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Alkylations and Competing Rearrangements in the Aluminum Chloride Catalyzed Reactions of Secondary Alkyl Chlorides with Arenes[1]

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Aluminum chloride catalyzed alkylations of benzene and p-xylene by 2- and 3-chloropentane and 2- and 3-chlorohexane have been studied. The alkylations are accompanied by simultaneous isomerization of the chloroalkanes and rearrangement of the product arylalkanes. At 25°, rearrangement of the arylalkanes to an equilibrium composition is the dominant product-determining factor. At −20°, this rearrangement is minimized and product composition is determined by isomerization of the chloroalkanes and competitive alkylation by the isomeric chloroalkanes. The order of mixing the reactants affects the product composition at 0 and −20°. Rough kinetic analysis of alkylations of benzene and p-xylene by 2- and 3-chlorohexane indicates that the rates of isomerization and alkylation of the chloroalkanes are of the same order of magnitude. The rate of alkylation by 2-chlorohexane is estimated to be about 2–3 times the rate of alkylation by 3-chlorohexane. Alkylations with $AlCl_3 \cdot CH_3NO_2$ catalyst at 25° took place without product isomerization; rates of alkylation were reduced more than rates of chloroalkane isomerization. Comparison is made of the present results from chloroalkane alkylations and isomerizations with analogous reactions of alkenes.

There have been numerous reports of alkylations of arenes with secondary alkylating agents. However, because of the analytical methods employed in some of the older work, the analysis of isomeric phenylalkanes has led to some questionable and contradictory results.

Ipatieff, Pines, and Schmerling[2] alkylated benzene with both 1-pentene and 1-pentanol using 80% sulfuric acid as a catalyst. Their report of a 60% 2-phenylpentane and 40% 3-phenylpentane product was the first report of such a reaction mixture from this type of alkylation. Pines, Huntsman, and Ipatieff[3] reported 76% 2-phenylpentane and 24% 3-phenylpentane from the reaction of 3-pentanol and benzene in the presence of $AlCl_3$ at 25–35°. 2-Pentanol was reported to yield 60% 2-phenylpentane and 40% 3-phenylpentane. Streitweiser, Stevenson, and Schaeffer[4] studied the alkylations of benzene with isomeric pentanols using BF_3 catalyst. Both 2- and 3-pentanol gave identical product mixtures containing 65% 2-phenylpentane, 25% 3-phenylpentane, and 10% 2-methyl-2-phenylbutane. These workers suggested a carbonium ion type alkylating species and stated that the 2- and 3-phenylpentane ratio was probably determined by the rearrangement of the carbonium ion prior to alkylation.

Ipatieff, Pines, and Schmerling[2] reported a mixture containing 60% 2-phenylpentane and 40% 3-phenylpentane from the alkylation of benzene with 1-pentene and sulfuric acid. However, Axe[5] and Simons and Archer[6] reported 2-phenylpentane as the only reaction product from 2-pentene and BF_3 or HF. Olson[7] found 37% 2-phenylhexane and 63% 3-phenylhexane from benzene and 1-hexene with sulfuric acid, a complete reversal from the results from 1-pentene reported by Ipatieff et al.[2] Alul has studied the alkylation of benzene by 1-dodecene, trans-6-dodecene,[8,9] and 8-methyl-1-nonene[10] with various catalysts, and has discussed the influence of catalyst type and medium polarity on the distribution of products. A comparison of the alkene

reactions with those of the chloroalkanes in this work will be given later.

Rearrangements of sec-phenylalkanes have also been previously investigated. Burwell and Shields[11] found that $AlCl_3$ caused complete racemization of optically active 2-phenylpentane after only 10 min at room temperature. No 3-phenylpentane was detected in the reaction mixture. They postulated that the racemization occurred via a rapid hydride ion transfer. The interconversion of 2- and 3-phenylpentane occurred more slowly and was ascribed to disproportionation to dipentylbenzene and benzene followed by the reverse of this reaction. However, Roberts and co-workers[12,13] have suggested that the rearrangements of 2- and 3-phenylpentane as well as the isotopic scrambling of 2-phenyl-2-^{14}C-butane occur via an intermediate phenylalkyl cation produced after hydride abstraction.

This paper is concerned with alkylations by 2- and 3-chloropentanes and 2- and 3-chlorohexanes and the relationship of the concomitant isomerizations of the chloroalkanes and the sec-phenylalkanes to the observed final compositions of the product mixtures.

Discussion

Alkylations of Benzene with 2- and 3-Chloropentane. Both 2- and 3-chloropentane isomerized rapidly in the presence of $AlCl_3$ at temperatures from −20 to 25° to a 64:36 equilibrium ratio (Table I). This 64:36 ratio very nearly represents a statistical distribution, since the chloropentanes have two carbon atoms to which chlorine may bond in the 2 position and one such carbon atom in the 3 position. When benzene was added to an isomerized chloropentane mixture at −20°, a very similar 66:34 distribution of 2-:3-phenylpentane resulted (run 6, Table II). The procedure of isomerizing a chloroalkane with $AlCl_3$, followed by addition of the arene, will be referred to as alkylation method B. When the order of addition of reactants was

Table I
Isomerization of 2- and 3-Chloroalkanes with Aluminum Chloride[a]

Starting chloroalkane	Temp, °C	Time, min	Product chloroalkanes[b]	
			% 2-	% 3-
2-Chloropentane	25	2	64	36
	−20	1	64	36
	−20	25	65	35
3-Chloropentane	25	2	64	36
	−20	1	64	36
2-Chlorohexane	−20	1	53	47
	−20	10	52	48
3-Chlorohexane	−20	1	52	48
	−20	10	52	48

[a] Mole ratio, chloroalkane:AlCl₃ 10:1. [b] Relative percentages of chloroalkane isomers: by ir for chloropentanes; by GLC for chlorohexanes.

