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NEW FRIEDEL–CRAFTS CHEMISTRY—XX

REPORTED LACK OF REARRANGEMENT IN ALKYLATIONS WITH PRIMARY ALCOHOLS AND ALUMINUM CHLORIDE

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Abstract—Aluminum chloride-catalyzed alkylations of benzene with 1-propanol, cyclobutylcarbinol, cyclopentylcarbinol, and cyclohexylcarbinol have been reported to take place without any rearrangement of the alkylating species. We have now reinvestigated these alkylations and have found that in every case isomerizations occur which are consistent with expected rearrangements of intermediate carbonium ions or equivalent complexes.

The relative amounts of *n*-propyl- and isopropylbenzene obtained from 1-propanol depend on the severity of the conditions; long heating results in disappearance of isopropylbenzene from the liquid reaction mixture owing to much more rapid dealkylation of this isomer than of n-propylbenzene. The major product from cyclobutylcarbinol is cyclopentylbenzene; from cyclopentylcarbinol, cyclohexylbenzene; and from cyclohexylcarbinol, a mixture of isomeric methylphenylcyclohexanes. These reactions are now shown to be consistent in mechanism with other aluminum chloride-catalyzed alkylations with primary alkyl derivatives.

INTRODUCTION

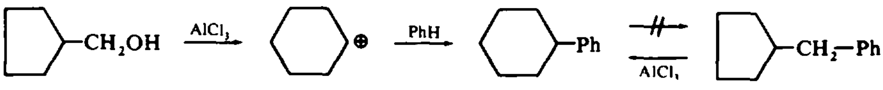
One of the long-standing mysteries of Friedel–Crafts chemistry has been the reports that alkylations with certain primary alcohols take place without rearrangement when aluminum chloride is used as catalyst, whereas rearrangements expected of carbonium ion intermediates occur when "milder" catalysts such as sulfuric acid and boron trifluoride are employed.[1] For example, neopentyl alcohol was reported to yield neopentylbenzene with aluminum chloride catalyst,[1b] but *t*-pentylbenzene with sulphuric acid[1b] or boron trifluoride[1d] catalyst.

It has now been shown that the detection of the so-called "unrearranged product" in this case is actually the end result of multiple rearrangements.[2] The first rearrangement is one of the alkylating agent before attachment to the benzene ring so that the initial product is *t*-pentylbenzene. This hydrocarbon is isomerized by aluminum chloride, first to 2-methyl-3-phenylbutane and then to neopentylbenzene.[2b,c] Both sulfuric acid and aluminum chloride isomerize the alkylating agent, but only the latter catalyst is capable of isomerizing *t*-pentylbenzene.

Other primary alcohols that have been reported to alkylate benzene without rearrangement when aluminum chloride catalyst is used are 1-propanol,[1a] cyclobutylcarbinol,[1c] cyclopentylcarbinol,[1c] and cyclohexylcarbinol.[1c] 1-Propanol was reported to give only isopropylbenzene when 80% sulfuric acid was used as catalyst.[1a] Much more recently, alkylation with 1-propanol and aluminum chloride was found to give about equal amounts of *n*-propyl- and isopropylbenzene.[3] 1-

Pentanol and 1-hexanol have also been shown to give rearranged products of alkylation with aluminum chloride catalyst.[*]

There has been no challenge of the report that the cycloalkylcarbinols gave alkylation products with the original cycloalkylcarbinyl moiety intact, in spite of the fact that there was no proof of the structure of the products. An explanation for "non-rearrangement" such as that given for neopentyl alcohol is completely untenable for these reactions. For example, in the case of cyclopentylcarbinol, isomerization of the alkylating agent would be expected to produce a cyclohexyl cation (or complex), so that the initial alkylation product would be cyclohexylbenzene. However, in order for "unrearranged product" to be found, cyclohexylbenzene would then have to isomerize to benzylcyclopentane (Eq. 1), which is known not to occur. Actually, benzylcyclopentane is isomerized rapidly to cyclohexylbenzene by aluminum chloride, but this isomerizarion is practically irreversible.[5]

 (1)

The purpose of the present research was to repeat the alkylations with the cycloalkyl-carbinols and to identify the products rigorously using modern techniques of analysis and structure proof. Alkylations with 1-propanol have also been examined with the aim of explaining the contradictory reports existing in the literature.[1a, 3]

