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Modern Friedel–Crafts Chemistry. Part 24.† Alkylation of Benzene with 1,2-Dibromo-3-chloro-2-methylpropane in the Presence of Lewis and Brønsted Acid Catalysts‡

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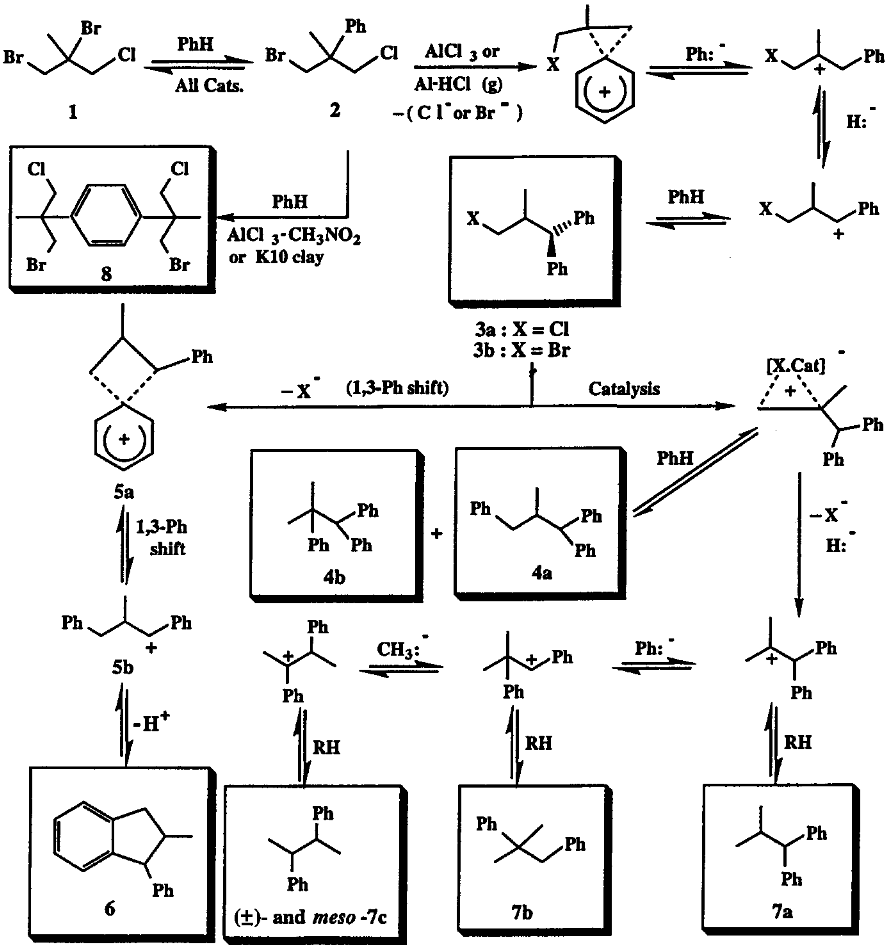
The major alkylation products of benzene with 1,2-dibromo-3-chloro-2-methylpropane are 1-X-2-methyl-3,3-diphenylpropane (X = Cl, Br) with $AlCl_3$ and 1,4-bis-(1-bromo-3-chloro-2-methylpropyl)benzene with $AlCl_3$–CH_3NO_2 or K10 montmorillonite (K10 Clay); minor products include di- and tri-phenylated butanes and/or 2-methyl-1-phenylindane.

The alkylation of benzene with multifunctional reagents constitutes an important part of Friedel–Crafts chemistry.[1,2] In this paper, we present the alkylation of benzene with 1,2-dibromo-3-chloro-2-methylpropane **1** under both Lewis and Brønsted acid catalyses. The results are depicted in Table 1 and their mechanistic rationale in terms of carbocation transformations is formulated in Scheme 1.



Scheme 1 (X = Cl or Br)

With reference to Table 1 and Scheme 1, the alkylation of benzene with **1** gave product mixtures consisting of varying proportions of 1-chloro- and 1-bromo-2-methyl-3,3-diphenylpropanes **3a**,**b**, 1,1,2- and 1,1,3-triphenyl-2-methylpropanes **4a**,**b**, 1-phenyl-2-methylindane **6**, 1,1- and 1,2-diphenyl-2-methylpropanes **7a**,**b**, (±)- and *meso*-2,3-diphenylbutane **7c** and 1,4-bis-(1-bromo-3-chloro-2-methylpropyl)benzene **8**, depending on catalyst type and the reaction conditions.

Commenting on these results, several points have to be emphasized:

(1) The results of entry 4 are worthy of comparison with earlier ones from the corresponding trichloride which report the product to be *meso*-**7c** (33.4% yield) mixed with two unidentified liquid isomers.

(2) The formation of **8** as the major product in entries 5–7 may be attributed to the mild catalytic activity of $AlCl_3$–CH_3NO_2 and K10 montmorillonite (K10 Clay) which can induce reaction only at the tertiary site. However, a longer reflux time with K10 montmorillonite appears to enhance dealkylation of **8** to **3b** (see entry 8).

(3) The dominance of **3b** over **3a** in all the reactions is explicable in terms of the known greater reactivity of Cl as compared to Br in Friedel–Crafts reactions.[1]

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†Part 23: Reference 2.

