ammonium chloride was refluxed for 3.5 hr. The reaction mixture was cooled and filtered, and the filtrate evaporated to a solid. The solid was recrystallized from hexane (5°) to give white needles of the acetal **4**, 7.0 g (57%), mp 84–86°. The ir and nmr spectra of this product were identical with corresponding spectra of the acetal isolated in the oxidation reactions.

B. Of 3,5-Di-*tert*-butyl-2-hydroxybenzaldehyde.—A mixture of 0.39 g (0.0016 mol) of 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde, 5 g (0.04 mol) of trimethyl orthoformate, 3 ml of absolute methanol, and 0.05 g of ammonium chloride was refluxed for 36 hr. The reaction mixture was cooled and filtered, and the filtrate evaporated to the liquid acetal, 0.436 g (97%). The ir and nmr spectra of this product were identical with the corresponding spectra of the acetal isolated from the oxidation of 4,6-di-*tert*-butyl-*o*-cresol.

Preparation of 2,6-Di-*tert*-butyl-4-methoxymethylidene Quinone Methide (3a).—A mixture of 11.7 g (0.05 mol) of 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde (**5**), 30 ml of trimethyl orthoformate, 30 ml of absolute methanol, 30 ml of xylene, and 0.5 g of ammonium chloride was refluxed 1 hr. Approximately 0.5 the total volume of the reaction mixture was removed by distillation. The residual solution was refluxed for an additional 2 hr. Filtration of the cooled reaction mixture and evaporation of the filtrate in vacuum gave an orange solid. Crystallization of the product from petroleum ether (bp 60–110°) gave orange needles of the quinone methide (**3a**), 7.5 g (60%), mp 136–138° (lit.[11] mp 136–138°).

Reaction of 3a with Methanol.—A solution of 0.86 g (0.0034 mol) of **3a** in 15 ml of absolute methanol was stirred at 25° for 1 hr. The characteristic orange color of this quinone methide was instantaneously discharged upon dissolving in methanol and a colorless solution resulted. Evaporation of the solvent gave a quantitative yield of the dimethyl acetal **4**, mp 81–83°.

Registry No.—**1**, 128-37-0; **4**, 23093-16-5; manganese dioxide, 1313-13-9; lead dioxide, 1309-60-0.

(11) E. Muller, R. Mayer, U. Heilmann, and K. Scheffler, *Justus Liebigs Ann. Chem.*, **645**, 66 (1961).

New Friedel–Crafts Chemistry. XXIII. The Mechanism of the Aluminum Chloride Catalyzed Rearrangement of *tert*-Pentylbenzene to 2-Methyl-3-phenylbutane

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Transalkylations between *tert*-pentylbenzene (**1a**) and toluene and between *p-tert*-pentyltoluene (**1b**) and benzene have been effected by $AlCl_3$–CH_3NO_2 without significant isomerization of the *tert*-pentyl group. When transalkylations between **1a** and toluene were repeated, but with the addition of a molar equivalent of isopropyl chloride, extensive isomerization of the *tert*-pentyl group occurred. Treatment of 2-chloro-3-methyl-3-phenylbutane (**10a**) with $AlCl_3$–CH_3NO_2 and methylcyclohexane produced a mixture of **1a** and 2-methyl-3-phenylbutane (**2a**). Reaction of 1,2-dibromo-2-methylpropane (**13**, X = Br) with benzene and $AlCl_3$–CH_3NO_2 yields a mixture of two diphenylbutanes, whereas 1,3-dichloro-3-methylbutane, under similar conditions, gives no diphenylpentane. Treatment of 1-chloro-2-methyl-2-phenylpropane (**14**, X = Cl) with $AlCl_3$–CH_3NO_2 and methylcyclopentane gave isobutylbenzene but no *sec*-butylbenzene. On the basis of the transalkylation results and of the behavior of **10a**, **13**, and **14**, we conclude that the rearrangement of **1a** to **2a** takes place by a hydride abstraction process concerted with phenyl participation, producing a phenonium ion intermediate, followed by a second hydride transfer to the phenonium ion from the side chain of another arene molecule.