Table II
Alkylations of Benzene with 2- and 3-Chloropentane[a]

Method[b]	Chloropentane	Temp, °C	Time, min	Run no.	Product phenylalkane[c]	
					% 2-	% 3-
A	2-Chloropentane	25	1	1	73	27
			155		74	26
		−20[d]	1	2	72	28
			5[e]		72	28
			20		73	27
A	3-Chloropentane	25	1	3	73	27
			155		74	26
		−20[d]	1	4	65	35
			5[e]		66	34
			155		68	32
			90[f]	5	72	28
			155[f]		74	26
B	2-Chloropentane	−20[d]	1	6	66	34
			120		65	35

[a] Mole ratio benzene:chloropentane:AlCl₃ 4:1:0.1.
[b] Method A, AlCl₃ added to benzene plus chloropentane; method B, AlCl₃ added to chloropentane followed by addition of benzene. [c] Relative percentages determined by GLC.
[d] Hexane added to reactions at −20° to prevent freezing.
[e] Reaction >90% as measured by disappearance of chloropentane. [f] An additional quantity of AlCl₃ equal to original charge added after 45 min.

changed, different phenylalkane distributions resulted. Addition of AlCl₃ to a solution of chloroalkane and arene will be referred to as alkylation method A. Alkylation of benzene with either 2- or 3-chloropentane at 25° by method A yielded a 74:26 distribution of 2-:3-phenylpentane (runs 1 and 3, Table II). When the reaction temperature was reduced to −20°, 2-chloropentane gave the same distribution of 2-:3-phenylpentane (run 2, Table II); however, 3-chloropentane gave an initial distribution of 65:35, which changed to 68:32 upon standing for 2.5 h (run 4, Table II). When fresh catalyst was added to a 3-chloropentane alkylation reaction mixture after 45 min, the product distribution changed from 65:35 to 74:26 (run 5, Table II).

In order to determine the extent to which isomerization of the phenylalkane affects the final distribution of products from an alkylation reaction, alkylations of benzene with 2- and 3-chloropentane were carried out by method A but in the presence of 2- or 3-phenylhexane.[14] Reactions were carried out at 25, 0, and −20°. The results from the experiments at 0 and 25° are set out in Table III. It may be seen that a constant proportion of 2-:3-phenylpentane of 73:27 was reached in the first minute at 25°, and rearrangement to a constant proportion of 2-:3-phenylhexane of 63:37 was reached in 15 min. At 0° the constant proportion

of 2-:3-phenylpentane was reached in ca. 15 min and the constant proportion of 2-:3-phenylhexane was reached in ca. 25 min when 2-phenylhexane was present at the start, and in ca. 60 min when 3-phenylhexane was present at the start. In the experiments carried out at −20°, a constant proportion of 2-:3-phenylpentane of 71:29 was reached in 5–10 min, and no rearrangement of 2- or 3-phenylhexane occurred in up to 2 h. Thus, with the reasonable assumption that the susceptibility toward rearrangement of 2- and 3-phenylpentane is essentially the same as that of 2- and 3-phenylhexane, one can conclude that the distribution of alkylation products from 2- and 3-chloropentane at −20° is determined in part by isomerization of the chloroalkanes preceding attachment to the benzene ring, but not by rearrangement of the phenylpentanes. The slightly higher proportion of 2-phenylpentane (73 ± 2% vs. 71 ± 2%) produced

Table III
Alkylations of Benzene with 2- and 3-Chloropentane in the Presence of 2- or 3-Phenylhexane[a]

Chloropentane	Phenylhexane	Temp, °C	Time, min	Phenylpentane		Phenylhexane	
				% 2-	% 3-	% 2-	% 3-
2-	2-	0	1	67	33	100	0
			15[b]	74	26	70	30
			25[b]	74	26	64	36
2-	3-	0	1	71	29	0	100
			15	74	26	27	73
			60[b]	74	24	62	38
3-	2-	0	1	70	30	100	0
			15	75	25	76	24
			25[b]	74	26	63	37
3-	3-	0	1	69	31	0	100
			15	75	25	27	73
			60	75	25	61	39
2-	2-	25	1	72	28	95	5
			15[b]	75	25	63	37
2-	3-	25	1	73	27	3	97
			15[b]	75	25	63	37
3-	2-	25	1	73	27	96	4
			15[b]	76	24	63	37
3-	3-	25	1	71	29	3	97
			15[b]	75	25	64	36

[a] Mole ratio benzene:chloropentane:phenylhexane:AlCl₃ 4:1:0.1:0.1. [b] No further change after 120 min. [c] No further change after 90 min.

