates. The results are given in Table 2.

Although it is likely that the optimal catalyst would be different for different substrates, with more acidic catalysts giving better results for deactivated substrates and less acidic ones giving better results for activated substrates in accord with the comments relating to Table 1, it is clear from the results in Table 2 that K10 can produce good yields of 1-arylalk-2-enes from a range of substrates of moderate activity. Furthermore, hydrogenation of compounds 5 according to Scheme 2[13] was straightforward and quantitative. Thus, the two-step sequence represented by Schemes 1 and 2 provides a new, high-yielding and convenient route to 1-arylalkanes (6). It should prove to be of considerable significance.

$$C_5H_{11}\overset{.}{C}H=CHCH_2Ar \xrightarrow[Pd/C\,cat.]{H_2} C_5H_{11}CH_2CH_2Ar$$

5 (*E*)   6
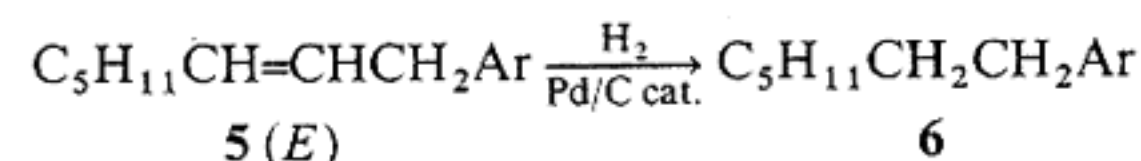
Scheme 2

We also note that solids which generally exhibit Brønsted acidity act to produce allylic substitution rather than addition to the double bond, in contrast to the reported situation with soluble acids.[2b]

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