Alkylations of benzene with *tert*-pentyl chloride,[2–4] isopentyl bromide,[3] 1-chloro-2-methylbutane,[5] and 2-chloro-3-methylbutane[5] have been found to give mixtures of *tert*-pentylbenzene (**1a**) and 2-methyl-3-phenylbutane (**2a**). When aluminum chloride was used as catalyst, the pentylbenzene isomers were produced in an apparent equilibrium proportion of 15–18% **1a** and 85–82% **2a**. However, when the reactions were catalyzed by only trace amounts of aluminum chloride[4] or by weaker alkylation catalysts such as BF_3,[3] $ZrCl_4$,[3] $AlCl_3$–CH_3NO_2,[2,5] or $FeCl_3$,[2] *tert*-pentylbenzene was the sole or major product. These results have been explained in terms of initial alkylation by *tert*-pentyl cation (which is produced by rapid ionization and/or isomerization of the isomeric pentyl halides) to give *tert*-pentylbenzene (**1a**), followed by a slower rearrangement of **1a** to 2-methyl-3-phenylbutane (**2a**) brought about by the stronger catalysts.[3,5,6] In a recent paper,[5] we described two plausible mechanisms for the subsequent isomerization of **1a** to **2a**, but we concluded that the data available at that time did not allow a choice between the two possibilities.

The alternative mechanisms for rearrangement of **1a** to **2a** may be presented as shown in Scheme I. The first, which may be referred to as an *intermolecular* mechanism, involves the dealkylation–rearrangement–realkylation sequence **1a** → **3** → **4** → **2a**.[7–9] The second, which may be referred to as an *intramolecular* mechanism (since the rearranging side chain never becomes separated from the aromatic ring) involves a hydride abstraction, which may or may not be concerted with phenyl participation *via* a phenonium ion, **5a**,[5] or with methyl participation *via* a methyl-bridged cation, **6a**. If the hydride abstraction is not a concerted process, the classical ions **7a**, **8a**, and **9a** may be involved. We have now obtained additional experimental data which we believe constitute definitive evidence for the most probable pathway for the rearrangement of **1a** to **2a**.

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(1) Robert A. Welch Postdoctoral Fellow, on leave from Assiut University, Assiut, U. A. R.

(2) M. Inatome, K. W. Greenlee, J. M. Derfer, and C. E. Boord, *J. Amer. Chem. Soc.*, **74**, 292 (1952).

(3) L. Schmerling and J. P. West, *ibid.*, **76**, 1917 (1954).

(4) B. S. Friedman and F. L. Morritz, *ibid.*, **78**, 2000 (1956).

(5) R. M. Roberts and S. E. McGuire, *J. Org. Chem.*, **35**, 102 (1970).

