

## Modern Friedel-Crafts Chemistry. XVIII. Alkylation of Benzene with 1,2-Dibromo-2-methylpropane, 1-Chloro-2-methyl-2-phenylpropane, 3-Chloro-2-methyl-1-propene and 1-Bromo-2-methyl-1-propene

ALI ALI KHALAF\* and HASSAN A. ALBAR

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

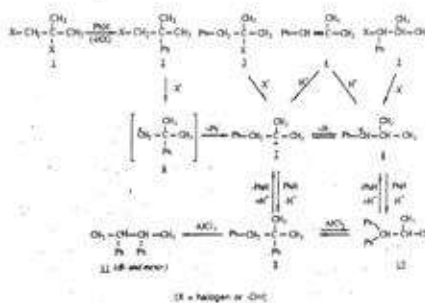
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Alkylation of benzene with the title compounds gave similar product mixtures containing isomeric 1,2-diphenyl-2-methylpropane (9), 1,1-diphenyl-2-methylpropane (10) and *dl*- and *meso*-2,3-diphenylbutane (11) in alkylations catalysed by appreciable amounts of  $\text{AlCl}_3$  or  $\text{Al-HCl}_{(g)}$  and of 9 and 10 only in alkylations catalysed by the milder catalysts  $\text{AlCl}_3\text{-CH}_3\text{NO}_2$ ,  $\text{ZrCl}_4$  and  $\text{TiCl}_4$ . In almost all cases, 9 and 10 were always produced in an apparent equilibrium ratio of approximately 2 : 1. These new results disproved numerous earlier reports claiming the products from these reactions to contain only 9 and *meso*-11 depending on catalyst and conditions. Mechanistic interpretations are given to account for the results.

In previous publications, Khalaf and Roberts<sup>1-5</sup> found that alkylation of benzene with systems 1-5 (Scheme 1) gave similar product mixtures consisting of 1,2-diphenyl-2-methylpropane (9), 1,1-diphenyl-2-methylpropane (10) and *dl*- and *meso*-2,3-diphenylbutane (11) in alkylations catalysed by large amounts of  $\text{AlCl}_3$  and of the first two isomers (9 and 10) only in alkylations catalysed by just trace amounts of  $\text{AlCl}_3$  or by weaker catalysts such as  $\text{AlCl}_3\text{-CH}_3\text{NO}_2$  or  $\text{FeCl}_3$ . Furthermore, in all cases, isomers 9 and 10 were invariably produced in an equilibrium ratio approximating 2 : 1. Khalaf and Roberts<sup>2-4</sup> rationalised their findings in terms of the carbocation transformations summed up in Scheme 1 wherein 6 presents a transient highly energetic species and 7 and 8 constitute a rapidly equilibrating cationic pair of which 7 is more stable.

In view of the sound assumption that other benzene alkylations anticipated to involve carbocations 6, 7 and/or 8 as reaction intermediates should show similar behaviour<sup>3-5</sup>, numerous old

literature reports appear to be quite anomalous. Examples of these are to be found in the reports that benzene alkylations with 1,2-dichloro- or 1,2-dibromo-2-methylpropane<sup>7</sup>, 1-chloro-2-methyl-2-phenylpropane<sup>8</sup>, 3-chloro-2-methyl-1-propene<sup>7,8</sup> and 1-bromo-2-methyl-1-propene<sup>9</sup> in the presence of  $\text{AlCl}_3$ ,  $\text{Al-HCl}_{(g)}$  and/or  $\text{ZrCl}_4$  catalysts gave product mixtures in which diphenylated butane isomers 9 and *meso*-11 could only be recognised. The presence of either one or both of isomers 10 and *dl*-11 passed totally unnoticed.