Table IV
Alkylations of Benzene with 2- and 3-Chlorohexane[a]

Method[b]	Chlorohexane	Temp, °C	Time, min	Run no.	Percent reaction[c]	Recovered chlorohexane[d]		Product phenylhexane[d]	
						% 2-	% 3-	% 2-	% 3-
A	2-Chlorohexane	25	1	1				63	37
			120					60	40
		−20[e]	1	2	33	90	10	65	35
			3		71	51	49	65	35
			5		90–95	50	50	65	35
			20		100			64	36
			120					64	36
			240[f]					63	37
			240[g]					62	38
A	3-Chlorohexane	25	1	3				59	41
			120					61	39
		−20[e]	1	4	17	17	83	55	45
			3		29	22	78	55	45
			5		43	25	75	54	46
			20		94	50	50	55	45
			120		100			57	43
			240[f]	5				62	38
			240[g]					62	38
B	2-Chlorohexane	−20[e]	1	6				56	44
			120					57	43
B	3-Chlorohexane	−20[e]	1	7				56	44
			120					57	43

[a] Mole ratio benzene:chlorohexane:$AlCl_3$ 4:1:0.1. [b] Method A, $AlCl_3$ added to benzene plus chlorohexane; method B, $AlCl_3$ added to chlorohexane followed by benzene addition. [c] Determined by GLC from disappearance of chlorohexane. [d] Relative percentages determined by GLC. [e] Hexane added to reactions at −20° to prevent freezing. [f] An additional quantity of $AlCl_3$ equal to original charge added after 2 hr. [g] Reaction allowed to warm to 25° after 2 hr.

at 25° may be attributed to some rearrangement after attachment of the pentyl group to the ring, since rearrangement of the phenylhexanes obviously does occur under the reaction conditions. Another factor affecting the distribution of products of the alkylations is the relative rates at which the 2- and 3-chloropentanes react with benzene. This will be discussed in later sections.

Alkylations of Benzene with 2- and 3-Chlorohexane. When $AlCl_3$ was added to neat 2- or 3-chlorohexane, an equilibrium product distribution of 52:48 of 2-:3-chlorohexane resulted (Table I). This ratio is very near the 50:50 statistical distribution, since with the chlorohexanes there are an equal number of 2- and 3-carbon atoms to which chlorine can bond. When benzene was added to either 2- or 3-chlorohexane and $AlCl_3$ at −20° (alkylation method B, runs 6 and 7, Table IV), a 56:44 distribution of 2-:3-phenylhexane resulted. Alkylation by method A at 25° gave a product distribution of 61:39 of 2-:3-phenylhexane from either 2- or 3-chlorohexane (runs 1 and 3, Table IV). This higher 2-:3-phenylhexane product ratio may well be explained in terms of rearrangement of the phenylhexanes after attachment of the hexyl groups, as the data of Table III show that this occurs quite rapidly at 25°.

However, no phenylalkane rearrangement occurs at −20°, and it should be noted that the alkylations by both 2-chloropentane and 2-chlorohexane by method A at −20° also gave products higher in 2-phenylalkane content than either the equilibrium ratio of 2-:3-chloroalkanes (Table I) or the ratio of 2-:3-phenylalkanes produced by method B (compare runs 2 and 6, Table II, and runs 2 and 6 or 7, Table IV). The alkylations by both 3-chloropentane and 3-chlorohexane by method A at −20° gave product distributions lower in 2-phenylalkane content (run 4, Table II, and run 4, Table IV). These results are probably due to differences in *rates* of alkylation by 2- and 3-chloroalkanes in the reactions carried out by method A. Alul[9] has suggested that the 2 cation reacts faster than the 3 cation in dodecene alkylations of benzene catalyzed by $AlCl_3$ and $AlCl_3$–

CH_3NO_2, and a more rapid alkylation by the 2 cation has also been proposed in alkylation of benzene by chloropentadecanes.[15,16]

Further information about the competitive reactions of alkylation and isomerization can be obtained by a rough kinetic analysis of the data in Table IV. On the basis of the results from the alkylations with 2- and 3-chloropentane in the presence of 2- or 3-phenylhexane at −20°, we can assume that no appreciable isomerization of the products occurs after alkylation by 2- and 3-chlorohexanes. In the experiments identified by runs 2 and 4 of Table IV, the amount and identity of the isomeric chlorohexanes remaining in the reaction mixtures were determined after various times, and the extent of the alkylation could thus be calculated. Using these data and the proportion of 2- and 3-phenylhexanes produced at the times samples were taken for GLC analysis, we can calculate approximate values for the competitive processes of isomerization of chlorohexanes and their simultaneous reactions with benzene, using the following expressions.

$$A_2 = \frac{R}{100} P_2$$

A_2 = mole percent of 2-chloroalkane which has alkylated benzene without isomerization at time t; R = mole percent reaction of 2-chloroalkane at time t, both alkylation and isomerization; P_2 = mole percent 2-phenylalkane produced at time t.

$$I_2 = \frac{(100 - R)}{100} C_3 + \frac{R}{100} P_3$$

I_2 = mole percent of 2-chloroalkane which has isomerized at time t (based on both recovered chloroalkane and phenylalkane resulting from alkylation by isomerized chloroalkane); C_3 = mole per cent 3-chloroalkane in remaining chloroalkane at time t; P_3 = mole percent 3-phenylalkane produced at time t.