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Table 1 Products from alkylation of benzene with compound **1**

	Reactants		Conditions			Product composition (%)[a]							
												Other products	
Entry no.	**1** (mol)	PhH (mol)	Catalyst (mol)	Time (t/h)	Temp. (T/°C)	**3a**	**3b**	**4a,b**	**7a**	**7b**	**7c**	Identified	Unidentified[b]
1	0.11	1.1	$AlCl_3$ (0.011)	1	25	12	51	3	2	5	2	**6** (13)	12
2	0.11	0.5	$AlCl_3$ (0.011)	24	25	2	69	2	1	2	3	**6** (2)	19
3	0.11	1.1	$AlCl_3$ (0.02)	24	25	1	86	2	1	1	3	—	6
4[c]	0.23	2.3	Al (2%)/HCl (g)	14	25	8	31	4	2	5	7	—	43
5	0.11	1.1	$AlCl_3$/(0.02)/CH_3NO_2 (0.06)	24	25	2	3	—	—	—	—	**8** (79)	16
6	0.02	0.2	K10 Clay (2.0 g)	12	Reflux	5	13	—	—	—	—	**8** (63)	19
7	0.02	0.2	K10 Clay (2.0 g)	24	Reflux	2	16	3	1	2	—	**8** (44)	32
8	0.02	0.2	K10 Clay (2.0 g)	43	Reflux	2	38	3	1	2	—	**8** (4)	50

[a] Product identifications and percentage compositions of various products are based on combined IR, ^{1}H NMR, GC and GCMS analyses. [b] Most FriedelCrafts reactions are complex and the presence of unidentifiable components is always expected; the number of unidentifiable components ranged from 3 in some cases (*e.g.*, entry no. 3) to 14 in other cases (*e.g.*, entry no. 4). [c] Parallels old work by Dolgov and Larin[3] in which 1,2,3-trichloro-2-methylpropane was the alkylating agent.

(4) The formation of **6** *via* intermediates **5** finds analogy in an earlier paper co-authored by one of us.[4]

Experimental

IR spectra were recorded on a Nicolet Magna 520 FT-IR spectrometer, ^{1}H NMR spectra were recorded on a Bruker DPX-400 FT-NMR spectrometer, GC–MS data were obtained with a Shimdazu QP-5000 mass spectrometer and microanalyses were performed on a 2400 Perkin Elmer Series 2 CHNS analyser.

Preparation of 1,2-*Dibromo*-3-*chloro*-2-*methylpropane* **1**.—Addition of bromine (0.2 mol) to stirred methallyl chloride (0.1 mol) over 1 h followed by stirring at room temperature for 48 h gave the desired product **1**: δ_H ($CDCl_3$) 1.98 (s, 3 H, CH_3), 4.02 (s, 4 H, $2\times CH_2$).

Alkylation Procedures.—These were similar to those published in earlier papers.[2]

Spectral Data for New Alkylation Products.—The ^{1}H NMR and MS data for **3a**, **3b**, **6** and **8** are as follows:

Compound **3a**: δ_H ($CDCl_3$) 1.03 (d, 3 H, *J* 7 Hz, CH_3), 2.53–2.89 (m, 1 H, C*H*CH_3), 3.16–3.67 (m, 2 H, C*H*Ph_2 and *H*CHX), 3.79 (d, 1 H, *J* 9 Hz, CHX) and 7.03–7.41 (m, 10 H, Ar-H); *m/z* (%), 244/246 (M^+, 12/3), 208 (M^+ −HCl, 08), 193 (04), 178 (10), 167 (100), 152 (53), 115 (15), 103 (05), 91 (23), 77 (09), 65 (12), 51 (19).

Compound **3b**: δ_H ($CDCl_3$) identical with that of **3a**; *m/z* (%), 288/290 (M^+, 06/06), 208 (M^+ −HBr, 04), 193 (02), 178 (04), 167 (100), 152 (23), 115 (08), 102 (02), 91 (12), 77 (07), 65 (05).

Compound **6**: δ_H ($CDCl_3$) 1.26 (d, 3 H, *J* 7 Hz, CH_3), 2.48 (m, 1 H, C*H*CH_3), 2.74 (m, 1 H, C*H*C_6H_4), 3.21 (dd, 1 H, C*H*C_6H_4), 3.84 (d, 1 H, *J* 7 Hz, C_6H_4C*H*Ph) and 7.12–7.43 (m, 9 H, Ar-H); *m/z* (%), 208 (M^+, 90), 193 (M^+ $-CH_3$, 22), 180 (11), 179 (100), 165 (09), 149 (20), 130 (13), 115 (20), 105 (26), 91 (28), 77 (09), 57 (11) (Found: M^+, 208.12520. $C_{16}H_{16}$ requires M_r, 208.304).

Compound **8**: δ_H ($CDCl_3$) 1.32 (s, 6 H, $2CH_3$), 3.63 (s, 8 H, $4CH_2$), and 7.09–7.22 (m, 4 H, Ar-H); *m/z* (%), 414/422 (M^+, 0/0), 370 [M^+ −(Cl—CH_2), 5], 335/341 [M^+ −($ClCH_2+2CH_3$), 8], 300–304 [M^+ −(Cl+Br), 12], 286–290 [M^+ −(Br+$ClCH_2$), 13], 256–260 (18), 221–223 (28), 179–181 (19), 143 (63), 125 (53), 105 (84), 91 (100), 77 (81), 65 (89), 53 (73).

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