

Catalytic activity of K10-montmorillonite in reaction of arenes with some mono- and di-functional alkylating agents, mostly derived from isobutane and isobutene^{*}

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Received 13 March 1995; revised and accepted 11 September 1995

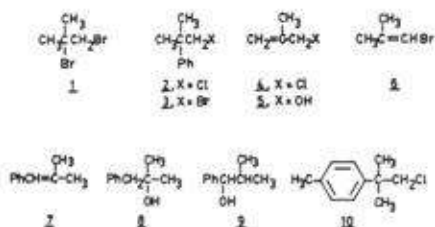
K10-montmorillonite has been tested as Friedel-Crafts catalyst in the alkylation of benzene, toluene and anisole with one or more of the alkylating agents 1-10. The reaction products consisted essentially of 1,1- and 1,2-diaryl-2-methylpropane derivatives (e.g. 11 and 12 respectively) together with side products resulting from transalkylation, monoalkylation, hydride transfer and elimination. K10-montmorillonite has also been used to catalyse the alkylation of naphthalene with benzyl alcohol whereby a mixture of α - and β -benzyl naphthalene is obtained. The results, explained in terms of carbocation transformations, show K10-montmorillonite to be a mild catalyst with no subsequent side-chain isomerising ability just like FeCl₃, AlCl₃-CH₃NO₂, TiCl₄ and ZrCl₄.

Over the years, clay minerals have attracted much attention of both catalyst and organic chemists¹⁻⁴. However, their application to Friedel-Crafts reaction is still very limited as only a few scattered reports can be traced in the literature⁵⁻¹⁰. Inspired by the theoretical and industrial importance of the Friedel-Crafts reactions as well as by the economical, environmental and practical (set-up and work-up) advantages of the heterogeneous solid clay catalysts, we examined the application of K10-montmorillonite as Friedel-Crafts catalyst in the reaction of benzene, toluene and anisole with some mono- and difunctional alkylating agents especially those derived from isobutane and isobutene (1-10). In doing this, our primary aim has been to compare the behaviour of this catalyst with other conventional Lewis and Bronsted Friedel-Crafts catalysts such as

AlCl₃, AlCl₃-CH₃NO₂, FeCl₃, TiCl₄, ZrCl₄, BF₃, H₂SO₄, H₃PO₄, etc.

Results and Discussion

The conditions and results of arene alkylation with 1 to 10 are compiled in Tables I and II. The identification of products was established by TLC, IR, ¹H NMR, GC and in some cases also by GC-MS analyses.



Careful examination of the results of Table I reveals considerable similarities between the alkylation behaviour of compounds 1-4 and 6-9. For example: (i) all alkylations showed obvious dependence on reaction variables such as catalyst ratio (*cf.* SI Nos. 4 and 5), time (compare *cf.* SI Nos. 5 and 6; 12 and 13; 18 and 19), temperature (*cf.* SI Nos. 1 and 6; 7 and 9; 10 and 13; 22 and 23) and (ii) apart from other compounds, all effective reactions gave diphenylisobutane fractions consisting of isomers 11 and 12 in an apparent equilibrium ratio approximating 2:1 (*cf.* SI Nos. 3-6, 9, 11-13, 15-19, 23-26) (Eqn 1).

Comparison of the present results with those of similar alkylations induced earlier¹⁷ by other catalysts reveals that K10-montmorillonite is a catalyst with no side-chain isomerising ability just like the mild FeCl₃, AlCl₃-CH₃NO₂, TiCl₄ and ZrCl₄ catalysts. Thus, it did not cause any isomerisation of 11 or 12 to *dl* and *meso*-2,3-diphenylbutane as did the strong AlCl₃ catalyst.

Referring back to Table I, several interesting observations are worthy of emphasis and special comments: (i) except for methallyl alcohol (5) which did not alkylate (*cf.* SI Nos. 20 and 21), all other alkylations of benzene took effect only at reflux temperature, (ii) most alkylations were suppressed by added *pet.* ether (b.p. 40-60°C), (*cf.* SI Nos. 2, 3, 8,

^{*} Part XXII of the series of Modern Friedel-Crafts Chemistry. This work was presented in part at the Second International Conference on Chemistry in Industry, sponsored jointly by the Saudi Arabian International Chemical Sciences Chapter of the ACS and Bahrain Society of Chemist, October 24-26, 1994, Vol 2 (1994), Process and Refining Division, Paper No. 1085.