Analogous expressions can be used to calculate A_3 and

Table V
Alkylation vs. Isomerization in Alkylations of Benzene[a]
and p-Xylene[b] with 2- and 3-Chlorohexane at −20°

Arene	Rxn time, t, min	$A_2{}^c$	$I_2{}^d$	A_2/I_2	$A_3{}^c$	$I_3{}^d$	A_3/I_3	A_2/A_3
Benzene	1	21	18	1.2	7.7	23	0.33	2.8
	3	46	39	1.2	13	32	0.41	3.5
	5	60	37	1.6	20	37	0.54	3.0
p-Xylene	3	10	14	0.72	3.0	15	0.20	3.3
	10	23	27	0.85	7.5	28	0.27	3.1
	20	31	34	0.91	15	35	0.43	2.1

[a] Data for benzene calculations from Table IV. [b] Data for p-xylene calculations from Table VII. [c] Mole percent of chloroalkane which has alkylated without isomerization. [d] Mole percent of chloroalkane which has isomerized, including that which has alkylated benzene or p-xylene (see text).

Table VI
Alkylations of p-Xylene with 2- and 3-Chloropentane[a]

Method[b]	Chloropentane	Temp, °C	Time, min	Run no.	Product p-xylylpentane[c] % 2-	% 3-
A	2-Chloropentane	0	15	1	75	25
			120		75	25
		−20[d]	1	2	67	33
			3		66	34
			5		65	35
			20		67	33
			120		67	33
A	3-Chloropentane	0	15	3	75	25
			120		75	25
		−20[d]	1	4	48	52
			3		50	50
			5		52	48
			20		57	43
			120		64	36
B	2-Chloropentane	−20[d]	1	5	61	39
			120		62	38
B	3-Chloropentane	−20[d]	1	6	62	38
			120		62	38

[a] Mole ratio p-xylene:chloropentane:AlCl₃ 4:1:0.1. [b] Method A, AlCl₃ added to p-xylene plus chloropentane; method B, AlCl₃ added to chloropentane followed by p-xylene addition. [c] Relative percentages determined by GLC. [d] Hexane added to reactions at −20° to prevent freezing.

I_3, and from these expressions, values of A_2/I_2 and A_3/I_3 can be calculated. A tabulation of these values for the reactions of 2- and 3-chlorohexane with benzene and AlCl₃ at −20° appears in the top part of Table V.

The values of A_2/I_2 at 1 and 3 min indicate that alkylation and isomerization take place at almost equal rates for 2-chlorohexane, whereas the values of A_3/I_3 at the same times show that the rate of alkylation by 3-chlorohexane is only 0.3–0.4 times the rate of its isomerization to 2-chlorohexane. Since the rates of isomerization are approximately equal ($I_2{:}I_3 = 18{:}23$ and 39:32), this means that the relative rates of alkylation by 2-chlorohexane and 3-chlorohexane are ca. 3:1 ($A_2/A_3 = 2.8$–3.5).

Alkylations of p-Xylene with 2- and 3-Chloropentane. The alkylation of p-xylene by method B at −20°, using either 2- or 3-chloropentane, gave a 62:38 distribution of 2-:3-p-xylylpentane (runs 5 and 6, Table VI). This is slightly different from the 64:36 distribution produced by equilibrating the neat chloropentanes (Table I), as was found in the case of method B alkylation of benzene, also.

The alkylation by method A at 0° using either 2- or 3-chloropentane gave a 75:25 distribution of 2-:3-p-xylylpentane (runs 1 and 3, Table VI). This distribution undoubtedly arises from product isomerizations, since the p-xylylpentanes do interconvert at 0° (Experimental Section). No p-xylene alkylations were run at temperatures above 0° because methyl reorientation to m-xylylpentanes becomes a competing process.

Alkylation at −20° using method A gave quite different results for 2-chloropentane and 3-chloropentane. 2-Chloropentane and p-xylene initially gave a 67:33 distribution of 2-:3-p-xylylpentane (run 2, Table VI); after 2 h this distribution was unchanged. 3-Chloropentane initially gave a 48:52 distribution of 2-:3-p-xylylpentane. After 2 h this distribution had changed to 64:36 (run 4, Table VI). Since no product isomerization occurs at −20°, there is clearly competition between alkylation and chloropentane isomerization prior to alkylation. The fact that there is initially a much higher 2-p-xylylpentane content produced from 2-chloropentane than 3-p-xylylpentane content produced from 3-chloropentane suggests that the 2-chloropentane alkylates faster than the 3-chloropentane in this system, too.

Alkylation of p-Xylene with 2- and 3-Chlorohexane. The alkylation of p-xylene with 2-chlorohexane at −20° using method B yielded a 53:47 distribution of 2-:3-p-xylylhexane (run 5, Table VII). This is very near the 52:48 equilibrium distribution for the neat chlorohexanes reported in Table I.

