65. Catalysis of *Friedel-Crafts* Alkylation by a Montmorillonite Doped with Transition-Metal Cations

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Catalysts are obtained by exchange of the interstitial cations in the K 10 montmorillonite. They are applied to *Friedel-Crafts* alkylations with halides, alcohols, and olefins. They are quite effective even with unactivated hydrocarbons. Isomer distribution depends little on the catalyst used. Thermodynamic equilibration does not take place, the reactions appear to be kinetically controlled. Efficiency of the catalysts bears no apparent relation to that of the corresponding *Lewis* acids under homogeneous conditions, and it depends on the nature of the alkylating agent. Zr(IV) and Ti(IV), in general, give the best results.

Introduction. – Catalysis of organic reactions by inorganic solids [1] is an important new dimension of preparative organic chemistry. Thus, it is natural that it should concern itself with the *Friedel-Crafts* reaction [2–5]. This is not only one of the major reactions in organic and industrial chemistry [5], it is also a reaction that demands catalysis [3–5]. *Olah* has surveyed the *Lewis* acids used as catalysts in the *Friedel-Crafts* reaction, and he has provided a scale for their efficiency [6]. However, use of standard *Lewis*-acid catalysts is frought with problems such as their handling, the necessity of using large amounts with alcohol substrates [3], not to mention the isomerizations they often trigger. For such reasons, and also because of a greater ease of setup and workup, solid catalysts have excited much interest. They include resins such as *Nafion-H* [7–8], the graphite-aluminum-chloride intercalate [9], modified alumina [10] as well as a number of phyllosilicates (clays) [11–15]. These latter heterogeneous catalysts, while inexpensive by comparison with the *Nafion-H* polymer, have shown drawbacks such as a requirement for rather drastic reaction conditions, or a need for activated aromatics such as phenols. For these reasons, we have sought to devise an improved heterogeneous clay catalyst for *Friedel-Crafts* alkylations. We had already reported that such a system, consisting of the K 10 montmorillonite doped with ferric ions, can perform arylation directly on a saturated hydrocarbon, adamantane serving as the test substrate [16]. To further explore the scope and limitations of such catalysts for aromatic alkylations, we have now performed a more systematic survey of the potency of various transition-metal cations associated with the K 10 clay, and we report here the various improvements (lowering of the amount of catalyst, decrease of polyalkylation, improved regioselectivity [17], *etc.*) they lead to.

Results. – a) *Alkyl Halides*. Percentages of conversion are plotted as a function of time for benzylation of benzene with $PhCH_2Cl$ *(Fig. a)*; for alkylation of toluene with cyclohexene *(Fig. b)*, and for benzylation of benzene with $PhCH_2OH$ *(Fig. c)*, in the presence of 10 different catalysts. There are marked differences. In the first case, Fe(III),

Zn(II), Cu(II), and Zr(IV), all metal ions except Cu(II) in the second case, and all metal ions except Co(II) and Zn(II) in the last case are seen to give rise to acceptable rates of conversion.