RESULTS AND DISCUSSION

Alkylations with 1-*propanol*

Our earlier observation of the greater case of dealkylation of isopropylbenzene than of *n*-propylbenzene[6] suggested an explanation for the results of alkylation with 1-propanol and aluminum chloride. The conditions employed by Ipatieff *et al.*[1a] (110–120°, 1 hr) and Nield[3] (80°, 6·5 hr) were quite severe, and it seemed possible that the initial major product was isopropylbenzene, as expected, but that the prolonged heating with aluminum chloride decomposed it by dealkylation more rapidly than *n*-propylbenzene. Thus, the relative amount of the latter isomer became increasingly larger until it was the only isomer detected by the qualitative identification technique of the early work (preparation of a derivative).[1a]

This explanation is confirmed by the results presented in Table 1. In reaction mixtures stirred at room temperature for 24–60 hr, isopropylbenzene was the major product (74–77%). When the reaction mixtures were heated, the relative amount of isopropylbenzene decreased and that of *n*-propylbenzene increased until, in the second experiment after 7 hr, *n*-propylbenzene was the major alkylation product. Gas evolved during the course of the heating, collected and analyzed by gas chromatography (GLPC), was found to consist mainly of propane, although an appreciable amount of

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[*] Khakimov and Tsukervanik reported 1-, 2-, and 3-Phenylpentane as products from 1-pentanol. They also reported isomerization of 2-phenylpentane to 3-phenylpentane by heating with aluminum chloride at 80° for 5 hr but they did not observe the presence of 1-phenyl-2-methylbutane; cf. R. M. Roberts and Y. W. Han, *J. Am. Chem. Soc.* **85**, 1168 (1963).

isobutane was produced during the second and third hours of heating.* Significant amounts of the fragmentation products[7] ethylbenzene and toluene were also found in the liquid reaction mixture.

TABLE 1. ALKYLATION OF BENZENE WITH 1-PROPANOL AND ALUMINUM CHLORIDE

	Experiment 1			Experiment 2		
	S1[a]	S2[b]	FRM[c]	S1[a]	S2[b]	FRM[c]
Time at 25°, hr	60	60	60	24	24	24
Time at 80°, hr	—	1	8	—	1	6
Composition, %[d]						
Me—Ph	—	1	11	—	—	7
Et—Ph	—	3	28	—	2	23
i-Pr—Ph	77	46	29	74	99	64
n-Pr—Ph	23	51	29	26	34	38
s/*i*-Bu—Ph[e]	—	—	2	—	—	2

[a] First sample from reaction mixture.
[b] Second sample from reaction mixture.
[c] Final reaction mixture.
[d] Determined from relative GLPC peak areas.
[e] *sec*-Butyl- and isobutylbenzene were not resolved by the GLPC column (SE-30 silicone gum rubber).

Alkylations with cycloalkylcarbinols

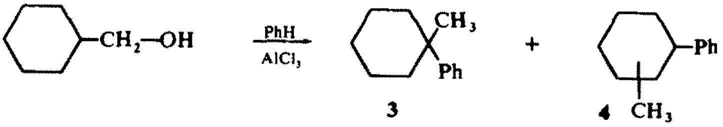
As anticipated, the results of the reinvestigation of the alkylations with the cycloalkylcarbinols showed that these reactions did *not* take place without accompanying rearrangement. Cyclobutylcarbinol gave cyclopentylbenzene (**1**), cyclopentylcarbinol gave cyclohexylbenzene (**2**), and cyclohexylcarbinol gave 1-methyl-1-phenylcyclohexane (**3**) and other methylphenylcyclohexanes (**4**) as major products.

(2)

1

(3)

2



(4)

3 **4**

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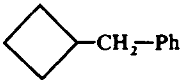
[*] Isobutane was previously observed as a gaseous product when 1,3-diphenylpropane was heated with $AlCl_3$.[7] The detection of this alkane, as well as that of *sec*- butylbenzene and/or isobutylbenzene among the liquid products (Table 1), is indicative of the complex sequence of dealkylations, carbonium ion additions, rearrangements, fissions, realkylations, and further dealkylations which must occur when arenes are heated with $AlCl_3$.

With respect to the possible "unrearranged products" (**5**, **6**, and **7**), it may be stated that they were present in very minor amounts, if at all. **6** was identified as a trace component (< 1%) in reaction mixtures from cyclopentylcarbinol, and **7** may have been among the unidentified products (*ca.* 10%) from cyclohexylcarbinol. There was no evidence of the presence of **5** in the product from cyclobutylcarbinol.



