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Alkylation of Benzene with Isoparaffin–Alkyl Chloride Mixtures[1]

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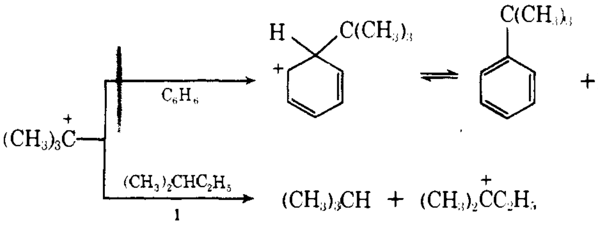
Abstract: The product formed by the alkylation of benzene with *tert*-butyl chloride at room temperature in the presence of an isoparaffin and aluminum chloride consists not only of *tert*-butylbenzene but also of alkylbenzene in which the alkyl group is produced from the isoparaffin. For example, the gradual addition of *tert*-butyl chloride to a stirred mixture of benzene, isopentane, and the catalyst yields chiefly pentylbenzenes during the early part of the experiment; the relative quantity of *tert*-butylbenzene increases as the addition proceeds. On the other hand, when a secondary alkyl chloride, isopropyl chloride, is reacted with benzene and isopentane, isopropylbenzene is the chief product, pentylbenzenes being formed in only minor amount. Alkylation of benzene by saturated hydrocarbons does occur even with a primary alkyl chloride if it isomerizes readily to a tertiary chloride (1-chloro-3,3-dimethylbutane) or yields a very active primary cation (benzyl chloride). The reaction mechanism and the reasons for the differences between the types of alkyl chlorides are discussed.

The aluminum chloride catalyzed alkylation of aromatic hydrocarbons with alkyl chlorides has been intensively investigated since Friedel and Crafts first reported that pentylbenzene is formed by the action of aluminum chloride on a solution of pentyl chloride in benzene.[2] It is the purpose of the present paper to show the marked effect on the course of the reaction of paraffins and cycloparaffins which contain tertiary carbon atoms. The literature does contain some examples of the reaction of benzene with isoparaffins and alkylcycloparaffins during its alkylation with olefins[3,4] or *tert*-alkyl fluorides,[5] but the reactions are not adequately discussed.

The product formed by the alkylation of benzene with *tert*-butyl chloride at room temperature in the presence of aluminum chloride and a saturated hydrocarbon containing a tertiary carbon atom consists not only of the expected *tert*-butylbenzene, but also of the alkylbenzene isomers produced by alkylation of the benzene with a moiety derived from the saturated hydrocarbon. Thus, the dropwise addition of *tert*-butyl chloride to a stirred mixture of benzene, isopentane, and aluminum chloride at room temperature (expt 1) resulted in the formation of isobutane and of liquid product containing approximately equal amounts of *tert*-butylbenzene and pentylbenzenes (chiefly the *sec*-isopentyl isomer, 2-methyl-3-phenylbutane). The pentylbenzenes were the principal products during the early part of the experiment; the relative quantity of *tert*-butylbenzene increased as the experiment proceeded, presumably because the relative proportion of available isopentane decreased. The final liquid product contained approximately equal quantities of *tert*-butylbenzene and the pentylbenzenes.

The reaction may be explained by the following pathway, which involves hydride transfer (hydrogen-chlorine exchange):

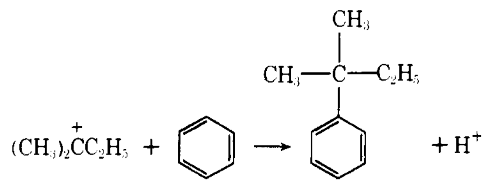
$$(CH_3)_3CCl + AlCl_3 \rightleftharpoons (CH_3)_3C^+ + AlCl_4^-$$



