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ALKYLATIONS WITH ISOBUTYL ALCOHOL AND ISOBUTYL CHLORIDE UNDER "DRASTIC" CONDITIONS

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Abstract—Alkylations of benzene with isobutyl alcohol and isobutyl chloride using massive amounts of aluminum chloride gave low yields of butylbenzene mixtures composed of mainly t-butylbenzene, but also containing minor amounts of isobutyl- and sec-butylbenzene. Alkylations with t-butyl chloride under similar alkylation conditions also yielded isobutyl- and sec-butylbenzene.

It is shown that reasonable explanations of these results can be given without resort to the *ad hoc* theory that drastic experimental conditions reverse the usual order of isomerizations.

Previously we reported that a careful study of alkylation of benzene by isobutyl chloride and aluminum chloride gave t-butylbenzene as the exclusive monoalkylation product at temperatures from 80° to $-18°$.[1] More recently we showed that alkylation of *p*-xylene by isobutyl chloride gave low yields of isobutyl- and sec-butyl-*p*-xylene.[2] The formation of isobutyl and sec-butyl derivatives from isobutyl chloride and *p*-xylene, but not from benzene, was ascribed to steric hindrance to attachment of t-Bu groups *ortho* to Me groups in *p*-xylene, a factor which allows alkylation by the less bulky primary and secondary Bu groups to become appreciable.

Nield has described alkylations of benzene by isobutyl derivatives (ethers, alcohols, chlorides) in which mixtures of isobutyl- and sec-butylbenzene were produced.[3] In these alkylations the reaction conditions were vigorous in terms of temperature, time, and amount of aluminum chloride. This is necessary to effect any alkylation in the case of the alcohols and ethers, but not for chlorides. As we have shown in the preceding paper,[4] the number and type of products from aluminum chloride-catalyzed alkylations with alcohols are strongly affected by the experimental conditions, particularly the amount of catalyst. For example, the ratio of n-propyl- and isopropylbenzene produced from 1-propanol depends on the extent to which isopropylbenzene, the initial major product, undergoes preferential dealkylation. We believe that the results from alkylations with isobutyl derivatives described by Nield are also attributable partly to subsequent reactions of the initial products.

In discussing his results,[3b] Nield mentions the *ad hoc* theory of Baddeley invoked to explain the finding of 2-methyl-3-phenylbutane as the major product from alkylation of benzene with t-pentyl chloride and aluminum chloride;[5] i.e. "secondary alkylation is faster and less reversible" (than tertiary alkylation).[6, 7] Nield further states that "it is, of course, under the more drastic conditions that the reversal of the usual order of isomerization, primary → secondary; primary (iso) → tertiary, would be expected." There is no theoretical basis for this statement, and indeed it is not relevant to Nield's data, since he accepts the direct rearrangement of sec-butylbenzene to isobutylbenzene,[8] and the finding of isobutylbenzene produced from isobutyl alkylating agents requires no isomerization at all.

It is quite possible that the isobutylbenzene found in alkylations with isobutyl alcohol, ether, and chloride comes from direct reaction of the isobutyl alcohol–catalyst complex with benzene, before any isomerization has occurred, but there is no obvious reason why "drastic" conditions should favor direct reaction or, particularly, rearrangement of tertiary to primary alkylating agents. On the other hand, it seemed to us that the use of massive amounts of aluminum chloride and high temperatures in alkylation reactions are just the circumstances expected to lead to subsequent reactions of arenes such as rearrangements, dealkylations, and fragmentations.[8–10]

We had observed some isobutyl- and/or sec-butylbenzene to be produced from t-butylbenzene by heating with a smaller amount of aluminum chloride at 100° for 3 hr.[10] The present paper describes some alkylations of benzene with isobutyl chloride, isobutyl alcohol, and t-butyl chloride using an excessive amount of aluminum chloride (1·5 mol $AlCl_3$/mol RX), and separate treatments of t-butylbenzene with a 1·5 molar ratio of aluminum chloride under alkylation conditions.