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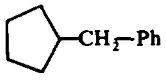

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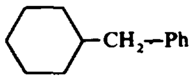

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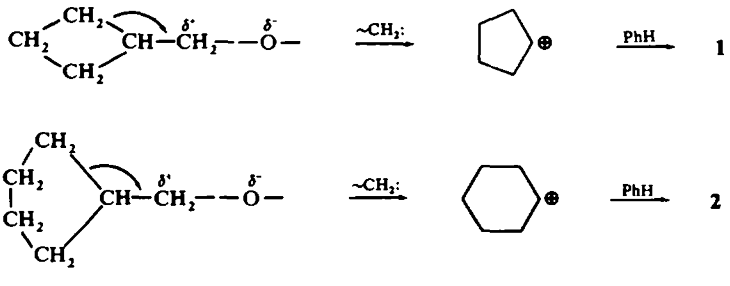
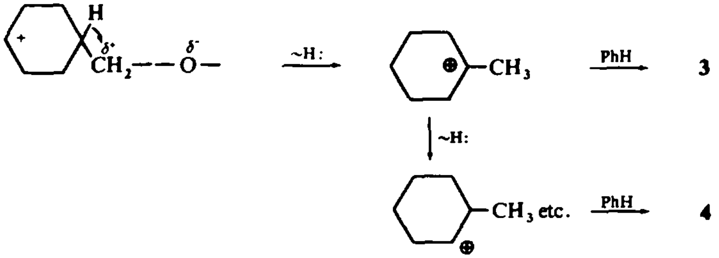
Huston and Goodemoot[1c] stated that the order of increasing reactivity of the cycloalkylcarbinols was cyclohexyl-<cyclopentyl-<cyclobutylcarbinol. This statement was apparently based on the observation that cyclobutylcarbinol alkylated benzene readily at room temperature whereas the other two did not, but they also reported that cyclopentylcarbinol gave a higher yield of product than cyclobutylcarbinol in reactions carried out at 75–80°. In restudying these reactions, we found that the proportion of catalyst to cycloalkylcarbinol has such a profound effect on the extent and direction of the reaction that a blanket statement on relative reactivity of the cycloalkylcarbinols is meaningless.

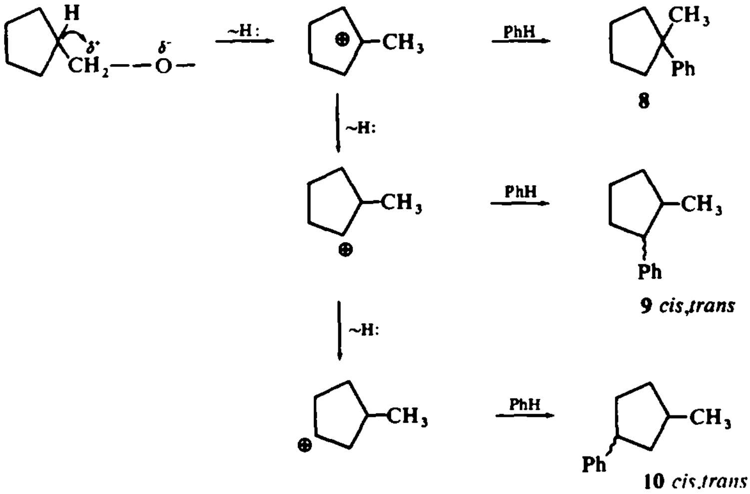
When the molar ratio of $AlCl_3$–ROH was 0·34 or below, no alkylation occurred even at 75–80° with cyclobutylcarbinol and cyclopentylcarbinol, and presumably would not with cyclohexylcarbinol. With ratios of 0·66 to 1·0, the best yields of **1** (46%), **2** (45%), and **3** (23%), were obtained. (Experiments II.A.1, II.B.2, and II.C.2). With higher ratios the yields of these products were lowered, with concomitant increases in the formation of isomers and other products (see below).

The exact nature of the complexes formed by interaction of aluminum chloride and alcohols is still uncertain,[8] but it is clear that a much larger molar proportion of aluminum chloride is required to produce an active alkylating agent from alcohols than from alkyl halides. Whatever the nature of the alcohol–aluminum chloride complexes, it is apparent from our results with the cycloalkylcarbinols that they behave as carbonium ion precursors. In the case of the cyclobutyl- and cyclopentylcarbinols, a shift of a ring methylene group takes precedence over a hydrogen shift. Apparently the release of angle and torsional strain in going from a 4-membered ring to a 5-membered ring, and from a 5-membered ring to a 6-membered ring, is more important than the formation of a tertiary carbonium ion by a hydrogen shift. However, in the case of cyclohexylcarbinol, a hydrogen shift takes precedence over ring enlargement to a 7-membered ring.