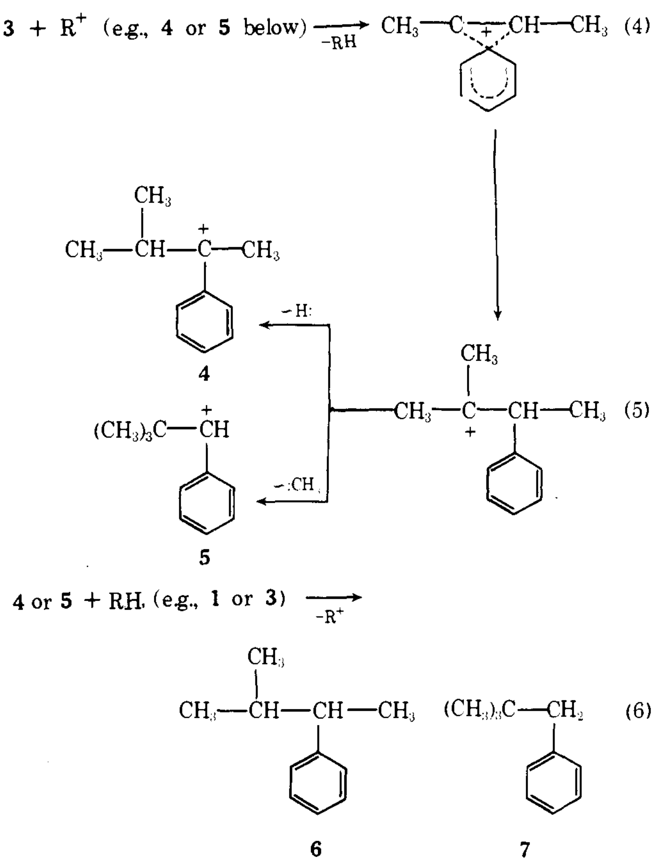
(1)

(2)

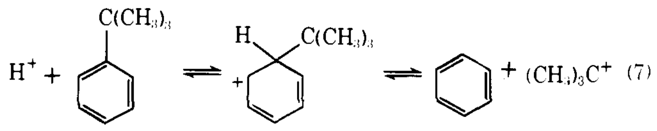
2



(3)



tert-Butyl cations may also be formed by dealkylation of primarily formed *tert*-butylbenzene:



Reaction of the *tert*-butyl ion with isopentane (cf. eq 2) leads to the production of isobutane and pentylbenzenes. In other words, alkylbenzene is formed from the paraffin solvent via reaction with either the alkyl chloride or the alkylbenzene. Equation 7 is confirmed by an early observation of Ipatieff and Pines[6] that *sec*- and *tert*-alkylbenzenes are dealkylated by the aluminum chloride catalyzed reaction with cyclohexane or decahydronaphthalene.

The hydrogen-chlorine exchange between an alkyl chloride and an isoparaffin in the presence of an aluminum halide has been shown to occur very readily.[7] The isomerization of *tert*-pentylbenzene (**3**) to *sec*-isopentylbenzene (2-methyl-3-phenylbutane, **6**) and neopentylbenzene (**7**) has been well established.[8-10]

Despite the fact that it has been shown that *tert*-butyl chloride and isopentane undergo rapid hydrogen-chlorine exchange when contacted with aluminum halide,[7] it was quite surprising to find that *tert*-butyl chloride (i.e., *tert*-butyl cation) apparently reacts more rapidly with isopentane than with benzene and that it induces the alkylation of the aromatic hydrocarbon by the isoparaffin.

In order to obtain further insight into the reaction, the alkylation of benzene with a higher molecular weight isoparaffin (3-methylhexane) and *tert*-butyl chloride was investigated. The alkyl chloride was slowly added (during 2 hr) in four equal portions to a stirred mixture of the aluminum chloride catalyst, 0.5 mol of the heptane, and 1.0 mol of benzene (expt 2). A sample of the product was removed for analysis by gas chromatography (GC) after each portion of alkyl chloride had been added. The first chromatogram showed that the initial alkylation product was solely heptylbenzene. The succeeding chromatograms indicated that (as with isopentane) proportionately more *tert*-butylbenzene was produced as the reaction progressed. The final product contained *tert*-butylbenzene in about 18 mol % yield and heptylbenzene (a mixture of at least four isomers) in about 12 mol % yield, the yields being estimated from the gas chromatographic analysis. The isobutane (**2**) yield was not determined.