Scheme 1

TABLE I-PRODUCTS FROM ALKYLATION OF BENZENE WITH COMPOUNDS 12-15

Sl. no.	Method	Reactants (mol)			Catalyst		Time, h	Temp, °C	Product composition (%) <sup>a</sup>				Other products	
		Alkyl agent	CaH <sub>2</sub>	MCH <sup>b</sup>	Kind	/mol			9	10	<i>di</i> -11	<i>meso</i> -11	Ident. no. (%)	Unident. %
(I) Alkylations with isobutylene dibromide (12)														
1 <sup>c</sup>	D	1	06	-	Al-HCl <sub>2</sub>	2.00%	24	25	26	10	06	17	16 (32) <sup>d</sup>	-
2 <sup>e</sup>	A	1	05	-	AlCl <sub>3</sub>	0.11	01	2-4	27	11	-	-	12 (54)	08
3 <sup>e</sup>	A	1	05	-	AlCl <sub>3</sub>	0.11	05	5-10	45	17	-	-	12 (33)	05
4 <sup>e</sup>	B	1	05	03	AlCl <sub>3</sub>	0.11	05	5-10	08	03	-	-	12 (74)	15
5 <sup>e</sup>	B	1	05	03	AlCl <sub>3</sub>	0.11	05	25	-	-	-	-	12 (87)	13
(II) Alkylations with neophyl chloride (13)														
6 <sup>e</sup>	A	1	10	-	TiCl <sub>4</sub>	0.20	48	25	43	11	-	-	2, X = Br (20)	26
7 <sup>e</sup>	A	1	10	-	ZrCl <sub>4</sub>	0.43	24	25	-	-	-	-	12 (89)	11
8 <sup>e</sup>	A	1	10	-	ZrCl <sub>4</sub>	0.43	01	55	62	29	-	-	12 (2)	07
9 <sup>e</sup>	B	1	10	10	ZrCl <sub>4</sub>	0.43	01	55	06	03	-	-	2, X = Br (37)	15
10 <sup>e</sup>	B	1	05	03	AlCl <sub>3</sub>	0.22	01	2-4	34	13	-	-	13 (20), 16 (23)	03
11 <sup>e</sup>	B	1	05	03	AlCl <sub>3</sub>	0.22	01	25	38	27	-	-	3, X = Cl (05)	-
12 <sup>e</sup>	A	1	05	-	CH <sub>3</sub> NO <sub>2</sub>	6.00	02	25	39	24	-	-	17 (01), 18 (01) <sup>f</sup>	-
13 <sup>e</sup>	B	1	05	-	ZrCl <sub>4</sub>	0.22	02	25	43	17	-	-	13 (09), 16 (07)	19
14 <sup>e</sup>	B	1	05	10	CH <sub>3</sub> NO <sub>2</sub>	6.00	01	25	36	13	-	-	17, 18 (traces)	-
15 <sup>e</sup>	B	1	05	10	ZrCl <sub>4</sub>	0.11	01	Reflux	23	11	-	-	13 (16), 16 (06)	15
16 <sup>e</sup>	C	1	-	10	ZrCl <sub>4</sub>	0.11	02	25	-	-	-	-	13 (20), 16 (12)	08
17 <sup>e</sup>	C	1	-	10	ZrCl <sub>4</sub>	0.11	06	Reflux	-	-	-	-	13 (25), 16 (07)	19
18 <sup>e</sup>	C	1	-	03	AlCl <sub>3</sub>	0.22	01	25	-	-	-	-	13 (01), 16 (11)	22
(III) Alkylations with methallyl chloride (14)														
19 <sup>e</sup>	A	1	10	-	AlCl <sub>3</sub>	0.22	05	25	58	26	04	08	16 (03) <sup>g</sup>	01
20 <sup>e</sup>	D	1	06	-	Al-HCl <sub>2</sub> (g)	2.00%	24	25	38	17	01	03	16 (18) <sup>h</sup>	23
21 <sup>e</sup>	A	1	10	-	AlCl <sub>3</sub>	0.11	05	25	60	28	-	-	16 (09)	03
22 <sup>e</sup>	B	1	10	03	AlCl <sub>3</sub>	0.11	02	2-4	45	14	-	-	13 (14), 16 (11)	14
23 <sup>e</sup>	B	1	10	-	AlCl <sub>3</sub>	0.11	05	25	47	27	-	-	17 (01), 18 (01) <sup>i</sup>	-
24 <sup>e</sup>	B	1	10	03	ZrCl <sub>4</sub>	0.22	01	Reflux	35	08	-	-	16 (12)	14
(IV) Alkylations with 1-bromo-2-methyl-propene (15)														
25 <sup>e</sup>	A	1	10	-	AlCl <sub>3</sub>	0.22	05	25	31	20	14	29	-	-
26 <sup>e</sup>	A	1	10	-	AlCl <sub>3</sub>	0.11	05	25	66	30	-	-	16 (14)	04
27 <sup>e</sup>	B	1	10	-	AlCl <sub>3</sub>	0.22	05	25	47	27	-	-	-	12