There were minor products from the reaction of cyclopentylcarbinol which indicate that a hydrogen shift does compete to some degree with the ring-enlarging methylene shift. These were methylphenylcyclopentane isomers, **8**, **9**, and **10**. The extent to which these isomers were produced was dependent on the $AlCl_3$–ROH molar ratio.



With a ratio of 1·0 (Experiment II.B.2), the yield of **2** was 45% and the combined yield of **8**, **9**, and **10** was ca. 4%. With a ratio of 1·75, the relative proportion of **8**, **9**, and **10** to **2** rose to ca. 38 :62 (Table 2). The yield of "unrearranged product" (**6**) was never higher than about 1%. In one experiment (II.B.1), another minor product was observed and tentatively identified as cyclopentylcarbinyl cyclohexyl ether (**11**).

The results of a detailed study of the effects of varying the $AlCl_3$–ROH molar ratio in the reaction of cyclopentylcarbinol with benzene are presented in Table 2. In the reactions with higher $AlCl_3$–ROH ratios. It may be seen that the reaction is faster at 30° with higher $AlCl_3$–ROH ratios than at 77° with the lower $AlCl_3$–ROH ratio. However, it should be noted that the 1·75 ratio produced the high proportion of methylphenylcyclopentane isomers mentioned above. Also in this reaction mixture were found larger amounts of lower-boiling by-products, identified as methylcyclopentane and cyclohexane, which may arise from dealkylation of methylphenylcyclopentanes and cyclohexylbenzene. There was a remarkable change in the proportion of these two cycloalkanes present in the 0·5-hr and 3-hr reaction mixtures; methylcyclopentane predominated at the earlier time and cyclohexane at the later time (in the experiment with $AlCl_3$–ROH = 0·85 methylcyclopentane was the major isomer

TABLE 2. ALKYLATION OF BENZENE WITH CYCLOPENTYLCARBINOL AND ALUMINUM CHLORIDE

AlCl$_3$–ROH, moles	0·60[a]			0·85[b]			1·75[b]	
Temp., °C	77			30[c]			30[c]	
Time, hr	4	8	24	3	5	12	0·5	3
Starting Material and Products[d]								
Cyclopentylcarbinol, %	47	29	10	74	26	2	46	<1
Cyclohexanol, %	2	1	<1	3	1	0	<1	0
Cyclohexyl chloride, %	36	45	0	7	0	0	0	0
Methylphenylcyclopentanes, %	1	2	2	1	1	1	0	38
Benzylcyclopentane, %	<1	<1	<1	<1	<1	<1	<1	<1
Cyclohexylbenzene, %	13	22	86	15	71	96	54	61
Cycloalkanes[e]					0·004	0·006	0·08	0·3
Methylcyclopentane: Cyclohexane (ratio)[f]					91:9	93:7	83:17	22:78

[a] 4·4 g cyclopentylcarbinol and 14·6 g benzene used as starting material.

[b] 2·2 g cyclopentylcarbinol and 7·3 g benzene used as starting material.

[c] The temperature was 20° for the first 0·5 hr.

[d] Analysis by GLPC using 10% Carbowax 20M column.

[e] Estimated combined yield of methylcyclopentane and cyclohexane compared to cyclohexylbenzene

[e] as 1.

[f] Analysis by GLPC using Bentone-34 column.

throughout). The increase in the proportion of cyclohexane in the experiment with the highest catalyst to carbinol molar ratio may represent an approach toward the equilibrium proportion of the two cycloalkanes.[9]

In the alkylation with cyclohexylcarbinol by the procedure of Huston and Goodemoot,[1c] a slightly better yield than they reported was obtained (10% *vs.* 7%), but the products were 1-methyl-1-phenylcyclohexane (**3**), 88%; *cis*-1-methyl-2-phenylcyclohexane (**12**), ca. 2%; and unidentified material, ca. 10%. A reaction in which the AlCl$_3$–ROH molar ratio was higher (1·0 rather than 0·70) gave a 27% yield of alkylation products consisting of 84% **3**, 4% of **12**, and 12% of unidentified material.