The relative amount of 3-methylhexane in the reaction mixture did influence the formation of heptylbenzenes. This was shown by the results of an experiment in which double the above amount of 3-methylhexane was used, half being mixed with the *tert*-butyl chloride, and the resulting solution being added gradually to the stirred mixture of catalyst, benzene, and the remaining 3-methylhexane (expt 3). The final yield of *tert*-butylbenzene was decreased to about 13 mol % while the yield of heptylbenzenes was increased to about 15 mol %.

The entire alkylation product was formed via hydrogen transfer when the saturated hydrocarbon was methylcyclohexane. The addition of *tert*-butyl chloride to aluminum chloride and an equimolar mixture of benzene and methylcyclohexane produced an 80% yield of (methylcyclohexyl)benzene and no *tert*-butylbenzene (expt 4). GC showed that the product consisted of about 20% of one isomer [the tertiary compound, (1-methylcyclohexyl)benzene] and 80% of another, probably (2-methylcyclohexyl)benzene.[8b]

When the secondary alkyl chloride, isopropyl chloride, was used instead of the tertiary chloride, *tert*-butyl chloride, less hydrogen transfer occurred and the isoparaffin was involved to only a minor extent. For example, when isopentane was the isoparaffin, isopropylbenzene was obtained in 54 mol % yield and pentylbenzene in only 4 mol % yield (expt 5). The isopropyl chloride (cation) reacts with benzene far more rapidly than with isopentane. This confirms observations (made during the study of isoparaffin alkylations) concerning the relative reactivity of isobutane with secondary and tertiary alkyl cations.[11]

Much hydrogen transfer did occur when a primary chloride, 1-chloro-3,3-dimethylbutane, was added to an approximately equimolar mixture of benzene, isopentane, and a catalytic quantity of aluminum chloride at 25° (expt 6). Pentylbenzene, consisting of about 55% *sec*-isopentylbenzene, 25% neopentylbenzene, and 20% *tert*-pentylbenzene, was obtained in 40 mol % yield and hexylbenzenes (2,2-dimethyl-3-phenylbutane and less 2,3-dimethyl-2-phenylbutane)[5a] in only 6 mol % yield.

2,3-Dimethylbutane was isolated in 86% yield; its formation by the reaction of 1-chloro-3,3-dimethylbutane (cation) with isobutane is inherent in the aluminum chloride catalyzed alkylation of isobutane with ethylene.[12] Formation of 2,3-dimethylbutane also explains the greater reactivity of isopentane with the primary alkyl chloride (1-chloro-3,3-dimethylbutane) than with the secondary alkyl chloride (isopropyl chloride). The cation formed from the hexyl chloride undergoes rearrangement to a tertiary alkyl cation far more readily than it adds to benzene. The so-formed tertiary ion abstracts a hydride ion from isopentane more rapidly than it adds to benzene. Hence, pentylbenzenes are formed in larger amount than are hexylbenzenes.

Hydrogen transfer resulting in alkylation of benzene by the saturated hydrocarbon also was the predominant reaction when a primary chloride which did not yield tertiary cation but formed a very active primary cation was used. Addition of benzyl chloride to 1.0 mol of benzene and 1.8 mol of methylcyclopentane in the presence of aluminum chloride at room temperature resulted in the production of toluene and (methylcyclopentyl)benzenes (expt 7). The