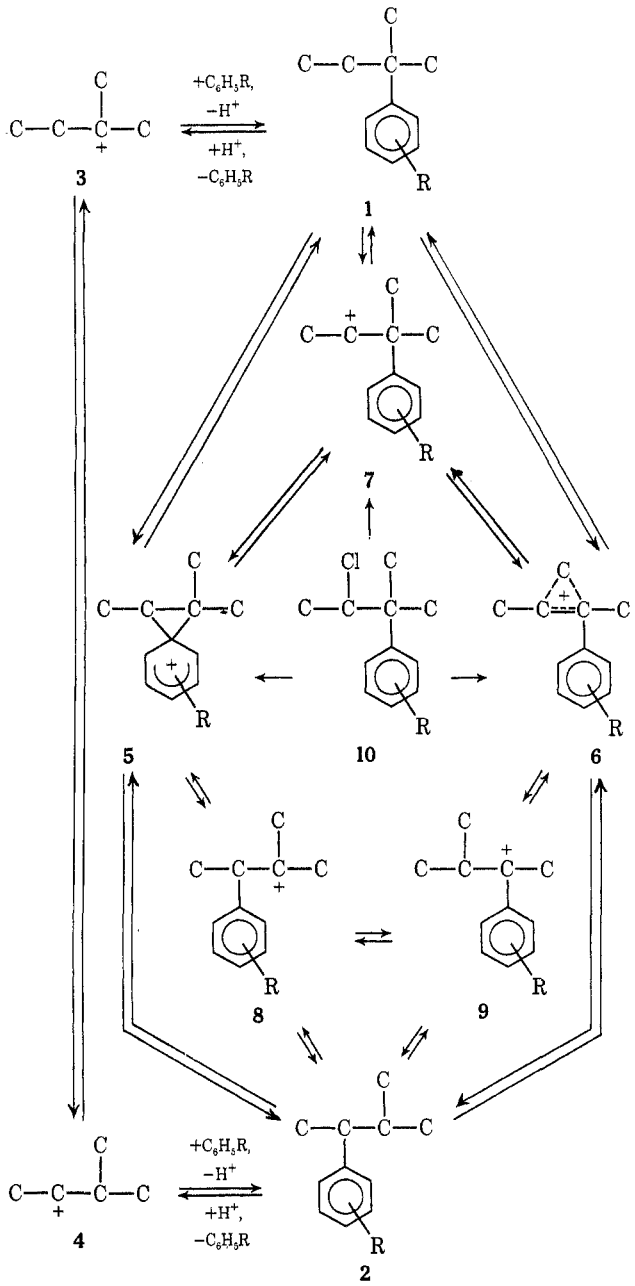
(6) L. Schmerling, J. P. Luvisi, and R. J. Welch, *J. Amer. Chem. Soc.*, **81**, 2718 (1959).

(7) B. S. Friedman, F. L. Morritz, C. J. Morrisey, and R. Koncos, *ibid.*, **80**, 5867 (1958).

(8) G. Baddeley, *Quart. Rev. (London)*, **8**, 355 (1954).

(9) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, N. Y., 1959, p 450.

SCHEME I



1a, R = H; **1b**, R = *p*-CH_3; **1c**, R = *m*-CH_3; etc.

Transalkylations of sec- and *tert*-alkylarenes are known to take place readily in the presence of mild catalysts such as $FeCl_3$[10] and $AlCl_3$–CH_3NO_2,[11–14] but processes involving hydride abstraction require a stronger catalyst and/or more strenuous conditions.[3–7] Thus, one logical explanation for the rearrangement of **1a** to **2a** by $AlCl_3$ but not by $AlCl_3$–CH_3NO_2 is that the modified catalyst is not capable of the hydride abstraction which is required for the intramolecular rearrangement mechanism. An alternative explanation in terms of the intermolecular mechanism is that the rate of dealkylation (**1a** → **3**) is so slow with $AlCl_3$–CH_3NO_2 catalyst that only **1a** is found as the product of kinetic control of alkylation, whereas with $AlCl_3$ catalyst the rate of dealkylation becomes significant, and **2a** is found as the product of equilibrium control.[15] Thus, if it could be demonstrated that dealkylation of **1a** takes place readily, even when the modified catalyst is used, the second explanation would be discredited and the intramolecular mechanism for rearrangement catalyzed by the unmodified $AlCl_3$ would be supported.

Results and Discussion

We have now demonstrated that dealkylation of **1a** takes place readily in the presence of $AlCl_3$–CH_3NO_2, by carrying out transalkylations between **1a** and toluene. The *tert*-pentyl group was also transferred from *p-tert*-pentyltoluene (**1b**) to benzene. The conditions and results of these transalkylations are summarized in Tables I and II.