When the reaction was carried out using a molar ratio of AlCl$_3$–ROH = 1·2 at a lower temperature (ca. 28° rather than 77°), and with a different order of mixing the reactants, a remarkable change in product composition was found. 1-Methyl-1-phenylcyclohexane (**3**) was no longer the major product, nor was *cis*-1-methyl-2-phenylcyclohexane (**12**), but it appeared to be a mixture of other methylphenylcyclohexane isomers (**4**). The NMR spectrum of this product, which was separated from **3** and **12** by preparative gas chromatography, was similar to that of *trans*-1-methyl-4-phenylcyclohexane,[10] but the possible presence of *cis*-1-methyl-4-phenyl-, *trans*-1-methyl-2-phenyl-, and *cis*- and *trans*-1-methyl-3-phenylcyclohexane cannot be excluded. The relative proportion of **3**:**4**:**12** at the end of 31 hr reaction time was approximately 9:76:15.

We have not attempted to determine which of the changes in reaction conditions may be responsible for the difference in the proportion of isomeric methylphenylcyclohexanes produced by the alkylation with cyclohexylcarbinol. Although this observation was interesting, the major significance of the results from this carbinol, as well as the other carbinols and 1-propanol, is that carbonium ion rearrangements do accompany these alkylations, and thus these reactions do not represent anomolous exceptions to the general pattern of aluminum chloride-catalyzed alkylations.

The nature of the rearrangements

The explanation of the "rearranged products" from these alkylations with primary alcohols has been given in the preceding discussion in terms of isomerizations of the carbonium ion (or equivalent complexes) corresponding to the original alcohols, followed by alkylation of benzene by the more stable carbonium ions produced by isomerization. There is another possible interpretation that should be mentioned. Alkylation might proceed directly, so that the "unrearranged product" is formed with kinetic control, but then isomerizes more slowly to the "rearranged product", which is the product of equilibrium control. The isomerization to the more stable product might occur by a dealkylation-realkylation mechanism, in which case the rearrangement actually takes place via the carbonium ions we have considered, or it might occur by other routes not involving dealkylation.*

The equilibrium proportion of n-propyl- and isopropylbenzene in the presence of aluminum chloride has been estimated to be approximately 9:1.[12] Benzylcyclopentane is known to rearrange to phenylcyclohexane.[5] Thus, it is possible that the rearrangements occur *after* initial alkylations have afforded "unrearranged products". The experimental results from 1-propanol do not allow a clear choice between rearrangement before and rearrangement after alkylation. However, a mechanism in which benzylcyclopentane (**6**) is formed initially in any significant amount appears highly unlikely on the basis of our results, since **6** was never found to comprise as much as 1% of the product mixture even in reactions of short duration at low temperature (Table 2).

The subject of rearrangement of alkylbenzenes via direct or dealkylation-realkylation mechanisms is discussed in more detail elsewhere.[13]

EXPERIMENTAL

IR spectra were recorded on a Beckman IR-5A instrument. NMR data were obtained using a Varian A-60 spectrometer with TMS as internal standard and CCl_4 as solvent unless noted otherwise. Chemical shifts are given in δ (ppm) units. Analytical GLPC was carried out using either a Beckman GC-2A or a Wilkens Aerograph A-600 instrument; preparative GLPC separations were made using a Wilkens A-700 (Autoprep) instrument. Details of columns are given in the individual experimental descriptions. Capillary mps are uncorrected.

Cyclobutylcarbinol was synthesized by standard procedures.[14, 15] Cyclopentylcarbinol, cyclohexylbenzene, and cyclohexylcarbinol were commercial products. Cyclopentylbenzene, benzylcyclopentane, 1-methyl-1-phenylcyclopentane, *cis*- and *trans*-1-methyl-2-phenyl-cyclopentane, and *cis, trans*-1-methyl-3-phenylcyclopentane were synthesized by standard procedures; their structures were confirmed by IR, NMR, and mass spectra.[15] All starting materials were >95% pure by GLPC analysis.

I. *Alkylations with 1-propanol.* To a mixture of 20 g (0·33 mol) 1-propanol and 120 g (1·5 mol) dry benzene (to which had been added 3 drops of water) was added, in 10-g batches, 87 g (0·68 mol) anhydrous $AlCl_3$ (B. and A., Technical). The reaction mixture became dark brown, HCl was evolved, and the benzene refluxed for a moment. After the reaction mixture had been stirred for 60 hr at room temp, a 15-ml sample was removed by a pipet, decomposed with cold water and HCl, and the organic

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* Such routes have been proposed for the rearrangement of sec-butylbenzene to isobutylbenzene, of *t*-pentylbenzene to 2-methyl-3- phenylbutane, and of *n*-propyl-β-^{14}C-Benzene to *n*-propyl-α-^{14}C-benzene.[11]

material was extracted into ether. The main reaction mixture was heated to 75–80° and, after 1 hr, an 8-ml sample was taken by pipet and worked up as before. The main reaction mixture was heated an additional 7 hr, allowed to cool to room temp, decomposed with cold water and HCl, and worked up in the same manner as the samples. The ether sols from the final reaction mixture and the samples were dried over $CaCl_2$ and subjected to GLPC analysis, with the results shown in Table 1.