To further evaluate the catalysts, we have selected benzylation of benzene by PhCH₂Cl as a test reaction *(Table 1)*. Five of the catalysts, including the unexchanged K10 montmorillonite, effect the full conversion of the starting PhCH₂Cl. Among the
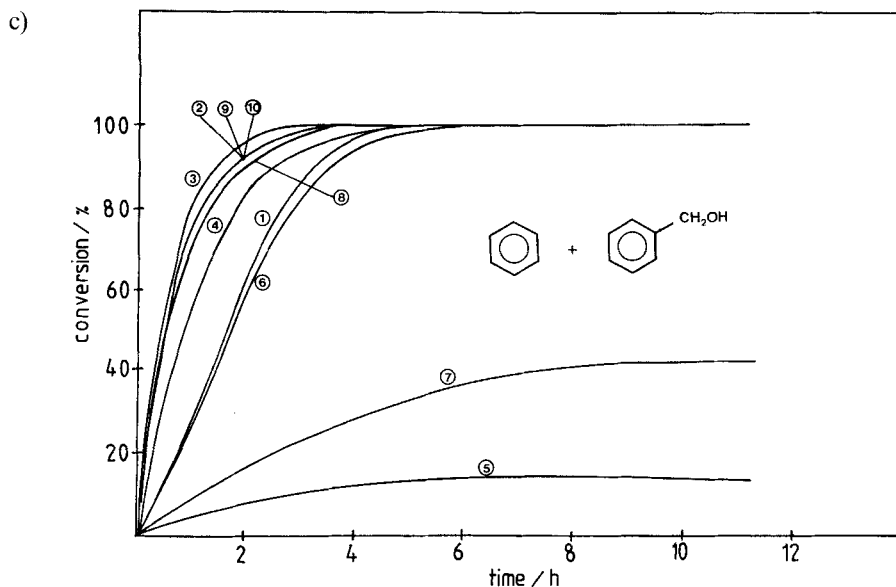
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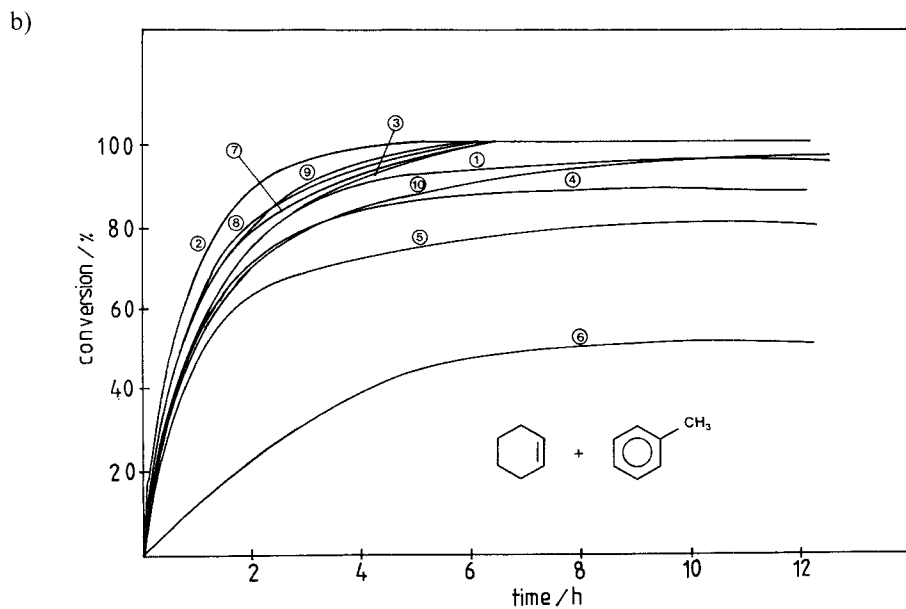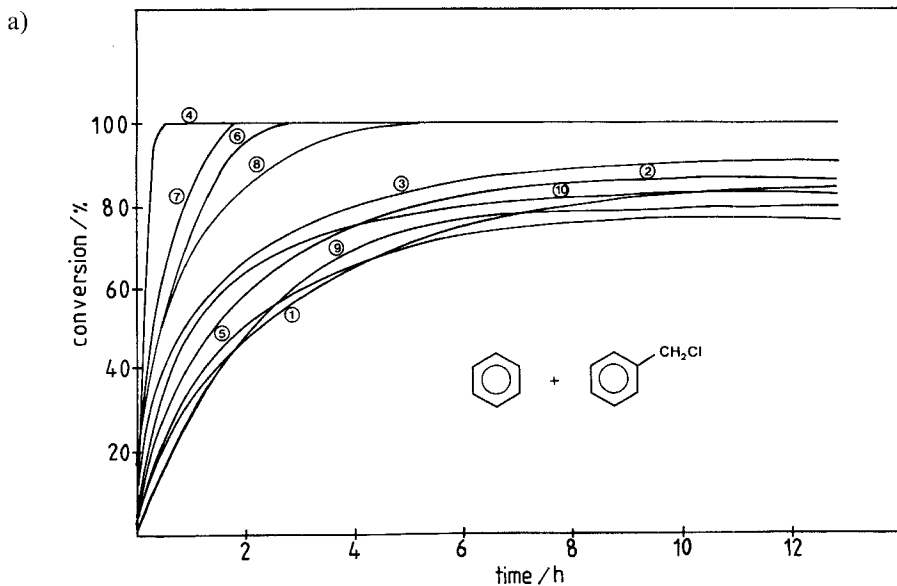
Figure. *Conversion percentage* vs. *time for alkylation of aromatics with PhCH₂Cl (a), cyclohexene (b), and PhCH₂OH (c), in presence of doped clay catalyst.* ① K10, ② K10-Al(III), ③ K10-Ti(IV), ④ K10-Fe(III), ⑤ K10-Co(II), ⑥ K10-Cu(II), ⑦ K10-Zn(II), ⑧ K10-Zr(IV), ⑨ K10-Nb(V), ⑩ K10-Ta(V).