It is evident from the results of experiments 1, 2, and 3 that the *tert*-pentyl group was transferred without significant internal rearrangement. The pentyltoluenes present in the reaction mixtures after 24 hr (experiments 2 and 3) apparently represent an equilibrium composition of 67–70% *m*- and 30–33% *p-tert*-pentyltoluene. This equilibrium proportion was verified by allowing *p-tert*-pentyltoluene to react with $AlCl_3$–CH_3NO_2, whereby the same proportion of isomers was produced (see Experimental Section). An equilibrium mixture of the related isomeric *tert*-butyltoluenes was shown to contain about 64% *m*- and 36% *p-tert*-butyltoluene.[12]

A transalkylation between 2-methyl-3-*p*-tolylbutane (**2b**) and benzene was also carried out (experiment 4, Table I). The reaction was much slower, and extensive internal rearrangement of the alkyl group accompanied its transfer. This result is not surprising, since secondary alkyl groups are known to undergo dealkylation much more slowly than tertiary alkyl groups,[16] and the 3-methyl-2-butyl cation (**4**) so produced would be expected to rearrange partially to the more stable *tert*-pentyl cation (**3**) before alkylating benzene. It is interesting to note that the 2-methyl-3-*p*-tolylbutane underwent no reorientation to the meta isomer in this experiment, indicating that the reorientation of the secondary alkyl group is still slower than the transalkylation.

Since the transalkylation experiments have demonstrated that dealkylation of *tert*-pentylbenzene may take place readily in the presence of $AlCl_3$–CH_3NO_2, the failure to find rearrangement to 2-methyl-3-phenylbutane when this catalyst is used must be attributed to the relative rates of the alkylation of benzene by the tertiary carbonium ion, **3**, and of its rearrangement to the secondary carbonium ion, **4**. The first process (alkylation) must be extremely fast compared to the rearrangement. When *p*-xylene is alkylated with *tert*-pentyl chloride, the secondary pentyl xylene corresponding to **2** is produced because competition from alkylation of *p*-xylene by the *tert*-pentyl cation is vir-

(10) V. N. Ipatieff and B. B. Corson, *J. Amer. Chem. Soc.*, **59**, 1417 (1937).
(11) R. H. Allen, *ibid.*, **82**, 4856 (1960).
(12) G. A. Olah, M. W. Meyer, and N. A. Overchuk, *J. Org. Chem.*, **29**, 2310 (1964).
(13) R. L. Burwell, Jr., and A. D. Shields, *J. Amer. Chem. Soc.*, **77**, 2766 (1955), and references given there.
(14) G. A. Olah, S. H. Flood, and M. E. Moffatt, *ibid.*, **86**, 1060 (1964).
(15) The rates of isomerization of **3** to **4** and of the alkylation step 4 → 2 are presumably fast enough, since alkylation of *p*-xylene with *tert*-pentyl chloride and $AlCl_3$–CH_3NO_2 gives 2-methyl-3-*p*-xylylbutane (**2b**).[7]
(16) R. M. Roberts, E. K. Baylis, and G. J. Fonken, *J. Amer. Chem. Soc.*, **85**, 3454 (1963).

TABLE I

TRANSALKYLATIONS BETWEEN *tert*-PENTYLBENZENE AND TOLUENE AND BETWEEN *tert*-PENTYLTOLUENE AND BENZENE WITH $AlCl_3$–CH_3NO_2 CATALYST AT 25°

Expt no.	Reactants, mole ratios	Time, hr	Products, %[a] *tert*-Pentylbenzene	2-Methyl-3-phenylbutane	*p-tert*-Pentyltoluene	*m-tert*-Pentyltoluene	2-Methyl-3-*p*-tolylbutane
1[b]	*tert*-Pentylbenzene–toluene–$AlCl_3$–CH_3NO_2, 1:2:0.06:0.6; mixture was saturated with dry HCl gas.	1	99	0	1	Trace	0
		24	88	1	7	4	0
2	*tert*-Pentylbenzene–toluene–$AlCl_3$–CH_3NO_2, 1:3:1:6	1	93	0	5	2	0
		24	37	4	18	41	0
3	*p-tert*-Pentyltoluene–benzene–$AlCl_3$–CH_3NO_2, 1:3:1:6	0.25	50	0	35	15	0
		24	83	1	5	11	0
		48	82	2	4	12	0
4	2-Methyl-3-*p*-tolylbutane–benzene–$AlCl_3$–CH_3NO_2, 1:3:1:6	24	5.5	0.5	0	0	94
		48	10	2	0	0	88

[a] Benzene (expt 1 and 2) or toluene (expt 3) and products with retention times higher than monopentylarenes were produced in roughly the same amounts and never exceeded 2–3% of the total aromatics. [b] The conditions of this experiment are comparable to the alkylation conditions used by Roberts and McGuire. (See ref 5.)