Competition between alkylation and isomerization of the chlorohexanes prior to alkylation is apparent with p-xylene at both 0° and −20°. Using method A and 2-chlorohexane at 0°, the product initially contained a 61:39 distribution of 2-:3-p-xylylhexane (run 1, Table VII); after 2 h this distribution was 66:34. However, with 3-chlorohexane, the product distribution was initially 46:54 (run 3, Table VII); after 2 h the distribution had changed to 65:35. At 0° there is apparently competition between isomerization of the chlorohexanes, alkylation, and isomerization of p-xylylhexanes. At −20°, where p-xylylhexane isomerization does not occur, the competition between alkylation and isomerization of chlorohexanes using method A is even more pronounced. 2-Chlorohexane initially yielded a 64:36 distribution of 2-:3-p-xylylhexane (run 2, Table VII); after 2 h this distribution was slightly reduced in 2 content to a 61:39 ratio. The results from 3-chlorohexane were dramatically different—initially the distribution of 2-:3-p-xylylhexane was 39:61 (run 4, Table VII); this changed to 53:47 after 2 h. The data in Table VII on the alkylations at −20° allow calculation of A_2/I_2, A_3/I_3, and A_2/A_3. The values for these quantities are presented in Table V, lower part. The values for A_2/I_2 indicate that in the p-xylene system, as in the benzene system, the rates of alkylation and isomerization of 2-chlorohexane are nearly equal. Significantly smaller values for A_3/I_3 suggest that alkylation by 3-chlorohexane is slower than its isomerization. Values for A_2/A_3 indicate that 2-chlorohexane alkylates p-xylene at −20° approximately three times faster than 3-chlorohexane. This rate difference is about the same as for alkylation of benzene at −20° by 2- and 3-chlorohexane. The calculated values for I_2 and I_3 in both p-xylene and benzene media are very nearly equal at a given time, indicating that the rates of interconversion of 2- and 3-chlorohexane are almost the same.

Alkylations with Aluminum Chloride–Nitromethane Catalyst. The moderating effect of nitrobenzene and nitromethane upon aluminum chloride is well known. Alul reported that secondary dodecylbenzenes were not isomerized by AlCl₃·CH₃NO₂ even at the reflux temperature of benzene.[9] We found that 2- and 3-phenylpentane were not isomerized by this moderated catalyst at 25°. Thus we were

Table VII
Alkylations of *p*-Xylene with 2- and 3-Chlorohexane[a]

Method[b]	Chlorohexane	Temp, °C	Time, min	Run no.	Percent reaction[c]	Recovered chlorohexane[d] % 2-	% 3-	Product *p*-xylylhexane[d] % 2-	% 3-
A	2-Chlorohexane	0	1	1				61	39
			15					65	35
			120					66	34
		−20[e]	1	2				64	36
			3		16	90	10	65	35
			10		36	78	22	64	36
			20		50	70	30	61	39
			45		92	54	46	61	39
			120		100			61	39
A	3-Chlorohexane	0	1	3				46	54
			15					59	41
			120					65	35
		−20[e]	1	4				39	61
			3		5	14	86	39	61
			10		13	25	75	42	58
			20		26	33	67	44	56
			45		81	50	50	49	51
			120		100			53	47
B	2-Chlorohexane	−20[e]	1	5				53	47
			45					53	47

[a] The mole ratio *p*-xylene:chlorohexane:AlCl₃ 4:1:0.1. [b] Method A, AlCl₃ was added to *p*-xylene plus chlorohexane; Method B, AlCl₃ added to chlorohexane followed by addition of *p*-xylene. [c] Determined by GLC from disappearance of halide. [d] Relative percentages determined by GLC. [e] Hexane added to reactions at −20° to prevent freezing.

assured that we could eliminate the possibility of product isomerization by using AlCl₃·CH₃NO₂ catalyst at 25° for alkylations with chloropentanes and chlorohexanes, and thereby obtain an interesting comparison of the results with those from the alkylations in which unmoderated AlCl₃ was used at −20°. Table VIII presents the results of these alkylations with moderated catalyst.

In contrast to the alkylations of benzene with AlCl₃ at −20°, it made little difference whether method A or method B of mixing the reactants was used, or whether the 2- or 3-chloroalkane was the starting material. The products were 2- and 3-phenylpentane in a 74:26 ratio and 2- and 3-phenylhexane in a 66 ± 1:34 ± 1 ratio. These results indicate that adding nitromethane to aluminum chloride reduces the rate at which the chloroalkanes alkylate benzene much more than the rate at which they isomerize. Isomerization is therefore much faster than alkylation in the presence of the moderated catalyst, whereas the two processes are of comparable rate in the presence of unmoderated AlCl₃ (vide infra).

The alkylations of *p*-xylene in the presence of the moderated catalyst were more like those in which AlCl₃ alone was used; i.e., there was a difference in the product ratio depending on whether the 2- or 3-chloroalkane was the starting material in method A alkylations. This must mean that the alkylation of *p*-xylene competes more effectively than that of benzene with isomerization of the chloroalkanes in the presence of the moderated catalyst. In the alkylations of both benzene and *p*-xylene, the 2-chloroalkanes reacted more rapidly than the 3-chloroalkanes, as was the case with unmoderated AlCl₃ as catalyst.

