

MODERN FRIEDEL-CRAFTS CHEMISTRY. PART 25. FRIEDEL-CRAFTS ALKYLATION OF BENZENE WITH 3-CHLORO-2- (CHLOROMETHYL)-1-PROPENE¹

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The major alkylation products of benzene with 3-chloro-(2-chloromethyl)-1-propene (**1**) and H₂SO₄ catalyst were 1,1-di(chloromethyl)ethylbenzene (**2**), three simple isomeric dimers of **1** (structures **5a,b,c**) and five mixed isomeric dimers resulting from a combination of **4** with **6** (molecular formula **7**). With AlCl₃ or K10-montmorillonite clay catalyst, however, the major alkylation products were *cis*- and/or *trans*-2-methyl-1-phenylindan (**11**) and 1-chloro-2-methyl-3,3-diphenylpropane (**14**) proving that the latter two catalysts have dual Lewis-Brønsted catalytic activities.

INTRODUCTION

In continuation of our interest in Friedel-Crafts alkylations with multifunctional reagents,^{1,2} we report here the alkylation of benzene with 3-chloro-2-(chloromethyl)-1-propene (**1**).

RESULTS

Depending on catalyst type and reaction conditions several products were produced in varying ratios (see Table 1). Of these products, the following were identified mainly through GC-MS data: 1,3-dichloro-2-methyl-2-phenylpropane (**2**), 1,3-dichloro-2-benzylpropane (**3**), 3-chloro-2-benzyl-1-propene (**4**), three isomeric 1,5-dichloro-2,4-di(chloromethyl)-2-methyl-*x*-pentenes (**5a,b,c**) resulting from dimerisation of **1**, five isomeric monochloro compounds all showing molecular ion peaks at 374/376, base peaks at **297** and compatible with molecular formula C₂₆H₂₇Cl (**7**) that can result from a combination of **4** with **6**, 2-methyl-1,1,3-triphenylpropane (**10**) *cis*- and/or *trans*-2-methyl-1-phenylindan (**11**), 1-chloro-2-methyl-3,3-diphenylpropane (**14**), 2-methyl-1,1,2-triphenylpropane (**17**), 1,1-diphenyl-2-methylpropane (**18**) and 1,2-diphenyl-2-methylpropane (**19**).

DISCUSSION

The carbocation transformations believed to be responsible for the formation of these products are formulated in Scheme 1.

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Commenting on Table 1 and Scheme 1 the following points are worthy to be emphasised: (i) The reaction proceeds essentially at the double bond with Brønsted H_2SO_4 catalyst but at both the allylic carbon and the double bond with AlCl_3 or K10 clay catalyst, meaning that the latter two have dual Lewis-Brønsted catalytic activities.^{4,5} (ii) The proposed intermediacy of alkene **6** is based on expected behaviour rather than on actual detection. (iii) The carbocationic rearrangement of **12a** to **13** is enhanced by further removal of the positive charge away from the electronegative chlorine center resulting in a more stable carbenium ion **13**. (iv) The ionisation of the primary chlorine in **2** is assisted by phenyl participation and concurrent 1,2-phenyl shift^{2,5} (see **12b**) while that in **14** is assisted by concurrent 1,2-hydride shift *via* **15** to yield **16**; the involvement of primary carbocations in either case can thus be avoided (v). The proposed involvement of **16** as one of the carbocationic intermediates in Scheme 1 is experimentally augmented by the detection of hydrocarbons **18** and **19**.^{2,7} (vi) Indan **11** probably forms through the route **4** \rightarrow **6** \rightarrow **8** \rightarrow **9** \rightarrow **11**. Experimental support for this is currently gained through progressing research on the behaviour of $(\text{PhCH}_2)_2\text{C}(\text{CH}_3)(\text{OH})$ under Friedel-Crafts conditions. (v) The rearrangement of **11** to 2-methyl-2-phenylindan (**11a**) and 1-methyl-3-phenylindan (**11b**) under the employed conditions is proposed to result from phenyl and methyl migrations, respectively; both are common phenomena in Friedel-Crafts reactions.^{2,5,7,8}