Table 1. *Benzylation of Benzene by PhCH₂Cl*

Catalyst	Reaction time [h][a])	Half-life time [min]	Conversion of PhCH₂Cl [%][b])	Isolated yields in	
				Monoalkylation product [%]	Dialkylation product [%][c])
K10	15	144	98	48	27
K10-Al(III)	9	87	84	59	31
K10-Ti(IV)	5	54	90	66	20
K10-Fe(III)	0.25	8	100	57	27
K10-Co(II)	11	114	76	40	20
K10-Cu(II)	3.5	30	100	60	33
K10-Zn(II)	1.5	20	100	60	30
K10-Zr(IV)	5	30	100	52	29
K10-Nb(V)	14	129	70	44	20
K10-Ta(V)	8	63	78	50	32

[a]) Reaction times indicated are the ones after which conversion of PhCH₂Cl remains roughly unchanged.
[b]) Determined by GC.
[c]) Relative areas (uncorrected) of the GC signals compared to that of the monoalkylated product.

other five catalysts, the K10-Ti(IV) system stands out, because it leads to the best yield, even though conversion remains incomplete after 5 h. This apparent paradox may be explained by this catalyst offering the best compromise between reactivity and selectivity: even though the K10-Ti(IV) catalyst appears less active than its Fe(III) congener, it gives rise to a lesser amount of polyalkylation products. Another interesting and not unexpected conclusion is the pronounced influence of the phyllosilicate support. The catalytic

activities recorded here bear little relationship to those of the unsupported cations [6]. Let us remind the reader of the overall reactivity sequence of *Lewis*-acidic *Friedel-Crafts* catalysts [18]: $AlBr_3, AlCl_3 > GaCl_3 > FeCl_3 > SbCl_5 > ZrCl_4 > BCl_3, BF_3 > SbCl_5$.

By contrast, we find here for instance a superiority of Zr(IV) as compared to Al(III), when conversion and yield are taken both into consideration *(Table 1)*.

Yet, more significant are the improvements with respect to existing catalysts. Benzylation of benzene gave 40% yield with $TiCl_4$ as catalyst [19], and 45% [20] or 59% [2] when $AlCl_3$ was the catalyst. We found isolated yields of 66% (5 h), 57% (15 min), 60% (3.5 h), 60% (1.5 h), and 52% (5 h) using K10 exchanged with Ti(IV), Fe(III), Cu(II), Zn(II), and Zr(IV), respectively, as catalysts. Another such illustrative set of results is the *tert*-butylation of *m*-xylene by *t*-BuCl which proceeds with yields above 60% in a very short time (20 min) with our K10-Ti(IV), K10-Cu(II), and K10-Zr(IV) catalysts, whereas the yields earlier reported were in the 23–50% range [22–23].

Another relevant consideration is the amount of catalysts required *(Table 2)*. The potency of our catalyst is blatant, much smaller quantities are sufficient for good yields to

Table 2. *Comparison of the Amounts of Catalysts Required for Benzylation of Benzene by $PhCH_2Cl$*

Catalyst	Catalyst/$PhCH_2Cl$ (w/w)	Temp. [°C]	Reaction time [h]	Yield [%]
K10-Ti(IV)	0.008	80	15	60
K10-Fe(III)				
K10-Cu(II)	0.08	80	0.25–5	57–66
K10-Zr(IV)				
Al–HCl	0.13	25	18	63 [4]
$AlCl_3$	0.15	7		80 [4]
$AlCl_3$	0.5	–	–	45 [4]
Al_2HgCl_2	0.6	0	3	60 [4]
$TiCl_4$	1.1	80	–	40 [4]
$ZnCl_2$	10.8	80	12	30 [4]
Ag_2SO_4	1.2	80	4	50 [4]

Table 3. *Comparison of the Conversions Achieved with a Clay-Based Catalyst and with Standard Lewis Acids*