TABLE II

TRANSALKYLATION BETWEEN *tert*-PENTYLBENZENE AND TOLUENE AT 25°

Expt no.	Reactants, mol ratios	Time, hr	Products, %[a] *tert*-Pentylbenzene	2-Methyl-3-phenylbutane	*p-tert*-Pentyltoluene	*m-tert*-Pentyltoluene + 2-methyl-3-*p*-tolylbutane	2-Methyl-3-*m*-tolylbutane
5	*tert*-Pentylbenzene–toluene–$AlCl_3$, 1:1:0.1	1 min	54	3	16	26	1
		10 min	37	8	16	34	5
		2	20	29	8	23	20
		24	11	44	3	15	27
6	*tert*-Pentylbenzene–toluene–isopropyl chloride–$AlCl_3$–CH_3NO_2, 1:4:1:0.1:1	1	80	14	5	1	
		24	32	32	11	25	
7	*tert*-Pentylbenzene–toluene–isopropyl chloride–$AlCl_3$–CH_3NO_2, 1:4:1:1:5	0.25	51	20	12	17	
		1	26	25	16	33	
		24	20	25	8	37	10

[a] Products with retention times higher and lower than monopentylarenes were also produced but were not identified.

tually eliminated by steric hindrance.[7] The transalkylations of experiments 1–3 take place readily without appreciable incursion of the rearrangement of **3** to **4** because there is no such steric hindrance in alkylation of benzene and toluene by the *tert*-pentyl cation.

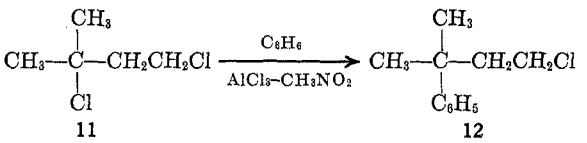
The demonstration of facile transfers of *tert*-pentyl groups between benzene and toluene molecules in the presence of $AlCl_3$–CH_3NO_2 with little or no isomerization of the pentyl group makes it appear unlikely that the effect of unmodified $AlCl_3$ in producing rearrangement of **1** to **2** is simply to increase the rate of dealkylation of **1**. More probably, the effect is to open up another mechanistic route from **1** to **2** by virtue of the hydride abstracting capability of $AlCl_3$. The results of experiment 5 (Table II) show that, although equilibrium is reached in transfer of pentyl groups between benzene and toluene in about 1 min, only 3% of rearrangement of **1** to **2** has occurred; the rearrangement of the *tert*-pentyl groups attached to both benzene and toluene then occurs progressively.

We have demonstrated previously[17] that the addition of an alkyl halide to $AlCl_3$ augments its hydride abstracting capability. When the transalkylations between *tert*-pentylbenzene and toluene were repeated, using $AlCl_3$–CH_3NO_2, but with the addition of 1 mol equiv of isopropyl chloride, extensive rearrangement of the pentyl side chain was observed (experiments 6 and 7, Table II). It is noteworthy that 14% of rearrangement of **1** to **2** occurred before significant para–meta equilibration of the *tert*-pentyltoluenes took place (experiment 6), in contrast to the results of experiments 2 and 5. Apparently the carbonium ion source provided by the isopropyl chloride, in conjunction with even the moderated catalyst, produces a medium capable of initiating and sustaining the hydride exchanges required for the intramolecular mechanism,[7] so that **1** → **2** rearrangement becomes faster than transalkylation and reorientation.

(17) R. M. Roberts, A. A. Khalaf, and R. N. Greene, *J. Amer. Chem. Soc.*, **86**, 2846 (1964).

