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No Contest : a Co-Reactant Deprived of Reactivity

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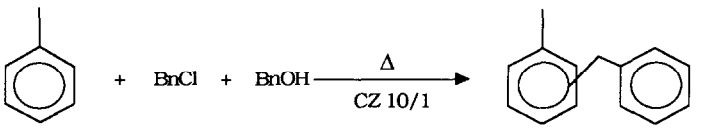
Abstract : *Whereas benzyl chloride is normally more reactive than benzyl alcohol toward aromatic hydrocarbons, at 20° C alkylation of toluene is totally inhibited in the presence of an equimolar mixture of the two benzylating agents and of a clay-based catalyst. At 80° C, all the alcohol molecules are first consumed. Then, and only then, at time t = 45 mn, the chloride molecules start their reaction.*

We show in another communication, that deals also with Friedel-Crafts alkylation of aromatic hydrocarbons by a benzylic reagent ($PhCH_2Cl$), in the presence of the "clayzic" catalyst, a reactivity inversion. In binary mixtures of toluene and mesitylene, the latter is benzylated preferentially, with high selectivity (greater than a factor six) ; while the former is more reactive when the two hydrocarbons are reacted separately[1].

We examine here the converse behavior, that of binary mixtures of two alkylating reagents ($PhCH_2Cl$ and $PhCH_2OH$), when reacted either separately or together with an excess of toluene as the aromatic substrate. Conditions are as in the preceding communication, *viz.* one-shot addition of the "clayzic" catalyst[1] (CZ ; 0.25g) to a mixture, pre-heated to the appropriate temperature, of benzyl chloride and/or benzyl alcohol (10 mmol total) and of toluene in excess (100 mmol). Conversion of benzyl chloride is monitored by GC, and a *n*-hexadecane internal standard is used to determine the yields of monobenzylated products. When benzyl *chloride* is the sole benzylation reagent, it reacts already at 20°C under these conditions. Whereas, when benzyl *alcohol* is the sole reagent, it demands a temperature of 110°C for reaction.

Table 1 Competition of Benzyl Chloride with Benzyl Alcohol.



100 mmol 5 mmol 5 mmol 0.250g m, o, p

Run	Temp. /°C	Time /mn	Conv. BzCl (%)	Conv. BzOH (%)	Yield[a] (%)
1	40	120	0	0	0
2	80	45	0	100	30
3	80	120	100	100	85[b]
4	90	5	0	50	10
5	90	10	10	100	40
6	90	20	100	100	90[b]
7	110	5	30	100	40
8	110	10	100	100	86

[a] monobenzylated products

[b] Formation of polyalcoylation side-products.

The results (Table 1) are nothing short of astounding :

(i) total inhibition of chloride reactivity at 20 and at 40° C (Run 1) ;

(ii) greater reactivity of the alcohol at 80 and at 90° C ;

(iii) at 80° C, one observes this *sequential* behavior : *first* the total conversion of the alcohol. *Then*, when it is over, *ie.* 45 mn after the start of the reaction (Runs 2-3), and *only then does conversion of the chloride start.*

Thus we have shown here that microscopic robots consisting of smectite clay-based catalysts effect the batch processing of chemicals.

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References

1 - Cornélis, A. ; Dony, C. ; Laszlo, P. ; Nsunda, K.M. ; preceding communication.

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