In conclusion, we should like to comment briefly on the relationship of our findings to those of others. Alul found widely different phenyldodecane isomer distributions produced from 1-dodecene and *trans*-6-dodecene alkylations with AlCl₃·HCl catalyst under conditions that excluded product isomerization (0–5°), indicating that alkylation was much faster than isomerization of dodecenes or intermediate carbonium ions.[9] He also noted that alkylating in nitromethane solution slowed down alkylation more than isomerization. Geiseler et al.[17] reported that 1-heptene iso-

Table VIII
Alkylations with Aluminum Chloride–Nitromethane Catalyst[a] at 25°

Arene	Method[b]	Chloroalkane	Time, min	Product arylalkane % 2-	% 3-
Benzene	A	2-Chloropentane	10	77	23
			45	74	26
	A	3-Chloropentane	10	72	28
			45	74	26
	B	3-Chloropentane	10	74	26
			30	74	26
	A	2-Chlorohexane	10	69	31
			45	67	33
	A	3-Chlorohexane	10	64	36
			45	65	35
	B	3-Chlorohexane	10	67	33
			30	67	33
p-Xylene	A	2-Chloropentane	15	71	29
			35	69	31
	A	3-Chloropentane	15	63	37
			35	61	39
	B	2-Chloropentane	10	68	32
			30	67	33
	A	2-Chlorohexane	10	67	33
			45	65	35
	A	3-Chlorohexane	10	54	46
			45	57	43
	B	2-Chlorohexane	10	60	40
			30	61	39

[a] Mole ratio arene:chloroalkane:AlCl₃:CH₃NO₂ 4:1:0.1:1. [b] Method A: catalyst complex was added to arene and chloroalkane. Method B: catalyst complex was added to chloroalkane, stirred for 10 min, then arene was added.

merized 3–7 times faster than it alkylated benzene when 100% H₂SO₄ was used as catalyst. Our results indicate that the rates at which 2- and 3-chloropentanes and 2- and 3-chlorohexanes isomerize and alkylate benzene and *p*-xylene in the presence of AlCl₃ are of the same order of magnitude; that is, they differ by no more than twofold or threefold. With AlCl₃·CH₃NO₂ catalyst, the rates of alkylation of benzene by the chloroalkanes are depressed much more than their rates of isomerization.

One must conclude from the foregoing summary that it is not safe to generalize about the relative rates of competing reactions, such as alkylation and isomerization of "carbonium ions" without reference to their source (alkene, haloalkane, etc.), the generating catalyst or reactant, the arene substrate, and the solvent medium, since all of these factors may have a strong influence on the results.

Experimental Section

The structure and purity of all starting materials and products were checked by GLC, ir, and NMR analyses.[18]

A. Synthesis of Chloroalkanes. The method described by Vogel[19] was used for preparation of all chloroalkanes from the corresponding alcohols. 2-Pentanol was purchased commercially. 3-Pentanol was prepared from 3-pentanone by the method of Weinstock and Lewis.[20] 2-Hexanol was prepared from methylmagnesium iodide and *n*-valeraldehyde, 3-hexanol from ethylmagnesium bromide and *n*-butyraldehyde. A Carbowax 20M (30%) column (12 ft × 0.25 in.) was used for GLC analysis of the alcohols. A Bentone-34 (5%) silicone gum rubber SE-52 (5%) column (10 ft × 0.125 in.) was used for GLC analyses of the chloroalkanes.

B. Synthesis of Authentic Hydrocarbons. 1. Phenylalkanes. Standard methods were employed. Acetophenone or propiophenone was condensed with the appropriate alkylmagnesium halide.[21] The resulting carbinol was hydrogenated in glacial acetic acid using palladium on charcoal catalyst to yield the desired phenylalkane.[22] The resulting ir and NMR spectra were as expected.

2. *p*-Xylylalkanes. Standard methods were employed. Reaction of 2-bromo-*p*-xylene, magnesium turnings, and the appropriate ketone in anhydrous either gave the corresponding dialkyl-*p*-xylylcarbinol. Hydrogenation in glacial acetic acid using a palladium on charcoal catalyst gave the desired *p*-xylylalkane.[22] The resulting ir and NMR spectra were as expected.

C. Isomerizations of Chloroalkanes. The chloroalkane was placed in a flask equipped with a magnetic stirrer, a drying tube, and, for the chlorohexanes, a septum to allow aliquots to be removed with a hypodermic syringe. The reactions were run in a dry ice–ethanol bath to maintain −20° or stirred at room temperature for the 25° isomerizations. In the chloropentane isomerizations the reactants were hydrolyzed by pouring onto ice. The organic phase was separated, washed with saturated sodium bicarbonate and then with brine, and dried over calcium chloride. The chloropentanes were isolated by distillation and analyzed by infrared using a Beer's law plot. The values of 2-chloropentane were obtained from the absorption peak at 745 cm⁻¹ and those of 3-chloropentane from that at 820 cm⁻¹. In the chlorohexane isomerizations a 0.25-ml aliquot was withdrawn after the desired time interval and quenched in a water-filled vial. The organic layer was analyzed directly by GLC without further purification. In all isomerizations the molar ratio of chloroalkane:catalyst was 10:1, the sample sizes of the chloroalkanes taken for isomerization were 0.05 or 0.1 mol. The results of these isomerizations are given in Table I.

Isomerizations of the chloroalkanes were also effected at 25° by AlCl₃·CH₃NO₂ (mole ratio chloroalkane:AlCl₃:CH₃NO₂ 10:1:10). The equilibrium proportions of the isomeric chloroalkanes were the same (± 1%) as when unmoderated AlCl₃ was used.