<sup>a</sup>Percentage composition of various products as determined by glc. <sup>b</sup>Methylcyclohexane (MCH). <sup>c</sup>Relative amounts of diphenylated butanes. <sup>d</sup>Most Friedel-Crafts reactions are complex and the presence of unidentifiable components is always expected; the number of unidentifiable components ranged from 1 in some cases (e.g. sl. no. 2) to 35 in some other cases (e.g. sl. no. 24). <sup>e</sup>Duplicate and correct old work by Doglov and Larin (Ref. 7) to check validity. <sup>f</sup>In contrast with Doglov and Larin (Ref. 7) only trace amounts of tert-BuPh could be detected. <sup>g</sup>Simulates and corrects old work by Schermerling *et al.* (Ref. 6) in which they used the dichloride as alkylating agent; apart from relative reactivity, both dihalides should give similar products. <sup>h</sup>Higher temperature was essential to enhance alkylation with the dibromide (cf. sl. no. 7). <sup>i</sup>Mainly the *para*-tertiary cycloalkyl derivative. <sup>j</sup>Duplicates an unpublished observation by Roberts and Khalaf (Ref. 13). <sup>k</sup>Includes minor amounts of *sec*- and *tert*-BuPh. <sup>l</sup>Duplicates and corrects old work by Schermerling *et al.* (Ref. 8). <sup>m</sup>Duplicates and corrects old work by Tsukervanik and Yuldasher (Ref. 9).

This work is aimed essentially at a modern reinvestigation of these early studies to find out any anomaly in the results. In doing so, we added more experimental support to our current views on this subject.

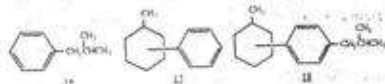
**Results and Discussion**

The conditions and results of benzene alkylations with 1,2-dibromo-2-methylpropane (isobutylene dibromide, **12**), 1-chloro-2-methyl-2-phenylpropane (neophyl chloride, **13**), 3-chloro-2-methyl-1-propene (methallyl chloride, **14**) and 1-bromo-2-methyl-1-propene (**15**) are all compiled in Table 1. These results were obtained through combined glc, nmr and ir spectral analysis of the product mixtures. Meanwhile, the experiments were designed to serve one or more of the following purposes : (i) to furnish reference samples necessary for characterisation, (ii) to check questionable earlier results, and (iii) to shed more light on some aspects of the reactions.

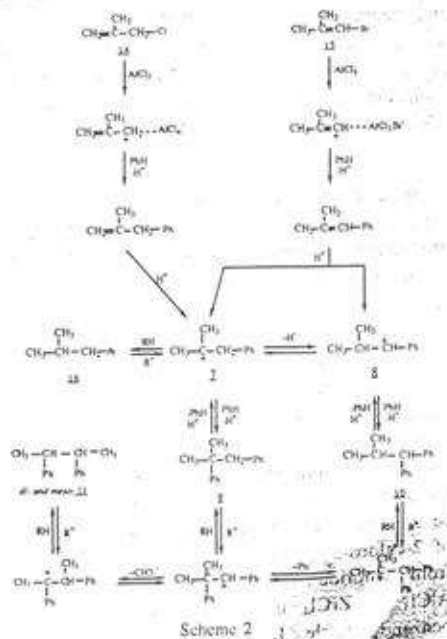
*General remarks :* Careful examination of the results (Table 1) reveals considerable similarities between the alkylation behaviours of compounds **12-15**. On the basis of these similarities the following generalisations can be drawn, (i) all alkylations showed obvious dependence on reaction variables such as time, temperature, catalyst type, reactants ratio and nature of solvent. (ii) Alkylations catalysed by the strong  $AlCl_3$  catalyst (added directly or generated *in situ*<sup>10</sup> from Al and  $HCl_{(g)}$ ) gave diphenylbutane fractions consisting essentially of isomers **9** and **10** mixed with diastereomers **11** in varying proportions depending on catalyst ratio, temperature and time (Table 1, sl. nos. 1, 19-22, 25 and 26). As evident, the relative amounts of both forms of **11** were increased by increasing time, temperature and catalyst ratio. (iii) Alkylations catalysed by weak catalysts such as  $CH_3NO_2$ - and methylcyclohexane-moderated  $AlCl_3$ ,  $ZrCl_4$  and  $TiCl_4$  gave diphenylbutane fractions consisting of isomers **9** and **10** only with none of the diastereomers **11** (Table 1, sl. nos. 2-9, 10-18, 23, 24, 27). (iv) Regardless of alkylating agent, catalyst type