In a second experiment the original procedure[1a] was modified slightly: double the amounts of reactants were used, the order of addition was changed, and the reaction mixture was blanketed with a N_2 atmosphere. All of the $AlCl_3$ was mixed with the benzene, and the 1-propanol was added with stirring during the course of 1 hr. No water was added. After the reaction mixture had been stirred under N_2 for 24 hr at room temp, a 25-ml sample was taken by pipet, decomposed and worked up as before. The main reaction mixture was heated to reflux and the flow of N_2 was stopped. Gases produced were led by a tube from the outlet of the reflux condenser through a series of two NaOH traps and then into an inverted one-l. separatory funnel filled with brine and immersed in a 4-l. beaker containing brine. A second 25-ml sample of the reaction mixture was taken after 1 hr of heating, and the first gas sample was collected during this time (2·63 l., 93% propane, 7% isobutane by GLPC). Heating was continued for an additional 2·5 hr and a second gas sample was collected (2·95 l., 81% propane, 19% isobutane); after this time the evolution of gas was very slow. After a total heating period of 6 hr, the reaction mixture was cooled to room temp and worked up in the usual way. A known amount of 2-phenylpentane was added to the ether sol of the final reaction mixture so that the yield of the alkylbenzenes could be estimated from the GLPC data. (Since the volume of the reaction mixture from which the samples were taken was not known accurately, exact yields could not be calculated.) The proportions of alkylbenzenes in the samples and in the final reaction mixture as determined by GLPC are given in Table 1. The overall yield of the methyl-, ethyl-, propyl- and butylbenzenes was about 30%. The total volume of propane and isobutane collected was about 0·25 mol, which would correspond to 38% dealkylation if all of the alkanes were produced via propyl- and butylbenzene intermediates.

II. *Alkylations with cycloalkylcarbinols.* The following general procedure was followed except as noted otherwise. Experiments A.1, B.1, and C.1 were carried out under the conditions described.[1c]

The alcohol was mixed with dry benzene in a flask equipped with a short condenser protected by a drying tube. The mixture was stirred with a Teflon-covered magnet and kept at 35 ± 2° or 77 ± 2° by an electrically-heated oil bath. Anhyd $AlCl_3$ (powdered, reagent grade, either Mallinckrodt or Allied) was added through the condenser during a period of about 5 hr, after which stirring was continued another 8 hr. The mixture was then quenched with crushed ice and water and the aqueous portion was separated and extracted with three portions of ether; the ether extracts were combined, washed with sat NaCl aq and dried over anhyd K_2CO_3. After removal of the ether, the products were distilled, using a micro-column (15-cm) and/or a kugelröhr. The distillate fractions were weighed and then analyzed by GLPC.

A. *Cyclobutylcarbinol*

1. $AlCl_3$–ROH = 0·66. Reaction between 5·0 g (58 mmol) cyclobutylcarbinol, 4·8 g (36 mmol) $AlCl_3$, and 20 g (256 mmol) benzene was carried out at 77°. The forerun of the distillation of the reaction mixture contained 1·75 g unchanged cyclobutylcarbinol, which was shown by GLPC (30% Cyanosilicone column) to contain ca. 1% cyclopentanol. The alkylation product was **1** in 25% yield, based on unrecovered cyclobutylcarbinol, identical with authentic material in GLPC retention time (30% Carbowax 20M Column) and NMR spectrum: (CCl_4) δ 1·3–2·2 (m, 8H, $C\underline{H}_2$), 2·6–3·2 (m, 1H, $C\underline{H}$), and 7·1 ppm (s, 5H, aromatic).*

A second alkylation at 35°, otherwise as above, gave **1** in 46% yield, based on unrecovered cyclobutylcarbinol (ca. 4% of the original alcohol was recovered; it was less than 1% isomerized to cyclopentanol).