Alkylating agent	Substrate	Clay-based catalyst	Reaction time (Conversion [%])	Corresponding Lewis-acid catalyst	$H^{\oplus}$ equiv. relative to the clay-based catalyst	Reaction time (Conversion [%])
$PhCH_2Cl$	Benzene	K10-Fe(III)	15 min (100)	$FeCl_3$	3	15 min (100)
					5	12 min (100)
		K10-Zn(II)	1.5 h (100)	$ZnCl_2$	5	24 h (45)
		K10-Co(II)	11 h (70)	$CoCl_2$	5	24 h (2)
$PhCH_2OH$	Benzene	K10-Ti(IV)	1 h (100)	$TiCl_4$	5	24 h (0)
		K10-Al(III)	1.2 h (100)	$AlCl_3$	5	24 h (3)
		K10-Nb(V)	1.2 h (100)	$NbCl_5$	5	24 h (5)
Cyclohexene	Toluene	K10-Al(III)	3 h (100; 30% polyalkylation)	$AlCl_3$	3	15 min (100; 60% polyalkylation)
					1	1 h (100)
		K10-Zr(IV)	6 h (100)	$ZrCl_4$	5	24 h (6)
		K10-Nb(V)	4 h (100; 25% polyalkylation)	$NbCl_5$	3	40 min (99; 35% polyalkylation)
					1	24 h (50)

be achieved. While it is convenient because inexpensive to use 1 g of metal-exchanged K10 catalyst per 0.1M of alkyl halide, we could reduce this amount to 75 mg per 0.1M without problem: for instance, alkylation of toluene by i-PrBr is performed with 97% conversion in 18 h, with the K10-Ti(IV) association.

We have examined also regeneration of the catalysts. The same K10-Fe(III) sample could be re-utilized up to five consecutive times with no loss in activity, and up to eight times with some lengthening of the reaction time, in benzylation of toluene by PhCH₂Cl.

We have also controlled that the presence of the acidic montmorillonite clay increases conversion with respect to standard *Lewis* acids such as TiCl₄ or AlCl₃ *(Table 3)*. We have done this comparison with halides, alcohols and olefins: in each case, greater amounts of the classical *Lewis* acids are required for the same conversion to be achieved, sometimes to an inpractical extent.

b) *Alcohols.* We start this section also by a survey of the capabilities of the K10 montmorillonite doped with a number of metallic cations *(Table 4)*. Interestingly, the catalysts with the best performance, *i.e.* K10-Ti(IV), K10-Nb(V), and K10-Ta(V) are not the same as with alkyl halides. Electing the Ti system as the catalyst, we have tested various primary, secondary, and tertiary alcohols *(Table 5)*, with results generally superior to those obtained with stoichiometric amounts of the standard *Lewis* acids [3b] [4].

Table 4. *Efficiency of Various Catalysts* (500 mg) *for Benzylation of Benzene by PhCH₂OH* (0.1M)

Catalyst	Reaction time [h][a]	Half-life time [min]	Yield [%][b]
K10	3.5	100	31
K10-Al(III)	1.2	36	36
K10-Ti(IV)	1.0	30	40
K10-Fe(III)	1.5	94	24
K10-Co(II)	12	> 300	7
K10-Cu(II)	3.5	105	31
K10-Zn(II)	12	> 300	8.6
K10-Zr(IV)	1.3	40	24
K10-Nb(V)	1.2	36	34
K10-Ta(V)	1.2	36	43
AlCl₃	48		50 [4]
AlCl₃	120		55 [4]
H₂SO₄	3		40–50 [4]
BF₃	–		15 [4]
P₂O₅	48		30 [4]
HF	–		65–70 [4]

[a]   This is the time after which conversion of the starting material remains roughly unchanged according to GC.
[b]   Determined by GC.

Table 5. *Alkylation of Aromatics by Alcohols in the Presence of K10-Ti(IV) as Catalyst* (2.5g for 0.1M of the alcohol)

Substrate	Alcohol	Reaction time [h]	Isolated yield [%]
Benzene	PhCH₂OH	0.45	54
	Cyclohexanol	18	51
	t-BuOH	2	7.4
Toluene	PhCH₂OH	0.2	60
	2-Pentanol	6	50
	3-Pentanol	6	60

The single exception is t-BuOH, the low yield is due presumably to formation of 2-methyl-1-propene which escapes from the reaction medium.

The regioselectivity of the reaction little depends on the catalyst *(Table 6)*, only *ortho-* and *para*-products form.