Table 1
Conditions and results of alkylation of Benzene with 3-chloro-2-(chloromethyl)-1-propene (**1**)

Sl No.	Reactants and Conditions					Product Composition (%) ^{a,b}
	Compd 1 (mole)	PhH (mole)	Catalyst (mole or g.)	Time (hrs)	Temp. °C	
1 ^c	0.16	2.2	H_2SO_4 (0.19)	03	25	2 (26.4), 5a (11.1), 5b (3.0), 5c (24.6), <i>trans</i> - 11 (2.3), <i>cis</i> - 11 (0.5), 11a ^d and 11b ^e (<i>traces</i>), 14 (6.3), unident (25.8).
2	0.11	1.1	AlCl_3 (0.01)	01	25	7 (at least five isomers, 23.0), 10 (6.7), <i>trans</i> - 11 (25.5), <i>cis</i> - 11 (1.0), 11a (0.5), 11b (1.0), 14 (20.0), 17 (12.6), unident (9.7)
3	0.02	0.2	K 10 clay (2.0 g.)	15	Reflux	2 (trace), 3 (trace), 5a (2), 5b (1), 5c (2), 7 (at least three isomers, 10.0), <i>trans</i> - 11 (14.0), 11a (0.5), 11b (2.0), <i>cis</i> - 11 (2.0), 14 (54.3), 18 (2.0), 19 (3.0), unident . (9.7).
4	0.02	0.2	K 10 clay (2.0 g.)	24	Reflux	2 (0.7), 3 (2.7), 5a (10.6), 5b (4.0) 5c (trace), <i>trans</i> - 11 (37.6), <i>cis</i> - 11 (1.5), 14 (25.1), 18 (1.3), 19 (0.8), unident . (15.7).
5	0.02	0.2	K 10 clay (2.0 g.)	40	Reflux	5 (7.4), 19 (1.1), <i>trans</i> - 11 (37.7), 11a (trace), 11b (30.0), 14 (37.4), 17 (1.6), unident . (11.8)..

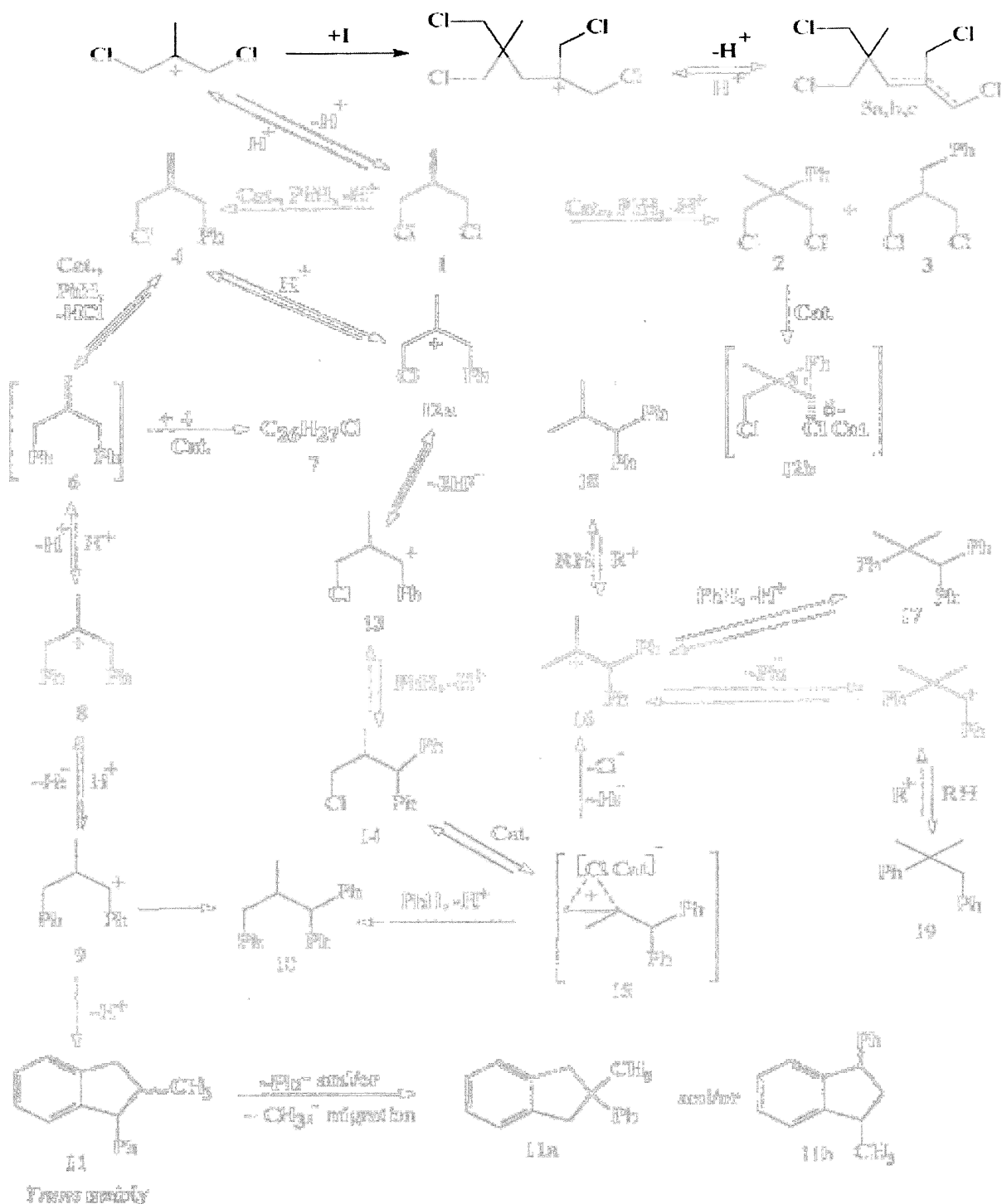
^a Percentage composition of various products as determined by GC-MS.