Table I—Conditions and results of alkylation of benzene with compounds 1-9 in the presence of K10-montmorillonite catalyst^a

Sl. No.	Method	Time (hr)	Temp. (°C)	Product Composition (%) ^b			
				Ph ₂ C ₆ H ₄ Isomers ^b		Other products	
				11	12	Ident. Compd No. (%)	Unident. Compd No. (%)
I. Alkylations with isobutylene dibromide (1)							
1	A	48	25	—	—	1(98)	02
2	B	09	Reflux	—	—	1(80), 3(08), 14(02), 15(01), 7(03)	06
3	B	48	Reflux	09	05	1(74), 3(03)	09
4 ^c	A	40	Reflux	19	08	1(54), 3(13), 14(05)	01
5	A	40	Reflux	29	12	1(29), 3(12), 14(04), 15(06), 7(04)	04
6	A	56	Reflux	46	26	1(13), 3(05), 7(04)	06
III. Alkylations with neophyl chloride (2)							
7	A	48	25	—	—	2(93)	07
8	B	30	Reflux	—	—	2(92), 13(03)	05
9	A	30	Reflux	29	12	2(39), 13(04), 15(08), 7(06)	02
II. Alkylations with neophyl bromide (3)							
10	A	48	25	—	—	3(98)	02
11	B	30	Reflux	10	04	3(83)	03
12	A	10	Reflux	34	11	3(31), 15(13), 7(02)	09
13	A	30	Reflux	64	29	3(01)	06
IV. Alkylations with methallyl chloride (4)							
14	A	48	25	—	—	4(97)	03
15	B	48	Reflux	12	06	4(78)	04
16 ^d	A	24	Reflux	19	10	4(29), 2(11), 13(04), 15(02), 7(04)	21
17 ^d	A	24	Reflux	15	07	4(05), 2(20), 13(06), 15(04), 7(22)	21
18	A	24	Reflux	30	13	4(23), 2(08), 13(03), 15(03)	20
19	A	72	Reflux	58	25	4(03)	14
V. Alkylations with methallyl alcohol (5)							
20 ^e	A	05	Reflux	—	—	5(09)	91
21 ^e	A	24	Reflux	—	—	—	100
VI. Alkylations with 1-bromo-2-methyl-1-propene (6)							
22	A	48	25	—	—	6(90)	10
23	A	40	Reflux	57	19	3(10), 14(07), 15(04)	07
VII. Alkylations with 2-methyl-1-phenyl-1-propene (7)							
24	A	30	Reflux	57	18	—	25
VIII. Alkylation with 2-methyl-1-phenyl-2-propanol (8)							
25	A	30	Reflux	38	18	—	44
IX. Alkylation with 2-methyl-1-phenyl-1-propanol (9)							
26	A	30	Reflux	32	16	—	52

^a Unless otherwise specified, reactants were as follows: alkylating agent (0.02 mole), benzene (0.2 mole) and K10-montmorillonite (2.0g).

^b Percentage composition of various products as determined by combined GLC and NMR data.

^c Most Friedel-Crafts reactions are complex and the presence of unidentifiable components is expected.

^d The amount of the K10-clay was 0.5 g instead of 2.0 g.

^e Alkylating agent (0.02 mole), benzene (0.1 mole) and K10-clay (4 g).

^f In these reactions: alkylating agent (0.02 mole), benzene (0.2 mole), and the K10-clay (4 g).

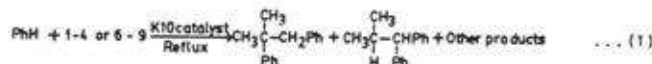
Table II—Additional alkylations and transalkylations of benzene, toluene and anisole

Sl no.	Method	Reactants ^a		Reaction conditions		Product composition ^b Compd No. (%)
		Alkyl. agent	ArH	Time (hr)	Temp. (°C)	
1	A	1	Ph-CH ₃	30	Reflux	1(08), 16(10), 17 ^c (54), 18 ^c (20), uniden. compds. (8).
2	A	10	Ph-CH ₃	20	Reflux	17 ^c (72), 18 ^c (22), uniden. compds. (06).
3	A	10	PhH	20	Reflux	11(21), 12(9), 19 ^c (41), 20 ^c (10), 21 ^c (6), uniden. compds. (13).
4	A	2	Ph-CH ₃	20	Reflux	17(16), 18(7), 19 ^c (43), 20 ^c (18), 21 ^c (16), uniden. compds. (10).
5	A	1	Ph-OCH ₃	12	Reflux	22 ^c (48), 23 ^c (31), uniden. compds. (21).
6	C	11+12	Ph-CH ₃	20	Reflux	19 ^c (19), 20 ^c (13), 21 ^c (12), 17 ^c (18), 18 ^c (12), uniden. compds. (26).
7	C	17+18	PhH	20	Reflux	12(14), 11(06), 19 ^c (40), 20 ^c (10), 21 ^c (04), uniden. compds. (26).