2. $AlCl_3$–ROH = 0·34. In this experiment, the $AlCl_3$ (1·25 g, 9·37 mmol) and benzene (10 g, 27·4 mmol) was added dropwise during ca. 0·5 hr. The mixture was stirred at room temp for 24 hr and then heated to 75° for 18 hr. Samples (1-ml) were withdrawn by pipet during the period of stirring at room temp and at the end of the heating period. After they were decomposed and extracted in the usual way.

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* Although it is possible that benzylcyclobutane (**5**) might have the same GLPC retention time as **1** and hence not show a separate peak (no authentic **5** was available to us), the NMR spectrum of the product identified as **1** showed no sign of a doublet expected for the benzylic hydrogens of **5**. The NMR spectrum of authentic benzylcyclopentane (**6**)[15] showed a clear doublet centered at δ 2·6 ppm ($J = 7$) for the benzylic hydrogens; hence, a significant amount of **5** mixed with **1** would be expected to show a doublet near δ 2·6 ppm.

their ether solutions were examined by GLPC. None showed the presence of products of alkylation by, or isomerization of, cyclobutylcarbinol.

B. *Cyclopentylcarbinol*

1. $AlCl_3$–ROH = 0·61. Reaction of 7·4 g (74 mmol) cyclopentylcarbinol, 6·0 g (45 mmol) $AlCl_3$, and 25 g (320 mmol) benzene was carried out at 77°. Distillation of the reaction mixture yielded 56% of the original amount of alcohol, which was partially (14%) isomerized to cyclohexanol. The alkylation product was **2** in 7% yield, based on unrecovered alcohol. A second product, detected in ca. 1% yield and isolated by preparative GLPC, was tentatively identified as **11**; IR (film) 1100 (broad), 1450, 1700, 1725 (C=O impurity), 2800, 2900; NMR (CCl_4) δ 0·9–2·2 (m, 19H, $C\underline{H}_2$ and $C\underline{H}$ of C_5 and C_6 rings), 3·2 (d, 2H, O—$C\underline{H}_2$), and 7·1 ppm (s, aromatic impurity, probably *trans*- **9t**, see below, ca. 2% indicated by GLPC); mass spectrum *m/e* (relative intensity) 182 (44), 100 (34), 83 (100), 82 (71), 67 (28), 57 (25), 55 (97), and 54 (12).

2. $AlCl_3$–ROH = 1·0. Reaction of 2·2 g (22 mmol) cyclopentylcarbinol, 2·9 g (22 mmol) $AlCl_3$, and 15 g (192 mmol) benzene at 77° yielded 45% **2**, ca. 2% *trans*- **9t**,[15]* and ca. 2% other methylphenylcyclopentane isomers (**8**, **9c**, **10c**, **t**).[15]† There was a trace (ca. 0·1%) of benzylcyclopentane (**6**) and about the same amount of recovered alcohol.

3. $AlCl_3$–ROH = 1·2. Reaction of 7·6 g (76 mmol) cyclopentylcarbinol, 12 g (90 mmol) $AlCl_3$, and 25 g (320 mmol) benzene at 77° yielded 19% **2**, ca. 2% of **9t**, ca. 2% of other isomers (**8**, **9c**, **10c**, **t**), a trace (ca. 0·3%) of **6**, and 7% of higher-boiling materials, thought to be diphenylcyclohexanes. A small amount of white, crystalline material, m.p. 169–172° was isolated in the work-up and was tentatively identified as 1,4-diphenylcyclohexane, lit.[16] m.p. 171–172°; NMR (CCl_4) δ 1·0–2·8 (broad multiplet, 10H, $C\underline{H}_2$ and $C\underline{H}$) and δ 7·14 ppm (s, 10H, aromatic).

C. *Cyclohexylcarbinol*

1. $AlCl_3$–ROH = 0·70. Reaction of 7·6 g (67 mmol) cyclohexylcarbinol, 6·2 g (46 mmol) $AlCl_3$, and 24 g (308 mmol) benzene at 77° gave a 10% yield of alkylation products, based on unrecovered alcohol (75% of the original alcohol was recovered, containing a trace of cyclohexanol). The alkylation products were separated by kugelrohr distillation followed by preparative GLPC (30% Cyanosilicone column) and shown to consist of 88% **3**: NMR (CCl_4) δ 1·13 (s, 3H, $C\underline{H}_3$), 1·2–2·2 (multiplet with spike at 1·4, 10H, $C\underline{H}_2$), and 6·9–7·5 ppm (m, 5H, aromatic);‡ ca. 2% of an isomer tentatively identified as *cis*- **12**: NMR (CCl_4) δ 0·7 (d, 3H, $J = 6$Hz, $C\underline{H}_3$), 1·1–2·0 (m, 10H, $C\underline{H}_2$, $C\underline{H}$), and 7·1 ppm (s, 5H, aromatic);‡ and ca. 10% of (an) unknown component (s).

