

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‡

Hassan A. Albar,* Ali A. Khalaf and Saleh O. Bahaffi

Department of Chemistry, Faculty of Science, King Abdulaziz University, P.O. Box 9028, Jeddah 21413, Saudi Arabia

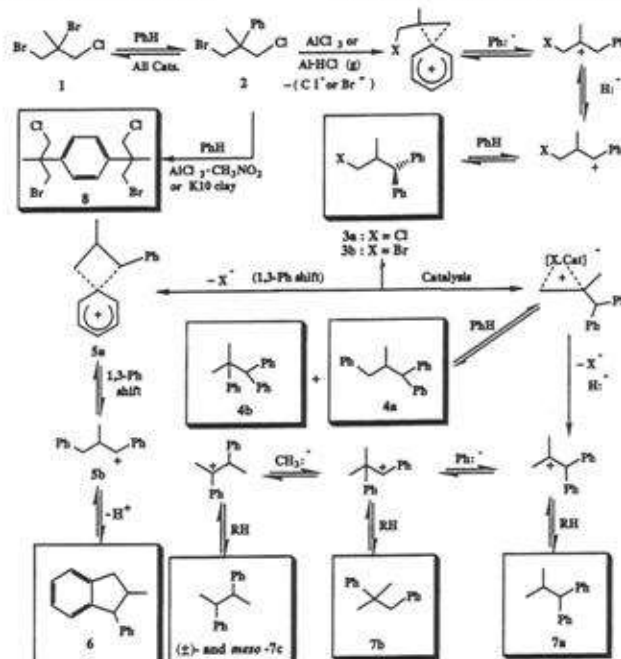
The major alkylation products of benzene with 1,2-dibromo-3-chloro-2-methylpropane are 1-X-2-methyl-3,3-diphenylpropane (X = Cl, Br) with AlCl_3 and 1,4-bis-(1-bromo-3-chloro-2-methylpropyl)benzene with $\text{AlCl}_3\text{-CH}_3\text{NO}_2$ or K10 montmorillonite (K10 Clay); minor products include di- 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.

butane **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



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**, (\pm)- and *meso*-2,3-diphenyl-

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 $\text{AlCl}_3\text{-CH}_3\text{NO}_2$ 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

*To receive any correspondence.

†Part 23: Reference 2.

‡This is a Short Paper as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1997, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

Table 1 Products from alkylation of benzene with compound 1

Entry no.	Reactants		Conditions		Product composition (%) ^a								
	1 (mol)	PhH (mol)	Catalyst (mol)	Time (h)	Temp. (T/°C)	3a	3b	4a,b	7a	7b	7c	Other products	
												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 ₃ NO 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

^aProduct identifications and percentage compositions of various products are based on combined IR, ¹H NMR, GC and GCMS analyses. ^bMost Friedel-Crafts 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). ^cParallels old work by Dolgov and Larin² 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. ¹H NMR spectra were recorded on a Bruker DPX-400 FT-NMR spectrometer. GC-MS data were obtained with a Shimadzu 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} (CDCl₃) 1.98 (s, 3 H, CH₃), 4.02 (s, 4 H, 2 × CH₂).

Alkylation Procedures.—These were similar to those published in earlier papers.¹

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

Compound 3a: δ_{H} (CDCl₃) 1.03 (d, 3 H, J 7 Hz, CH₃), 2.53–2.89 (m, 1 H, CHCH₃), 3.16–3.67 (m, 2 H, CHPh₂ and HCHX), 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} (CDCl₃) 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} (CDCl₃) 1.26 (d, 3 H, J 7 Hz, CH₃), 2.48 (m, 1 H, CHCH₃), 2.74 (m, 1 H, CHC₂H₅), 3.21 (dd, 1 H, CHC₂H₅),

3.84 (d, 1 H, J 7 Hz, C₂H₅CHPh) and 7.12–7.43 (m, 9 H, Ar-H); m/z (%): 208 (M⁺, 90), 193 (M⁺ – CH₃, 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; C₁₀H₁₄ requires M⁺, 208.304).

Compound 8: δ_{H} (CDCl₃) 1.32 (s, 6 H, 2CH₃), 3.63 (s, 8 H, 4CH₂), and 7.09–7.22 (m, 4 H, Ar-H); m/z (%): 434/422 (M⁺, 0/0), 370 [M⁺ – (Cl – CH₂), 5], 335/341 [M⁺ – (CICH₂ + 2CH₂), 8], 300–304 [M⁺ – (Cl + Br), 12], 286–290 [M⁺ – (Br + CICH₂), 13], 256–260 (18), 221–223 (28), 179–181 (19), 143 (63), 125 (53), 105 (84), 91 (100), 77 (81), 65 (89), 53 (73).

Received, 3rd June 1996; Accepted, 7th October 1996
Paper E16/03860C

References

- For reviews see: (a) R. M. Roberts and A. A. Khalaf, *Friedel-Crafts Alkylation Chemistry*, Marcel Dekker, New York, 1984; (b) *Friedel-Crafts and Related Reactions*, ed. G. A. Olah, Wiley, New York, 1963–1965.
- (a) A. A. Khalaf and H. A. Albar, *J. Indian Chem. Soc.*, 1995, 72, 87; (b) H. A. Albar, S. A. Basail and A. A. Khalaf, *Indian J. Chem. B*, 1996, 35, 161.
- B. N. Dolgov and N. A. Larin, *J. Gen. Chem. USSR*, 1950, 20, 450 (*Chem. Abstr.*, 1951, 45, 566f).
- A. A. Khalaf and R. M. Roberts, *J. Org. Chem.*, 1969, 34, 3571.