^a Reactants were as follows: alkylating agent (0.02 mole), benzene (0.2 mole) and K10-clay (2.0 g).

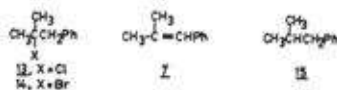
^b Product compositions were determined from a combination of GC, IR, NMR and in some cases GC-MS analyses.

^c Mixed with lesser amounts of the *meta*- and/or *ortho*- counterparts.



11 and 15), whether this was due to deactivation of the catalyst by the solvent and/or the lower reflux temperature is not yet clear, (iii) besides dialkylation products 11 and 12, most alkylations gave side products resulting from rearranged and non-rearranged processes including monoalkylation [e.g. 3 and 14 from 1 (*cf.* Sl No. 4); 2 and 13 from 4 (*cf.* Sl No. 16); 3 and 14 from 6 (*cf.* Sl No. 23)], elimination [e.g. 7 from 1, 2, 3 and 4 (*cf.* Sl Nos. 9, 12 and 17)], hydride transfer [e.g. 15 from 1, 2, 3 and 4 (*cf.* Sl Nos. 5, 9, 12 and 17)] and isomerisation of alkylating agents 2 to 13 (*cf.* Sl No. 9). In fact, when the alkylating agent neophyl chloride (2) was refluxed with K10 clay in pet. ether (40–60°C), it resulted in an isomerisation mixture composed of 2 and 13 in a percent ratio of 80:20. Mechanistic interpretations of the formation of products 11–15 in terms of intermediate carbocation transformations can be found in previous studies¹⁷.

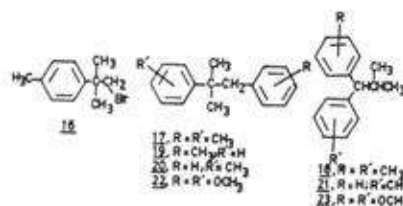
In connection with this work, we also investigated (*cf.* Sl No. 3) of toluene with 1, 2 and 10 (*cf.* Sl Nos. 1, 4 and 2) and of anisole with 1 (*cf.* Sl No. 5). The conditions and results of these alkylations are compiled in Table II and the structures of their products are formulated in Scheme I.



Parallel to the reactions of Table I, the reactions of Table II yielded products consisting essentially of *para*-oriented 1,1- and 1,2-diarylisobutane isomers (Scheme I) mixed with a varying amount of their *meta*- and/or *ortho*- oriented counterparts (*cf.* Sl Nos. 1, 2, 3 and 4). Of these reactions, 1 and 10 gave similar product mixtures consisting essentially of 1,1- and 1,2-di(*p*-tolyl)isobutanes (17) and (18) suggesting a common reaction intermediate (*cf.* Sl Nos. 1 and 2) as in Eqn. 2.

Likewise, each of reactions 3a and 3b of Table II (*cf.* Sl Nos. 3 and 4) gave five products of which 19, 20 and 21 were common resulting from straight alkylations (Eqn. 3). Besides, reaction 3a gave 11 and 12 (*cf.* Sl No. 3) and reaction 3b gave 17 and 18 (*cf.* Sl No. 4) as a result of subsequent transalkylations (*cf.* Sl Nos. 6 and 7) (Eqn. 4) (Scheme II).

Experimental support for these transalkylation pathways has been found in the finding that a product



Scheme I

Starting materials and reference samples

3-Chloro-2-methyl-1-propene (methallyl chloride, **4**), methallyl alcohol (**5**), 1-bromo-2-methyl-1-propene (**6**), isobutylbenzene (**15**), 1-chloro-1-phenylmethane (benzyl chloride) and benzyl alcohol were available commercially (Aldrich). 1,2-Dibromo-2-methylpropane (isobutylene dibromide, **1**)¹⁷ 1-chloro-2-methyl-2-phenylpropane (**2**)^{17b}, 1-bromo-2-methyl-2-phenylpropane (**3**)^{17b}, 2-chloro-2-methyl-1-phenylpropane (**13**), 2-bromo-2-methyl-1-phenylpropane (**14**), 2-methyl-1-phenyl-1-propanol (**7**), 2-methyl-1-phenyl-2-propanol (**8**), 2-methyl-1-phenyl-1-propanol (**9**) and 1-chloro-2-methyl-2-(4-tolyl)propane (**10**) were obtained as described earlier¹⁷.