Table 6. *Product Distribution in the Benzylation of $PhCH_3$ by $PhCH_2OH$ in the Presence of Various Catalysts*

Catalyst	Isomer distribution[a]		Catalyst	Isomer distribution[a]	
	o	p		o	p
K10-Co(II)	49	51	K10-Zr(IV)	37	63
K10-Zn(II)	44	56	K10-Ta(V)	40	60
K10	49	51	K10-Nb(V)	42	58
K10-Cu(II)	44	56	K10-Al(III)	40	60
K10-Fe(III)	41	59	K10-Ti(IV)	38	62

[a]   Isomer distribution is determined by GC and NMR, and by comparison with authentic samples of *o-, m-*, and *p*-methyl(diphenyl)methane.

c) *Olefins*. With olefins as alkylating agents, most catalysts present similar activities except for the surprisingly low performances by K10-Fe(III), K10-Cu(II), and K10-Co(II) *(Table 7)*.

Table 7. *Efficiency of Various Catalysts (2.5 g) for Alkylation of $PhCH_3$ by Cyclohexene (0.1M)*

Catalyst	Reaction time [h][a]	Half-life time [min]	Yield [%][b]
K10	8	50	44
K10-Al(III)	5	36	51
K10-Ti(IV)	7	50	51
K10-Fe(III)	20	60	37
K10-Co(II)	20	150	35
K10-Cu(II)	20	> 600	16
K10-Zn(II)	7	45	48
K10-Zr(IV)	7	45	48
K10-Nb(V)	6	45	48
K10-Ta(V)	8	60	57
AlCl₃	3		40
HF	–		74

[a]   The times after which conversion of cyclohexene remains roughly unchanged according to GC.
[b]   Determined by GC.

Selecting again the Ti system as catalyst, we have checked on various types of substrates that decent yields of alkylation products are obtained *(Table 8)*.

Table 8. *Alkylation of Aromatics by Cyclohexene (0.1M) in the Presence of K10-Ti(IV) as Catalyst (2.5 g)*

Substrate	Reaction time [h]	Isolated yield [%]	Product distribution[a]		
			o	m	p
Benzene	24	31	–	–	–
PhCH₃	16	51	17	12	71
PhOCH₃	3	85	73		27

[a]   Determined by NMR.

The regioselectivity of the reaction depends on the catalyst type, with a predominance of *para*-products while *ortho*- and *meta*-products form in comparable amounts *(Table 9)*.

Table 9. *Product Distribution in the Alkylation of PhCH₃ by Cyclohexene (0.1M) in the Presence of Various Catalysts(2.5 g)*

Catalyst	Product distribution[a]			Catalyst	Product distribution[a]		
	o	*m*	*p*		*o*	*m*	*p*
K10	23	16	61	K10-Cu(II)	29	20	51
K10-Al(III)	14	9	76	K10-Zn(II)	18	13	69
K10-Ti(IV)	17	12	71	K10-Zr(IV)	12	8	80
K10-Fe(III)	11	8	81	K10-Nb(V)	18	13	69
K10-Co(II)	18	13	69	K10-Ta(V)	9	6	85

[a]   Determined by NMR; ±2%.

We note that the catalyst consisting of K10 exchanged with Ta(V) gives very good results: good yields under moderate reaction times *(Table 7)* combined with a very large predominance of the *para*-product formed with a selectivity of 17:3 *(Table 9)*.

d) *Regioselectivity and Extent of Rearrangement*. An attractive feature of the catalysts investigated is the low proportion of rearrangement products whether intra- or intermolecular. This is apparent in the alkylation of benzene by the (chloromethyl)toluenes *(Table 10)*.

Table 10. *Product Distribution in the Alkylation of Benzene by (Chloromethyl)toluenes (0.1M) in the Presence of K10-Fe(III) as Catalyst (1 g)*

| (Chloromethyl) toluenes	Product distribution[a]		
	o	*m*	*p*
ortho	100	0	0
meta	0	100	0
para	0	0	100

[a]   Determined by NMR.