D. Alkylations of Benzene and *p*-Xylene with 2- and 3-Chloropentane and 2- and 3-Chlorohexane. Aluminum Chloride Catalyst. Two different methods were used to carry out these alkylations. The difference involved changing the order of addition of reactants. In method A the aluminum chloride was added to a stirred solution of the chloroalkane and arene. In Method B the aluminum chloride was added to the stirred chloroalkane, followed by addition of the arene. Alkylation results are presented in Tables II, IV, VI, and VII. Overall yields of alkylarenes were in the 70–80% range.

1. Alkylation by Method A. The reactions were carried out in a flask equipped with a magnetic stirrer, a condenser with drying tube, and a septum to allow aliquots to be withdrawn by syringe. The arene and chloroalkane were stirred at the desired temperature (25, 0, or −20°), and the aluminum chloride was added in one lot to begin the reactions. In the alkylations carried out at 0 and −20°, it was necessary to add hexane (20–35 g) to prevent freezing. In all the alkylations the ratio of arene:halide:aluminum chloride was 4:1:0.1; 0.05-mol samples of chloroalkanes were used. At desired intervals 0.25-ml aliquots were withdrawn, quenched in water-filled vials, and analyzed directly by GLC.

The determination of percent reaction was based upon disappearance of the chloroalkane which was traced by GLC analyses. The recovered chlorohexanes were analyzed for isomer distribution using a Bentone-34 (5%), silicone gum rubber SE-52 (5%) column (10 ft × 0.125 in.). The aromatic hydrocarbon isomer distribution was determined by GLC using a similar column of 5 ft × 0.125 in. dimensions.

2. Alkylation by Method B. The reaction vessel used was the same as that described in method A. Aluminum chloride was added to the chloroalkane being stirred at −20°. After 3 min the arene dissolved in hexane (20–35 g) and cooled to −20° was quickly added to the stirred aluminum chloride–chloroalkane mixture and a timer was started. A considerable amount of hydrogen chloride gas was evolved even though the same reaction using method A gave a slower reaction. At various time intervals, 0.25-ml aliquots were withdrawn, quenched in a water-filled vial, and analyzed directly by GLC. In all the alkylations the ratio of arene: chloroalkane:aluminum chloride was 4:1:0.1; 0.05-mol samples of chloroalkanes were used. In some of the alkylations, method B was used with only one of the isomeric chloroalkanes. This was all that was necessary, since it had been shown (Table I) that the neat 2- or 3-chloroalkanes instantaneously isomerize to the same mixture even at −20°.

3. Alkylations of Benzene with 2- and 3-Chloropentane in the Presence of 2- or 3-Phenylhexane (Method A).[14] Benzene (15.6 g, 0.20 mol), 2- or 3-chloropentane (5.33 g, 0.050 mol), and 2- or 3-phenylhexane (0.60 g, 0.0050 mol) were stirred at 0 or 25°. In the reactions carried out at −20°, enough hexane was added to keep the benzene from freezing. Aluminum chloride (0.67 g, 0.0050 mol) was added, and at the time intervals stated in Table III, 1-ml aliquots of the reaction mixture were withdrawn, quenched, and analyzed as before, using a 6 ft × 0.25 in. 10% Ucon column at 140°. The results are presented in Table III.

E. Tests of Rearrangement of Xylylpentanes under Alkylation Conditions. 2- or 3-*p*-xylylpentane (4.4 g, 0.025 mol), isopropyl chloride (2.0 g, 0.025 mol), *p*-xylene (10.6 g, 0.100 mol), and aluminum chloride (0.33 g, 0.0025 mol) were stirred at 0 and at −20° for 2.5 hr. The reaction mixtures were decomposed and a 5 ft × 0.125 in. Bentone-34 (5%)–silicone gum rubber (5%) column was used to separate the xylylpropanes produced from the xylylpentanes remaining. In the reactions run at −20°, neither 2- or 3-*p*-xylylpentane showed any rearrangement. In the reactions run at 0°, 2-*p*-xylylpentane underwent 5% rearrangement to 3-*p*-xylylpentane, and 3-*p*-xylylpentane underwent 22% rearrangement to 2-*p*-xylylpentane.

F. Alkylations with Aluminum Chloride–Nitromethane Catalyst. These were carried out as in section D except that the aluminum chloride was dissolved in nitromethane before adding it to the reactants according to methods A and B. The mole ratios, conditions, and results are presented in Table VIII.

Registry No.—Benzene, 71-43-2; 2-chloropentane, 625-29-6; 3-chloropentane, 616-20-6; aluminum chloride, 7446-70-0; 2-chlorohexane, 638-28-8; 3-chlorohexane, 2346-81-8; 2-phenylhexane, 6031-02-3; 3-phenylhexane, 4468-42-2; *p*-xylene, 106-42-3; 2-*p*-xylylpentane, 942-08-5; 3-*p*-xylylpentane, 4465-85-4.