^b Most Friedel-Crafts alkylations, especially those with multifunctional reagents, are complex and the presence of unidentifiable components is expected.

^c Duplicates and corrects earlier work by Gramenitskaya, Nikishin and Petrov³ who reported the product to consist only of **2**

^d The proposal of this structure was based on contrasting its GC-MS data with those of the traced and reported data for other methylphenylindan isomers.

^e Identified by comparison of its MS spectrum with that reported for 1-methyl-3-phenylindan in the data base supplied with the GC-MS instrument.



Scheme 1

EXPERIMENTAL

Materials and Instrumentation: The starting chemicals were all commercially available and were purchased from Aldrich Chemical Co. 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 and GC-MS data were obtained with a Shimadzu QP-5000 mass spectrometer.

Alkylation Procedures: These were similar to those published in earlier papers.^{1,4}

Mass Spectral Data for Reaction Products: The mass spectral data for most products were recorded and analysed putting emphasis on major and significant fragments. These MS data are given in the following:

Compound 2 m/z (rel. int. %); 202/204/206 (M^+ , 12, 07, 1.2); 153/155 (M^+ -CH₂Cl, 100/34); 117 (M^+ -CH₂Cl, -Cl, 65); 115 (33); 91 (PhCH₂, 50); 77 (Ph, 21); 65 (10.3); 51(33).

Compound 3: m/z (rel. int. %); 202/204/206 (M^+ , 13, 09, 1.4); 153/155 (M^+ -CH₂Cl, 05/1.5); 126/128/130 (M^+ -Ph, 40/14/04); 117 (11) 115 (12); 92 (18); 91 (PhCH₂, 100); 92 (18); 77 (Ph, 0.6); 65 (27); 51 (16).

Compound 4: m/z (rel. int. %); 166/168 (M^+ , 28/08); 131 (M^+ -Cl, 100); 129 (35); 117 (18); 116 (31); 115 (42); 103 (04); 91 (PhCH₂, 87); 77 (Ph, 53); 65 (39); 56 (21).

Compounds 5a,b,c: Three isomeric dimers of 1, designated, 5a, 5b and 5c were detected in the reaction mixtures from H₂SO₄ and K10 clay experiments. The MS data for these dimers were as follows:

Dimer 5a: m/z (rel. int. %); 248/250/252/254 (M^+ , 1.6/2.2/1.0/trace); 124/126/128 [M^+ , -(CH₂Cl)₂CH(CH₃), 19.0/11.2/2.0/Trace]; 89/91/93 (100/ 19.0/1.0); 77(4.0), 65 (3.5); 58(4.0); 53 (43.0).