DISCUSSION OF RESULTS

The first experiment of Table 1 was a repetition of Nield's alkylation with isobutyl chloride at 80°. We obtained a slightly higher yield of butylbenzenes (7% *vs.* 4·5%), but this product was not "mainly s- and iso-butylbenzenes" as reported, but contained only about 29% of these isomers. The ratio of isobutyl- to sec-butylbenzene (60/40) was similar to the equilibrium ratio produced by heating either of these arenes with aluminum chloride.[8b, 10] The extent of dealkylation (64% of the amount of isobutane theoretically obtainable from isobutyl chloride was collected) and the production of the fragmentation products ethylbenzene and isopropylbenzene were reminiscent of results from heating t-butylbenzene with aluminum chloride.[10] The large amount of

TABLE 1. ALKYLATIONS OF BENZENE (50 ml) WITH BUTYL CHLORIDES AND ALCOHOLS (0·1 mol) AND ALUMINUM CHLORIDE (0·15 mol)

	Temp., °C[a]	Products, Yield, %[b]				
		$i\text{-}C_4H_{10}$[c]	i-PrPh[d]	t-BuPh[d]	i/s-BuPh[d]	PePh[d]
i-BuCl[e]	80	64	2[f]	5	2[g]	48g[h]
i-BuCl	25	24	2	9	5	4
i-BuOH	80	70	0·3[i]	0·3	1	0
i-BuOH	25	0	trace	0·2	0·5	0
t-BuCl	25[j]	20	trace	34	1	0
t-BuCl	25	20	1	14	3	3

[a] The time of reaction at this temperature was 1·5 hr except as noted in *j*; [b] Percentage of theoretical yield based on the starting chloride or alcohol; [c] From direct volume measurement and GLPC identification; [d] From GLPC using a known weight of n-propylbenzene as internal standard; see Exptl section for description of columns; [e] In this expt, 1·0 mol isobutyl chloride, 1·5 mol $AlCl_3$, and 500 ml benzene were used, and the reaction mixture was fractionally distilled before GLPC analysis; [f] About 1% of ethylbenzene was also found; [g] 60% i-BuPh, 40% s-BuPh, by NMR analysis; [h] This material included all products with b.p. >185°; [i] About 0·1% of ethylbenzene was also found; [j] Reaction time 0·5 hr.

high-boiling residue probably contained not only some polyalkylated benzenes as reported by Nield, but also polyarylbutanes resulting from the hydride abstractions that are a part of the dealkylation reactions.[10] These results suggest that the major initial product of the alkylation with isobutyl chloride is t-butylbenzene, which, in the presence of the excessive amount of aluminum chloride, undergoes extensive dealkylation and fragmentations.

From the alkylation of benzene with isobutyl alcohol at 80°, Nield reported an 11% yield of butylbenzenes. We obtained a much lower yield, ca. 1% (Table 1, third experiment). The main reaction again was dealkylation (80%). The product distribution was similar to that from isobutyl chloride, except that the ratio of isobutyl- and/or sec-butylbenzene to t-butylbenzene was higher. This latter result may be attributed either to more direct alkylation by the alcohol (i.e., without rearrangement), or to more preferential dealkylation of t-butylbenzene.

Although it was already known that there was no observable temperature effect in alkylations with isobutyl chloride and normal amounts of aluminum chloride catalyst,[1] we tested alkylations with both isobutyl chloride and alcohol using a 1·5 molar equivalent of aluminum chloride at a lower temperature, 25° (Table 1, second and fourth experiments). There was little difference in the ratio of isobutyl- and/or sec-butylbenzene to t-butylbenzene formed from the alcohol, but the proportion of the primary and/or secondary isomers from the chloride was larger. Since the amount of dealkylation was much smaller at 25° than at 80°, it seems unlikely that preferential dealkylation is responsible for this different isomer distribution at the lower temperature.

Alkylations with t-butyl chloride at 25° were also tested (Table 1, fifth and sixth experiments). After a 0·5-hr reaction time, a small amount if isobutyl- and/or sec-butylbenzene was present, as well as t-butylbenzene. After 1·5-hr, a larger proportion of the primary and/or secondary isomers was found, although the extent of dealkylation was no greater (apparently nearly all of the dealkylation occurs in the early part of the reaction while the catalyst is most active[10]). These results suggested that some isobutyl- and sec-butylbenzene may indeed be produced by isomerization of initially formed t-butylbenzene.