and reaction conditions, most alkylations produced isomers **9** and **10** in a ratio approximating 2 : 1 respectively. While most alkylations gave isobutylbenzene (**16**) as a hydride-transfer product, alkylations conducted in the presence of methylcyclohexane (MCH) gave also varying amounts of (methylcyclohexyl)benzene (**17**, mainly the tertiary alkylate) and (methylcyclohexyl)isobutylbenzene (**18**, mainly the *para*-tertiary alkylate) (Table 1, sl. nos. 10, 11, 15-18, 22, 24). A sound explanation for the formation of these hydride-transfer products was offered by earlier workers<sup>6</sup>.

It is to be emphasised that the above remarks are all in conformity with our previous findings<sup>1-5</sup> for which the results of Table 1 offer further experimental support.



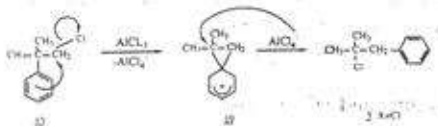
*Mechanistic interpretations :* A modern mechanistic view of the alkylation of benzene



with isobutylene dihalides (e.g. **12**) and neophyl halides (e.g. **13**) was presented in the previous publications<sup>1,2</sup>. Accordingly, we shall limit our present discussion to alkylations with the allylic methallyl chloride (**14**) and the vinylic 1-bromo-2-methyl-1-propene (**15**). The steps believed to be involved in these alkylations are presented in Scheme 2 with  $\text{AlCl}_3$  as a representative catalyst. As evident from Scheme 2, the first step in both the alkylations is suggested to involve reaction at the halide site. Although this suggestion is augmented by others<sup>5,11</sup>, it does not justify the elimination of the alternate possibility of attack at the unsaturation site for which practical evidence is found in the detection of neophyl chloride (**13**) under certain conditions (Table 1, sl. no. 22). The formation of isomers **9** and **10** in all reactions regardless of catalyst type and/or reaction conditions is expected<sup>1-5</sup> and is explicable in terms of the equilibration established between carbocations **7** and **8** prior to the alkylation step. The formation of diastereomers **11** is a post alkylation process involving isomerisation of **9** and/or **10** and requires a catalyst that is strong enough to abstract hydride ions<sup>1-6,12</sup>. Accordingly, diastereomers **11** are produced in alkylation catalysed by  $\text{AlCl}_3$  or  $\text{Al-HCl}_{(g)}$  but not by  $\text{AlCl}_3\text{-CH}_3\text{NO}_2$ ,  $\text{ZrCl}_4$ ,  $\text{TiCl}_4$  or  $\text{FeCl}_3$ .

Speaking of mechanisms, three relevant observations deserve special comments. Firstly, the production of isobutylbenzene (**16**) from reactions of neophyl chloride with methylcyclohexane and  $\text{AlCl}_3$  or  $\text{ZrCl}_4$  (Table 1, sl. nos. 15, 16, 17, 18) even in the absence of benzene disproves the claim<sup>6</sup> that route  $9 \rightarrow 7 \rightarrow 16$  (i.e. dealkylation of **9**) constitutes the only (or even the main) source for isobutylbenzene production. Instead hydride transfer to equilibrating carbocations **7** and **8** (resulting from routes  $14 \rightarrow 7 \rightleftharpoons 8 \rightarrow 16$  and  $15 \rightarrow 8 \rightleftharpoons 7 \rightarrow 16$ ) is believed to be a more sound source. Secondly, the production of 2-chloro-2-methyl-1-phenylpropane (**3**;  $\text{X} = \text{Cl}$ ) from chloride **13** with methylcyclohexane and  $\text{AlCl}_3$  or  $\text{ZrCl}_4$  in the presence or absence of benzene (Table 1, sl. nos. 10, 16, 18) adds

more experimental support to the view that removal of  $\text{Cl}^-$  ion from **13** is assisted by phenyl par-



ticipation and that phenonium ion **19** is involved as intermediate<sup>1,2,6</sup>. Nucleophilic attack on **19** by  $\text{Cl}^-$  ion (in the form of  $\text{AlCl}_4^-$  or  $\text{ZrCl}_5^-$ ) at the more stable tertiary site gives **3** ( $\text{X} = \text{Cl}$ ). Thirdly, the identification of neophyl bromide (**2**;  $\text{X} = \text{Br}$ ) among the products of alkylation of isobutylene dibromide (**12**) supports the view that the first step involves attack by benzene at the tertiary site as shown in Scheme 1.