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od B does not seem valid, since equilibrium control implies reversibility of alkylation, and the lack of rearrangement of phenylhexanes present in the chloropentane alkylations at −20° appears to refute this possibility. Of course one must remember that the reaction mixtures produced by both methods A and B are heterogeneous, and the isomeric chloroalkanes, catalyst, arene, and solvent (hexane) may be distributed quite differently in the reaction medium when the order of addition is changed. It is conceivable that in the reactions carried out by method B either (1) equilibration of the product phenylalkanes *does* occur even at −20°, or (2) there is not the same difference in rates of alkylation by 2- and 3-chloroalkanes in the reaction medium of method B as in the reaction medium of method A.

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Transfer Hydrogenation and Transfer Hydrogenolysis. IX. Hydrogen Transfer from Organic Compounds to Aldehydes and Ketones Catalyzed by Dihydridotetrakis(triphenylphosphine)ruthenium(II)

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In the hydrogen transfer from organic compounds to aldehydes and ketones, $RuH_2(PPh_3)_4$ was found to have an excellent catalytic activity under mild conditions. Ethers, hydroaromatic compounds, tertiary amines, and alcohols showed hydrogen donating ability, and the ability decreased in the order 2,5-dihydrofuran > tri-n-propylamine > benzyl alcohol > cyclohexanol > ethyl alcohol > tetralin ≈ 1,2-dihydronaphthalene > dioxane. The mechanism of hydrogen transfer from alcohols to the aldehydes was investigated. The data of the reaction can be accommodated by the rate expression of the form rate = $k[D][Cat]_0/(1 + K[RCHO])$, where [D], $[Cat]_0$, and [RCHO] are alcohol, catalyst, and aldehyde concentration, respectively. The kinetic isotope effect, $R_H/R_D = 0.9$, and other data suggests that the rate-determining step of the reaction is the coordination of the alcohols to the complex. The process of the hydrogen transfer from alcohols to aldehydes on the metal is also proposed.

In catalytic hydrogenation using transition metal complexes as catalysts, olefins have been mainly used as hydrogen acceptors and the reduction of other functional groups has received little attention. As for the reduction of aldehydes and ketones by molecular hydrogen, it has been reported that several cobalt,[1] iridium,[2] and rhodium[3] complexes have activities as homogeneous catalysts. In the catalytic transfer hydrogenation of aldehydes and ketones to alcohols, only primary and secondary alcohols seem to have been used as hydrogen donors, and transition metal salts,[4] $CoH_3(PPh_3)_3$,[5] $RhCl(PPh_3)_3$,[6] $RuCl_2(PPh_3)_3$,[7] and $IrCl_3[P(OMe)_3]_3$,[8] have been reported to have activity as homogeneous transition metal catalysts. However, no detailed studies of the mechanism of the reaction, including that of heterogeneous systems, have yet been carried out.

This study was undertaken to examine the transfer hydrogenation of aldehydes and ketones in detail.

Results and Discussion

Catalytic Activity of Some Phosphine Complexes. The catalytic activity of some representative phosphine complexes for the reduction of n-hexaldehyde was investigated. When a catalyst (0.02 M), benzyl alcohol (2.0 M), and n-hexaldehyde (1.0 M) were heated in bromobenzene at 120° for 150 min, the yield of n-hexyl alcohol was given as follows: $RuH_2(PPh_3)_4$, 0.90 M; $RuH_2(CO)(PPh_3)_3$, 0.78 M; $RuCl_2(PPh_3)_3$, 0.43 M; $RhH(PPh_3)_4$, 0.02 M; and $RhCl(CO)(PPh_3)_2$, $CoH[P(OPh)_3]_3$, and $MCl_2(PPh_3)_2$ (M = Fe, Ni, Co, Pd, and Pt) had no catalytic activity under this condition. $RhCl(PPh_3)_3$ showed no catalytic activity, because the complex was transformed to $RhCl(CO)(PPh_3)_2$

by the reaction with aldehyde[9] which has no catalytic activity. $RuH_2(PPh_3)_4$ was found to have the highest activity among complexes tried in this transfer hydrogenation, and the complex catalyzed the hydrogen transfer even at room temperature. In this study, $RuH_2(PPh_3)_4$ was used as a catalyst.

Hydrogen-Donating Ability of Some Organic Compounds. We have previously reported that cyclic ethers,[10] amines,[11] and alcohols[12] donate hydrogen to olefins in the presence of $RhCl(PPh_3)_3$, $RhH(PPh_3)_4$, or $RuH_2(PPh_3)_4$. The hydrogen-donating ability of some organic compounds to n-hexaldehyde was evaluated (Table I). 2,5-Dihydrofuran, benzyl alcohol, and cyclohexanol showed especially excellent hydrogen-donating abilities. Perhaps these compounds donate hydrogen rapidly and the resulted dehydrogenation products are relatively resistant to reduction. Other alcohols, hydroaromatic compounds, and ethers had almost the same hydrogen-donating abilities under the reaction condition. It is noteworthy that noncyclic ethers gave hydrogen in homogeneous catalysis, because such a phenomena seems not to be reported. When primary and secondary amines were used, n-hexyl alcohol was not detected and n-hexaldehyde disappeared. In the case of tertiary amines, the alcohol was obtained in good yield, but the amount of the surviving aldehyde was smaller than the theoretical one. These results show the existence of side reactions between the aldehyde and amines.

Analyses of the dehydrogenation products summarized in Table II clearly shows that the following reactions proceeded almost stoichiometrically without remarkable side reactions.