The experiments summarized in Table 2 show that such an isomerization can be detected, even at 25°. In the first experiment, no isomerization occurred, but when

TABLE 2. REACTIONS OF t-BUTYLBENZENE (0·10 mol) WITH ALUMINUM CHLORIDE (0·15 mol) IN BENZENE (50 ml) AT 25°

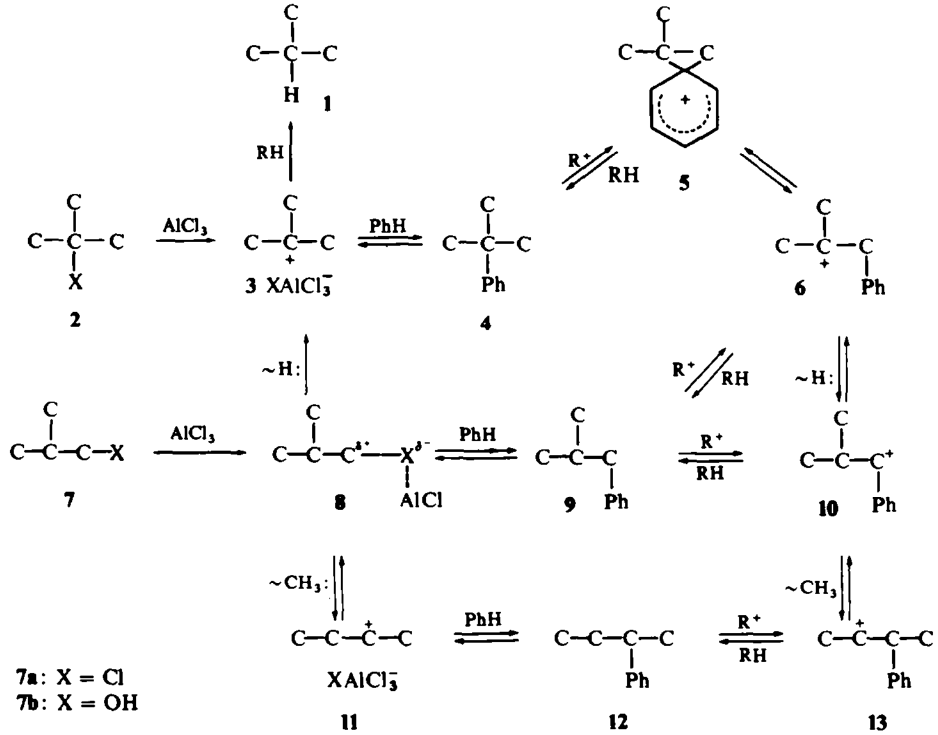
Other reactants	Reaction time, hr	Products, mol%[a]					
		i-C_4H_{10}[b]	i-PrPh[c]	n-PrPh[c]	t-BuPh[c]	i/s-BuPh[c]	Other
None	2	trace	0	0	63	0	–[d]
n-PrCl (0·10 mol)	1·5	66	14	4	11	1	1[g]
HCl[e]	1·5	74[f]	trace	0	32	1	–[d]

[a] Based on t-butylbenzene starting material; [b] From direct volume measurement and GLPC identification; [c] From GLPC using a known weight of n-propylbenzene as internal standard; [d] Not determined; [e] Gaseous HCl passed through reaction mixture continuously; [f] Contained 13% ethane and trace of propane.

alkylation conditions were simulated by the addition of n-propyl chloride or hydrogen chloride, isobutyl- and/or sec-butylbenzene were produced.

We believe that all of these results can be accommodated reasonably in terms of the mechanisms outlined in Scheme 1. Some isobutylbenzene (9) is produced by direct alkylation by isobutyl chloride or alcohol–aluminum chloride complex (8). A higher proportion of direct alkylation probably occurs with the alcohol than with the chloride because of a lesser tendency of the complex **8b** to separate into an ion pair which can isomerize before alkylation. It is also possible that a large amount of aluminum chloride accelerates the alkylation of benzene by the isobutyl chloride complex or ion pair (**8a**) more than its rearrangement to the tertiary ion pair (**3a**). This would explain the finding of some isobutylbenzene (9) in alkylations at low temperatures with large amounts of catalyst, whereas none is found with smaller amounts.[10] However, this postulate is not required to explain the results from isobutyl chloride, since the isobutylbenzene may arise from isomerization of initially-formed t-butylbenzene as described below. sec-Butylbenzene (12) is formed by isomerization of isobutylbenzene (9) via intermediates **10** and **13**[2, 8] and perhaps, in part, by rearrangement of **8** to **11** before alkylation. t-Butylbenzene (4) is produced by rearrangement of **8** to **3** before alkylation.