The regiospecificity of this reaction is maintained independently of the reaction time. This, together with the lack of isomerization, is consistent with kinetic control. Likewise, benzylation of toluene by PhCH₂Cl under the same conditions as in *Table 10* gives exclusively the *ortho*- and *para*-derivatives in 49 and 51% yields, respectively. This observation is reminiscent of results obtained with homogeneous catalysts such as AlCl₃ in CH₃NO₂ [6] [24]. Similarly, the various catalysts applied give rise to a predominance of *ortho*- and *para*-alkylation products with almost total exclusion of *meta*-isomers *(Table 11)*.

Table 11. *Product Distribution in the Benzylation of PhCl by PhCH₂Br (0.1M) in the Presence of Various Catalysts (1 g)*

Catalyst	Product distribution[a]		
	o	*m*	*p*
K10-Ti(IV)	38	traces	62
K10-Fe(III)	37	traces	63
K10-Cu(II)	37	traces	63
K10-Zn(II)	38	traces	62

[a]   Determined by GC and by comparison with authentic samples.

Scheme
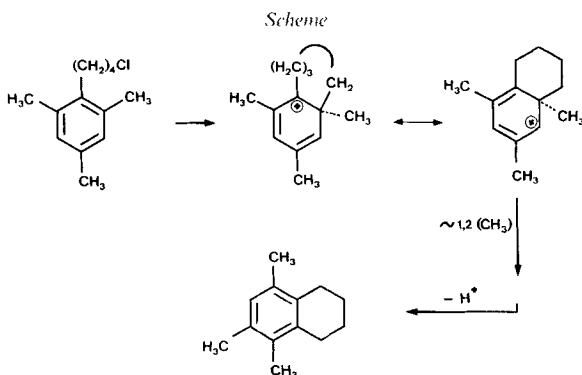
Only when the reaction is forced into rearrangement, if it is to proceed, rearrangement products occur. A nice example is the alkylation of mesitylene by 1-bromo-4-chloro-butane: we found the reaction to be apparently exclusively intramolecular with respect to alkylation, and to give rise to the 1,2,3,4-tetrahydro-5,6,8-trimethylnaphthalene only according to the plausible route shown in the *Scheme*.

Discussion. –- *Friedel-Crafts* alkylation of aromatic rings [2] with alcohols demands considerable quantities of the standard *Lewis*-acid catalysts [3]. We have solved this problem of considerable practical importance with the new catalysts presented here. That the overall best results, when one considers jointly halides, alcohols, and olefins as alkylation agents, are obtained with Ti(IV) and Zr(IV), *i.e.* with early transition metals, is not entirely unexpected. *Mukaiyama* paved the way a decade ago, when he reported the room-temperature formation of cyclohexylbenzene in 97% yield upon treatment of cyclohexanol with $TiCl_4$ in benzene [25].

The results reported here are especially gratifying with halides as alkylating agents, leading to good yields and preferential formation of the monoalkylation product. Alcohols give somewhat poorer results. In the presence of the modified clay catalyst, the reaction continues to conform to the classic carbocationic pathway: 2- and 3-pentanols give rise to the same product mixture albeit of differing compositions *(Table 12)*. The abysmal yield achieved with *t*-BuOH is due to the predominant and quantitative formation of the elimination olefin, 2-methyl-1-propene.

Table 12. *Isomer Distribution from the Alkylation of PhCH₃ (100 ml) with 2- and 3-Pentanol (0.1M) in the Presence of K10-Ti(IV) (5 g)*

Alcohol	Reaction time [h]	Yield [%]	Isomer distribution[a]
2-Pentanol	6	50	10:16:6:20:30:18
3-Pentanol	6	60	7:15:13:15:23:27

[a]   Six possible isomers occur: $(o, m, p) \times$ (2- or 3-pentyl).

The procedure has the asset of total simplicity: the aromatic hydrocarbon to be alkylated serves as its own solvent, workup consists merely of a filtration to remove the catalyst followed by solvent evaporation and/or a separation, as the case may be.

Conclusion. – To sum up, good conversion rates are achieved by using transition-metal-exchanged phyllosilicates such as the K10 montmorillonite as catalysts in *Friedel-Crafts* alkylations. The yields are improved significantly with respect to the standard *Lewis*-acid catalysts. Likewise, reaction times can be greatly reduced. The amounts of catalysts needed are much less than with the usual *Lewis*-acid catalysts, they can be reduced by up to three orders of magnitude on a weight-per-weight basis. The regeneration of the catalyst is feasible. The reactions are clean: little or no *meta*-products, absence of rearrangement, no polyalkylation. Some nice regioselectivities can be achieved. Thus, use of clay-based catalyst improves markedly this reaction, as it has done so already for a number of other important organic reactions [1].