Comparison of the results of this work (Table 1) with those reported for alkylations of compounds **12**<sup>6,7</sup>, **13**<sup>6</sup>, **14**<sup>7,8</sup> and **15**<sup>9</sup> reveals sharp contradictions. All earlier workers apparently believed that the diphenylbutane fractions from their reactions consisted just of the direct alkylate **9** mixed, in some cases, with little of the rearranged solid alkylate *meso*-**11**<sup>\*</sup>. Accordingly and without exception, they all overlooked the presence of *dl*-**11** in some others. The present results revealed that benzene alkylations with compounds **12**–**15** yielded diphenylbutane fractions consisting of isomers **9** and **10** with the weak catalysts  $\text{AlCl}_3\text{-CH}_3\text{NO}_2$ ,  $\text{AlCl}_3\text{-MCH}$ ,  $\text{ZrCl}_4$  and  $\text{TiCl}_4$  and of **9**, **10** and *dl*- and *meso*-**11** with the strong  $\text{AlCl}_3$  and  $\text{Al-HCl}_{(g)}$  catalysts. As such the old literature results are proved to be incorrect.

## Experimental

The instruments and techniques employed were similar to those reported earlier<sup>14</sup>.

*Starting materials and reference samples* : Methallyl chloride (**14**), 1-bromo-2-methyl-1-propene (**15**) and isobutylbenzene (**16**) were

\*Detection of this product is undoubtedly due to the fortuitous circumstances of its high m.p. and its low solubility in the medium.

available commercially (Aldrich). Isobutylene dibromide (12), neophyl chloride (13), 1,2-diphenyl-2-methylpropane (9), 1,1-diphenyl-2-methylpropane (10) and *dl*- and *meso*-2,3-diphenylbutane (11) were obtained as described earlier<sup>1,2</sup>. Compounds 17 (mainly the tertiary cycloalkyl isomer) and 18 (mainly the *para*-tertiary cycloalkyl isomer) were obtained through the respective  $\text{AlCl}_3\text{-CH}_3\text{NO}_2$  catalysed alkylations of benzene and isobutylbenzene with 1-methyl-1-cyclohexanol following standard procedures<sup>15</sup>: 17 nmr  $\delta$  ( $\text{CDCl}_3$ ) 1.12 (3H, s,  $\text{CH}_3$ ), 1.31-1.84 (10H, m,  $\text{CH}_2$ ) and 7.08-7.38 (5H, m, ArH); 18 nmr  $\delta$  ( $\text{CDCl}_3$ ) 0.83 (6H, d,  $J$  7 Hz,  $2 \times \text{CH}_3$ ), 1.15 (3H, s,  $\text{CH}_3$ ), 1.32-1.77 (10H, m,  $\text{CH}_2$ ), 1.88 (1H, m, CH), 2.50 (2H, d,  $J$  7 Hz,  $\text{CH}_2$ ) and 7.03-7.35 (4H, m, ArH).

**General alkylation procedures** : Four general methods were used, resulting in the data summarised in Table 1.

**Method A** : A solution of the alkylating agent in about one-third of the total amount of benzene was gradually added over a period of 0.5 h to a stirred mixture of the catalyst and the remainder of benzene. Stirring was continued at the desired temperature for the desired time. The reaction mixture was then hydrolysed by pouring into a stirred ice-cold 10% HCl. The hydrolysed mixture was extracted with ether, washed with dilute  $\text{NaHCO}_3$  solution and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . After distilling the ether under atmospheric pressure, the residue was subjected to glc, nmr and ir analysis.

**Method B** : The procedure was the same

as in method A with the exception that the required amount of  $\text{CH}_3\text{NO}_2$  and/or methylcyclohexane (MCH) was added to the catalyst prior to the addition of the alkylating agent.

**Method C** : Similar to method A with the exception that no reactant benzene was used. The amount of reactant MCH was divided between the catalyst and the alkylating agent.

**Method D** : The procedure applied previously by Doglov and Larin<sup>7</sup> was essentially used.

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