Scheme 1



The formation of isobutyl- and/or sec-butylbenzene in the alkylations with t-butyl chloride and in the treatments of t-butylbenzene with aluminum chloride under alkylation conditions requires additional consideration. The isomerization of **3** to **8** before alkylation, or subsequent to dealkylation of t-butylbenzene (**4**), is highly improbable. A more plausible pathway from **4** to **9** is via the intermediates **5**, **6**, and, possibly, **10**—none of which is a primary carbonium ion. The formation of the phenonium ion **5** involves participation of neighboring phenyl in hydride abstraction. Evidence for an analogous phenyl participation in alkylation with isobutylene dibromide has been reported previously.[11]

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EXPERIMENTAL

Gas chromatographic (GLPC) analysis of gaseous products was carried out at room temp on a Beckman GC-2A instrument using a ¼ in × 12 ft column containing 30% silicone gum rubber (SE-30) on firebrick. Identification was made by comparison of retention times of standard gas samples. Arene analyses were carried out at appropriate temps on a Wilkens Aerograph Hy-Fi instrument using a ¼ in × 5 ft column containing 5% Bentone-3 and 5% SE-52. Identification was made by comparison of retention times of authentic arenes; peak areas were calibrated from known mixtures. The NMR analysis of the butylbenzene fraction from the large-scale experiment (the first one in Table 1) was done on a Varian A-60 instrument. Use was made of a graph based on NMR data from known mixtures of sec-butyl- and isobutylbenzene in which the percentage of sec-butylbenzene was plotted *vs.* the ratio of peak area between δ1·09 and 1·25 ppm and between δ 6·70 and 7·50 ppm. It was necessary to add a correction to the peak area between δ 6·70 and 7·50 ppm due to the presence of t-butylbenzene in the sample.

The butyl chlorides and alcohols were checked for purity by GLPC. The t-butylbenzene was Phillips 99 mol % pure.

The reactions were carried out in a 3-necked flask equipped with a thermometer with its bulb in the liquid phase, a pressure-compensated addition funnel, and a reflux condenser. A drying tube ($CaCl_2$) was attached to the top of the reflux condenser and a Tygon tube led from the drying tube to a trap containing conc KOH aq. The exit gases from this trap were led into a large calibrated separatory funnel filled with saturated brine and immersed in the same soln contained in a large glass tank. The position of the funnel could be adjusted so that the inner and outer liquid levels could be equalized for volume measurements.

The benzene (previously dried by azeotropic distillation) and anhydrous $AlCl_3$ (reagent grade, powdered) were placed in the flask and stirred while the butyl alcohol or chloride was added dropwise during about 10 min. In the alkylations at 80°, an oil bath was employed. In the alkylation with isobutyl alcohol at 25°, it was necessary to cool the reaction mixture with an ice bath during the addition of the alcohol to maintain the temp at 25°. After the desired time, the contents of the reaction vessel were poured onto an ice-HCl mixture and stirred vigorously. The organic phase was separated. The aqueous phase was extracted twice with ether, and the ether extracts were combined with the main organic phase, which was then washed once with brine, twice with sat $NaHCO_3$ aq, and again with brine. After drying the organic product mixture over anhyd $CaCl_2$, it was subjected to GLPC analysis as described. The results of the alkylations are presented in Table 1.

The treatments of t-butylbenzene were carried out using the same equipment, and the reaction mixtures were worked up in the same way. In the first experiment, the benzene and $AlCl_3$ were mixed together initially and stirred while the t-butylbenzene was added dropwise. In the second experiment, an equimolar mixture of t-butylbenzene and n-propyl chloride was added to the benzene–$AlCl_3$ mixture. In the third experiment, a gas-bubbler inlet was added and a stream of dry HCl was passed in while the t-butylbenzene was added to the benzene–$AlCl_3$ mixture, and throughout the entire reaction period. The results of these reactions are presented in Table 2.

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