Table I. Alkylation of Benzene

	Reactants, mol							
Expt	C_6H_6	Satd	Hydrocarbon	RCl		$AlCl_3$, mol	Chief products	Yield, %[a]
1	1.0	i-C_5H_{12}	0.5	t-BuCl[d]	0.1	0.15	i-C_4H_{10}	
							$PhCMe_3$	
							PhC_5H_{11}[b]	
2	1.0	C_7H_{16}[c]	0.5	t-BuCl[d]	0.5	0.11	i-C_4H_{10}	
							$PhCMe_3$	18
							PhC_7H_{15}[e]	12
3	1.0	C_7H_{16}[c]	1.1	t-BuCl[d]	0.5	0.11	i-C_4H_{10}	
							$PhCMe_3$	13
							PhC_7H_{15}[e]	15
4	1.0	MCH[f]	1.0	t-BuCl	0.5	0.02	$PhCMe_3$	0
							$PhC_6H_{10}Me$	80
5	1.0	i-C_5H_{12}	1.5	i-PrCl[d]	0.5	0.11	$PhCHMe_2$	54
							PhC_5H_{11}	4
6	1.0	i-C_5H_{12}	1.3	NeoCl[g]	0.3	0.12	$Me_2CHCHMe_2$	86
							PhC_5H_{11}	40
							PhC_6H_{13}[h]	6
7	1.0	MCP[i]	1.8	BnCl[j]	0.5	0.11	PhMe	27
							PhC_5H_8Me	35
							Ph_2Me	12

[a] Molar yield. [b] Principally 2-methyl-3-phenylbutane and a smaller quantity of 2-methyl-2-phenylbutane. [c] 3-Methylhexane, Technical; Phillips Petroleum Co. [d] Added dropwise in four portions with intermediate GC after each portion. The yields given in the last column are those after all the alkyl chloride had been added. [e] Four GC peaks. [f] Methylcyclohexane. [g] Neohexyl chloride (1-chloro-3,3-dimethylbutane) prepared by the aluminum chloride catalyzed condensation of *tert*-butyl chloride and ethylene [L. Schmerling, *J. Am. Chem. Soc.*, 67, 1152 (1945)]. [h] Chiefly 2,2-dimethyl-3-phenylbutane and 2,3-dimethyl-2-phenylbutane. [i] Methylcyclopentane. [j] Benzyl chloride.

usual product of the alkylation of pure benzene with benzyl chloride (diphenylmethane) was obtained in lower yield.

It may be concluded that the Friedel-Crafts alkylation of benzene by alkyl chlorides is markedly changed when isoparaffins or alkylcycloparaffins are present.

Experimental Section

The experiments were carried out in a three-necked glass alkylation flask equipped with a mercury-sealed stirrer, a dropping funnel, and a condenser (see Table I for data). The alkyl chloride (occasionally dissolved in a portion of the saturated hydrocarbon) was added dropwise to a stirred mixture of the saturated hydrocarbon, benzene, and aluminum chloride at room temperature. The liberated hydrogen chloride was absorbed in a soda lime tower. The reaction product consisted of two liquid layers; the upper (usually an amber fluid) was separated from the viscous, red-brown lower layer, water-washed, dried, and submitted to gas-liquid chromatography (GC). The yields of products were estimated on the assumption that the peak areas of the compounds were proportional to the weight percent of the compounds; in other words, the yields were calculated on the assumption that all alkylbenzenes and other hydrocarbon products had the same response factor. Hence, the yields shown in Table I are not exact, but they do present semiquantitative information about the type of reaction which occurs when an alkyl chloride is added to a mixture of benzene and a saturated hydrocarbon in the presence of aluminum chloride.

As is usual in aluminum chloride catalyzed reactions, the viscous lower layer consisted chiefly of complexes of the catalyst and aromatic hydrocarbons (which were not included in the yields). This was proved in some cases by hydrolyzing the catalyst layer, water-washing the organic layer which separated, and performing a GC analysis of the dried product. In these experiments, it was found to contain the same compounds as the original upper layer.

A sample of the reaction product was passed through a 2 ft × 0.25 in. GC column containing 20% Carbowax 20M on Chrom P. The temperature was initially 70° and was programmed to 230° at 10°/min, using a helium flow rate of 50 ml/min. The peak retention times were compared with those of authentic compounds when the knowns were available. If not, they were isolated by preparative GC (Varian Aerograph Autoprep) and identified by infrared (Beckman IR-9), nuclear magnetic resonance (Varian A 60), and/or mass spectroscopy (CEC, Model 103C).

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