Dimer 5b: The fragmentation pattern was identical to that of 5a indicating a *cis-trans* relationship.

Dimer 5c: m/z (rel. int. %); 248/250/252/254 (M^+ , very weak); 158/160/162/164 (20.0/18.0/6.0/0.5); 123/125/127/124 (22.0/15.5/7.5/2.0); 122/124/126/128 (7.5/14.0/7.0/1.0); 90 (base peak, 100); 75 (medium); 53(strong).

Compounds 7: Five isomers of molecular formula 7 were detected. Their mass spectra were all similar showing a weak parent M^+ peak at 374/376 and a base peak at 297. The following MS data are representative of all isomers: m/z (rel. int. %); 374/376 (M^+ , 2.4, 1.0); 338 (M^+ -Cl, 8.2); 297 (M^+ -CH₃CHCH₂Cl, 100); 220 (9.0); 179 (28); 165 (3.2); 133 (7.5); 105 (4.0); 91 (PhCH₂, 16); 65 (1.8); 41 (8.0).

Compound 10: m/z (rel. int. %); 286 (M^+ , 7); 195 (M^+ -PhCH₂, 6); 178 (2); 168 (23); 167 (Ph₂CH, 100); 165 (24); 152 (16), 128 (2); 118 (11), 91 (PhCH₂, 42); 77 (Ph, 4); 65 (8); 51 (5).

Compound 11 (*cis* and *trans*): m/z (rel. int. %); 208 (M^+ , 89.7); 207 (9.3); 193 (M^+ -CH₃, 21.9); 180 (11.0); 179 (M^+ -C₂H₅, 100); 178 (31.5); 165 (9.0); 149 (19.7); 130 (13.4); 129 (12.6); 128 (3.6); 115 (19.6); 105 (26.0); 91 (PhCH₂, 28.0); 89 (3.9) (3.9); 77 (Ph, 9.1); 73 (4.8); 69 (8.7); 57 (10.6); 55 (7.8).

Compound 11a : m/z (rel. int. %); 208 (M^+ , 52); 192 (23), 193 (M^+ -CH₃, 59); 179 (M^+ -C₂H₅, 100); 178 (52); 165 (10); 130 (18); 115 (39); 103 (20); 91 (PhCH₂, 22); 89 (19); 77 (Ph,11); 65 (07); 51 (13).

Compound 11b m/z (rel. int. %); 208 (M^+ , 100); 193 (M^+ -CH₃, 66); 179 (M^+ -C₂H₅, 50); 178 (40); 165 (11); 152 (5); 130 (38); 115 (58); 103 (22); 95 (16); 91 (25); 89 (17); 82 (14); 77 (17); 65(11); 51 (15).

Compound 14: The mass spectral data of this compound was identical with that published before¹.

Compound 17: m/z (rel. int. %); 286 (M^+ , 0.0) 181 (1); 167 (Ph₂CH, 100); 152 (6.5); 115 (2); 91 (PhCH₂, 4); 77 (Ph, 1.5); 63 (2); 51 (2).

Compound 18: m/z (rel. int. %); 210 (M^+ , 10.1); 168 (13.4); 167 (Ph₂CH, 100); 166 (8.4); 165 (3.4); 153 (2.5); 152 (21.0), 139 (2.5); 128 (3.4); 115(10.1); 89 (2.5); 63(1.7); 43(2.5); 27 (3.4).

Compound 19: m/z (rel. int. %); 210 (M^+ , trace); 178(2.5); 120 (11.8); 119 [PhC(CH₃)₂, 100]; 118(14.3); 116 (5.9); 115(7.6); 103 (8.4); 92 (5.9); 91 (PhCH₂, 78.2); 89 (4.2); 79 (10.9); 78 (5.0); 77(Ph, 13.4); 65 (12.6); 63 (4.2); 51 (11.8); 41 (46); 39 (17.6); 27 (2.5).

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