2. $AlCl_3$–ROH = 1·0. Reaction of 7·6 g (67 mmol) cyclohexylcarbinol, 8·9 g (67 mmol) $AlCl_3$, and 24 g (308 mmol) benzene at 77° gave a 27% yield of alkylation products, based on unrecovered alcohol (53% of alcohol was recovered, of which 96% was cyclohexylcarbinol). The alkylation products were separated by kugelrohr distillation followed by preparative GLPC (30% Cyanosilicone column) and shown to consist of 84% **3**, ca. 4% *cis*- **12**, and 12% of two unidentified components.

3. $AlCl_3$–ROH = 1·2. A mixture of 22 g (160 mmol) $AlCl_3$ and 42 g (540 mmol) benzene was stirred at 28° and 15·2 g (133 mmol) cyclohexylcarbinol was added slowly through a condenser and then washed down with 6 g (77 mmol) benzene. The temp rose to 38° during the addition but returned to 28° within an hr. Samples (1-ml) were withdrawn after 4, 8, 11, 23 and 31 hr. These samples were decomposed and worked up as usual, and their ether sols were analyzed by GLPC.

The remaining main reaction mixture was decomposed and extracted as usual and then subjected to kugelrohr distillation. The distillate boiling in the range of the alkylation products was separated by

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* These methylphenylcyclopentane isomers were also encountered as minor products in the isomerization of benzylcyclopentane.[5] By GLPC they may be separated from cyclohexylbenzene (**2**) and benzylcyclopentane (**6**), and they produce two distinct GLPC peaks with different retention times. One of these peaks is due to *trans*-1-methyl-2-phenylcyclopentane, (**9t**) and the other to the remaining isomers (**8**, **9t**, **10c,t**).[15] Further details of their identification will be given in a paper in preparation.

† This NMR spectrum was very similar to that of authentic 1-methyl-1-phenylcyclopentane.[15]

‡ The Me doublet at δ 0·7 ppm is very similar to the corresponding doublet of authentic *cis*-1-methyl-2-phenylcyclopentane,[15] and the coupling constant ($J = 0·6$ Hz) is of the order expected for an axial Me group.[10]

preparative GLPC (30% Cyanosilicone column) into fractions which were large enough to yield NMR spectra. Compound **3** was a minor product, as was *cis*- **12**. The major product was apparently a mixture of other methylphenylcyclohexane isomers (**4**) which could not be further resolved by GLPC. The NMR of this fraction [(CCl_4) δ 0·9 (unsymmetrical doublet, 3H, $J \approx 4$Hz, $C\underline{H}_3$), 1·0–2·0 (broad multiplet, ca. 8H, $C\underline{H}_2$), 2·1–2·8 (broad multiplet, ca. 2H, $C\underline{H}$), and 7·2 ppm (multiplet, 5H, aromatic)]† was similar to that of *trans*- **13**,[11] but the other methylphenylcyclohexane isomers (*cis*-1,4-, *trans*-1,2-, *cis*- and *trans*-1,3-) may also be present. Several other very small peaks in the GLPC traces were indicative of other minor products, but these could not be identified.

The 1-ml samples taken at intervals during the reaction showed the same GLPC product components; **4** was the major component even in the first sample and its proportion increased as the reaction proceeded. The final (31-hr) proportion of **3**:**4**:**12** was ca. 9:76:15 by GLPC analysis.

D. *Cyclopentylcarbinol*

Studies of variations in the formation of intermediates and products with different catalyst–alcohol ratios. These experiments were carried out as in C. 3 above; i.e., the $AlCl_3$ and benzene were mixed first and the carbinol was added dropwise; 1-ml samples of reaction mixtures were taken after various reaction times and analyzed by GLPC. A reaction mixture in which the $AlCl_3$–ROH ratio was 0·34 gave no appreciable amounts (<1%) of alkylation products after 1 to 28 hr at 77°. The results of three other experiments are given in Table 2.

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* The NMR signal was quite low in the δ 2·6 ppm region where a sharp doublet would be expected for the benzylic hydrogens of benzylcyclohexane (**7**); thus, the presence of a significant amount of the "unrearranged product" (**7**) in this fraction is unlikely.