Experimental Part

General. M.p. (uncorrected): *Laboratory Devices, Melt-Temp apparatus.* NMR Spectra: *Bruker AM 300WB* and *Varian EM 360L.* MS: *Micromass 7070 F.*

1. *Preparation of Catalysts.* To 1 l of a stirred aq. soln. (1M) of $FeCl_3$, $CuCl_2$, $CoCl_2$, or $ZnCl_2$, or 1 l of an ethanolic solution (1M) of $ZrCl_4$, $TiCl_4$, $TaCl_5$, $NbCl_5$, or $AlCl_3$, 80 g of K10 clay are added. Stirring is maintained for 24 h. The clay suspension is centrifugated, and the supernatant solution is discarded. The clay catalyst is washed with distilled H_2O (suspension, stirring, centrifugation), and the washing cycles are repeated untill disappearance of Cl^- ions from the discarded H_2O. The clay, after drying overnight in an oven at 120°, is finely ground in a mortar.

2. *Alkyl Halides and Olefins as Alkylating Agents. General Procedure.* A 1M soln. of the alkylating agent in 100 ml of the aromatic is heated at reflux temp. in presence of the catalyst (1 g for the halides and 2.5 g for the olefins) for the time specified in the *Tables*. The reaction mixture is filtered, the solvent evaporated, and the residue distilled or recrystallized.

2.1. *Reaction between $PhCH_2Cl$ and Benzene.* B.p. 150°/15 Torr. Yields and reaction times: see *Table 1.* ^{1}H-NMR ($CDCl_3$) of diphenyl methane: 3.95 (*s*, 2 H); 7.2 (*m*, 10 H).

2.2. *Reaction between t-BuCl and m-Xylene.* B.p. 80°/15 Torr; 20-min reaction time with K10-Ti(IV), K10-Zr(IV), or K10-Cu(IV) for 60% yield. ^{1}H-NMR ($CDCl_3$) of 1-butyl-3,5-dimethylbenzene: 1.3 (*s*, 9 H); 2.3 (*s*, 6 H); 6.8 (*m*, 1 H); 7.0 (*m*, 2 H).

2.3. *Reaction between i-PrBr and $PhCH_3$.* B.p. 50–55°/5 Torr; 6-h reaction time with K10-Ti(IV), K10-Zr(IV) for 40% and 55% yields, respectively. ^{1}H-NMR ($CDCl_3$) for the mixture of the (isopropyl)(methyl)benzenes: 1.65 (*s*), 1.70 (*s*) (6 H); 2.70 (*s*), 2.80 (*s*) (3 H); 3.26 (*hept*, 1 H); 7.25–7.75 (*m*, 4 H).

2.4. *Reactions between (Chloromethyl)toluenes and Benzene.* 2.4.1. *o-(Chloromethyl)toluene and Benzene.* B.p. 104°/0.5 Torr; 24-h reaction time with K10-Fe(III) for 50% yield. ^{1}H-NMR ($CDCl_3$): 2.2 (*s*, 3 H); 4.0 (*s*, 2 H); 6.8–7.4 (*m*, 9 H).

2.4.2. *p-(Chloromethyl)toluene and Benzene.* B.p. 115°/5 Torr; 60-min reaction time with K10-Fe(III) for 70% yield. ^{1}H-NMR ($CDCl_3$): 2.3 (*s*, 3 H); 3.9 (*s*, 2 H); 6.8–7.5 (*m*, 9 H).

2.4.3. *m-(Chloromethyl)toluene and Benzene.* B.p. 117°/5 Torr; 30-min reaction time with K10-Fe(III) for 75% yield. ^{1}H-NMR ($CDCl_3$): 2.3 (*s*, 3 H); 3.9 (*s*, 2 H); 6.8–7.5 (*m*, 9 H).

2.5. *Reaction between $PhCH_2Cl$ and $PhCH_3$.* B.p. 110–115°/5 Torr; 5-min reaction time with K10-Fe(III) for 70% yield. ^{1}H-NMR ($CDCl_3$): 2.2 (*s*), 2.3 (*s*) (3 H); 3.9 (*s*), 4.0 (*s*) (2 H); 6.8–7.5 (*m*, 9 H).