¹H NMR data of new alkylation products

The ¹H NMR of the alkylation from toluene and isobutylene dibromide in the presence of either AlCl₃/CH₃NO₂ or K10 clay catalyst showed a mixture of two isomers **17** and **18**.

Isomer **17**: δ(CCl₄) 1.27 [s, 6H, C(CH₃)₂], 2.25 (s, 6H, 2CH₃), 2.76 (s, 2H, CH₂), 6.66-7.22 (m, 8H, Ar-H).

Isomer **18**: δ(CCl₄) 0.88 (d, 6H, J = 7 Hz, 2CH₃), 2.30 (s, 6H, 2CH₃), 2.49 (m, 1H, CH), 3.34 (d, 1H, J = 7 Hz, CH), and 6.54-7.38 (m, 8H, Ar-H).

The ¹H NMR of the alkylation from anisole and isobutylene dibromide in the presence of either AlCl₃/CH₃NO₂ or K10 clay catalyst showed a mixture of two isomers **22** and **23**.

Isomer **22**: δ(CCl₄) 1.27 (two overlapping s, 6H, 2CH₃), 2.70 and 2.83 (two overlapping s, 2H, (CH₂)₂), 3.60 (two overlapping s, 6H, 2OCH₃), 6.57-7.30 (two overlapping m, 8H, Ar-H).

Isomer **23**: δ(CCl₄) 0.84 (two overlapping d, 6H, J = 7 Hz, 2CH₃), 2.34 (two overlapping m, 1H, 2CH), 3.66 (two overlapping s, 6H, 2OCH₃), 3.87 (two overlapping d, 1H, J = 7 Hz, CH), 6.57-7.30 (two overlapping m, 8H, Ar-H).

Alkylation and transalkylation methods: General procedure

Unless otherwise specified in the footnotes of Tables I and II, the following general methods were essentially followed.

Method A—In a flask equipped with a magnetic stirrer, a pressure-equalising dropping funnel and a reflux condenser protected by a calcium chloride tube was placed K10-montmorillonite (2 g) and the arene (0.1 mole). A solution of the alkylating agent (0.02 mole) in the arene (0.1 mole) was introduced through the dropping funnel over a period of 10 min and the reaction mixture stirred at the desired temperature

for the desired time. After removing the heterogeneous catalyst by filtration and the solvent by evaporation, the residue was analysed by TLC, GLC, IR and NMR. The results obtained are summarised in Tables I and II.

Method B—The procedure was essentially the same as in method A with the exception that the reaction mixture was also furnished by pet. ether (b.p. 40-60°C, 20 mL) as a co-solvent.

Method C—A solution of a mixture of **11** and **12** (0.02 mole) in toluene (0.2 mole) or a mixture of **17** and **18** (0.02 mole) in benzene (0.2 mole) was added to K10-montmorillonite (2.0 g) taken in the reaction flask and the resulting mixture was heated under reflux for 20 hr. After the standard work-up, the residue was subjected to TLC, GC, NMR and IR analyses. The results are included in Table II.

Isomerisation of neophyl chloride (2) with K10-montmorillonite

A mixture of neophyl chloride (**2**, 0.02 mole), K10-montmorillonite (2.0 g), and pet. ether (b.p. 40-60°C, 20 mL) was heated under reflux for 18 hr. The heterogeneous catalyst was then removed by filtration. Evaporation of pet. ether left a residue which was shown by GC and NMR to be a mixture of **2**, **7**, **13** and **15** in a percent ratio of 60:15:14:9 with 2% of unidentified material. When the above reaction was performed in the absence of K10-montmorillonite catalyst, the starting neophyl chloride (**2**) was recovered unchanged.

Alkylation of benzene and naphthalene with benzyl alcohol and benzyl chloride in the presence of K10-montmorillonite

The procedure was essentially similar to method A above with the exception that CH₂Cl₂ was used as solvent in the case of naphthalene. Both alkylating agents gave diphenylmethane (ca. 90% yield) with benzene and a mixture of α- and β-benzyl-naphthalene (74% yield) in a ratio of 4:1 with naphthalene.

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