2.6. *Reaction between $PhCH_2Br$ and PhCl.* B.p. 145–150°/5 Torr; 45-min, 1.5-h, 6-h, and 6-h reaction-times with K10-Fe(III), K10-Zn(II), K10-Cu(II), and K10-Ti(IV), respectively, for 42%, 32%, 42%, and 35% yields, respectively. ^{1}H-NMR ($CDCl_3$): 3.9 (*s*, 0.8 H); 4.1 (*s*, 1.2 H); 6.9–7.6 (*s*, 9 H).

2.7. *Reaction between 1-Bromo-4-chlorobutane and Mesitylene.* M.p. (from EtOH) 44.5°; 24-h reaction time with 4 g of K10-Fe(III) as catalyst for 81% yield. ^{1}H-NMR ($CDCl_3$): 1.80–1.83 (*m*, 4 H); 2.14 (*s*, 3 H); 2.20 (*s*, 3 H); 2.29 (*s*, 3 H); 2.63–2.68 (*m*, 4 H); 6.87 (*s*, 1 H).

2.8. *Reaction between Cyclohexene and $PhCH_3$.* B.p. 105°/10 Torr. Reaction times and yields: see *Tables 7* and *8.* ^{1}H-NMR ($CDCl_3$): 1.30–1.75 (*m*, 5 H); 1.80–2.20 (*m*, 5 H); 2.45 (*s*), 2.49 (*s*) (4 H); 7.2–7.4 (*m*, 4 H).

2.9 *Reaction between Cyclohexene and Benzene.* B.p. 95°/5 Torr; 24-h reaction time with K10-Ti(IV) for 31% yield *(Table 8).* ^{1}H-NMR ($CDCl_3$): 1.0–2.2 (*m*, 10 H); 2.2–2.9 (*m*, 1 H).

2.10. *Reaction between Cyclohexene and $PhOCH_3$.* B.p. 120°/8 Torr; 3-h reaction time with K10-Ti(IV) for 85% yield *(Table 8).* ^{1}H-NMR ($CDCl_3$): 1.0–2.2 (*m*, 10 H); 2.3–3.0 (*m*, 1 H); 3.45 (*s*, 3 H); 6.6–7.4 (*m*, 5 H).

3. *Alcohols as Alkylating Agents.* A 1M soln. of the alcohol in 100 ml of the aromatic is placed in a flask equiped with a *Dean-Stark* apparatus, with 5 g of catalyst. The mixture is heated at reflux temp. for the time specified in the *Tables* and below. The mixture is filtered, the solvent is evaporated, and the residues are distilled.

3.1. *Reaction between PhCH$_2$OH and Benzene.* B.p. 150°/15 Torr; 27-min reaction time for 55% yield with K10-Ti(IV) as catalyst *(Table 4)*. ^{1}H-NMR: see *2.1.*

3.2. *Reaction between Cyclohexanol and Benzene.* B.p. 95°/5 Torr; 18-h reaction time for 51% yield with K10-Ti(IV) as catalyst *(Table 4)*. ^{1}H-NMR: see *2.9.*

3.3. *Reaction between t-BuOH and Benzene.* B.p. 170°, 2-h reaction time for 7.4% yield with K10-Ti(IV) as catalyst *(Table 4)*. ^{1}H-NMR (CDCl$_3$): 1.3 (*s*, 9 H); 5.7–6.3 (*m*, 5 H).

4. *Reaction between PhCH$_2$OH and PhCH$_3$.* B.p. 110–115°/5 Torr; 12-min reaction time for 60% yield with K10-Ti(IV) as catalyst *(Table 4)*. ^{1}H-NMR: see *2.5.*

5. *Reaction between 2-Pentanol and PhCH$_3$.* B.p. 37–40°/0.5 Torr; 6-h reaction time for 50% yield with K10-Ti(IV) as catalyst *(Table 12)*. GC and NMR are consistent with six isomeric (methyl)(pentyl)benzenes in the relative proportions 1.7:2.7:1:3.3:5:3.

6. *Reaction between 3-Pentanol and PhCH$_3$.* B.p. 37–40°/0.5 Torr; 6-h reaction time for 60% yield with K10-Ti(IV) as catalyst *(Table 12)*. GC and NMR are consistent with six (methyl)(pentyl)benzenes in the relative proportions 1:2:1.7:2:3.1:3.7.

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