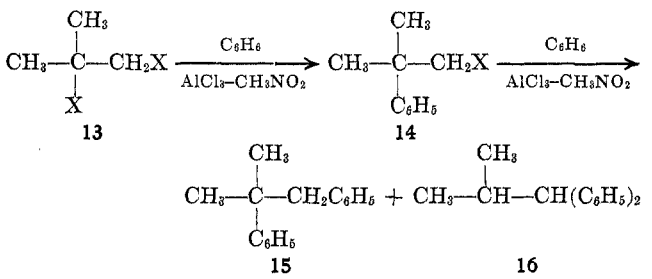
Consistent with this theory is the finding that 2-chloro-3-methyl-3-phenylbutane (**10a**) produced a mixture of *tert*-pentylbenzene (**1a**) and 2-methyl-3-phenylbutane (**2a**) upon treatment with $AlCl_3$–CH_3NO_2 and methylcyclohexane, which serves as a hydride donor. The proportion of **1a**:**2a** changes from an initial (5 min) value of 56:44 to 33:67 after 48 hr. Referring to Scheme I, one may rationalize the formation of these products in terms of the same intermediates (**5a**–**9a**) postulated for the intramolecular mechanism for rearrangement of **1a** to **2a**.

Turning now to the problem of deciding which of these intermediates constitute the most probable pathway for the intramolecular mechanism, we had on hand information pointing up the importance of phenyl participation in such reactions. 1,3-Dichloro-3-methylbutane (**11**) reacts with benzene in the presence of $AlCl_3$–CH_3NO_2 to produce 1-chloro-3-methyl-3-phenylbutane (**12**), and no diphenylpentane.[18] On the other



11 **12**

hand, treatment of either 1,2-dibromo-2-methylpropane (**13**, X = Br) or 1-chloro-2-methyl-2-phenylpropane (neophyl chloride, **14**, X = Cl) with $AlCl_3$–CH_3NO_2 yields a mixture of the two isomeric diphenylbutanes, **15** and **16**.[19] The failure of alkylation to occur at the



13 **14** **15** **16**

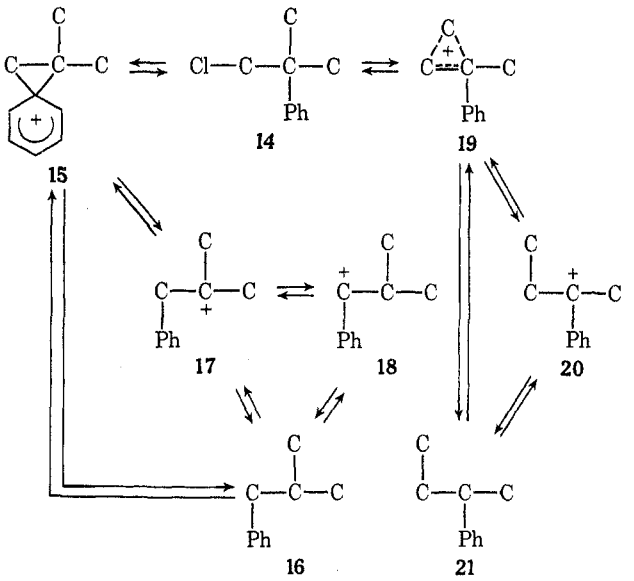
primary carbon atom in **12**, whereas it occurs readily in the reaction of **14** under the same experimental conditions, strongly suggests phenyl participation as a driving force in the latter case.

Additional evidence bearing on the probability of phenyl participation, to produce a phenonium ion intermediate (**5**), rather than methyl participation, to produce a bridged methyl intermediate (**6**), was obtained from a study of the reaction of **14** (X = Cl) with $AlCl_3$–CH_3NO_2 and methylcyclopentane, which may serve as a hydride donor. This system is similar to that containing **10a** in that both phenyl and methyl may participate in the hydride abstraction, but it is different in that different products should be formed after hydride donation, as shown in Scheme II. Phenyl participation should produce isobutylbenzene (**16**), whereas methyl participation should yield *sec*-butylbenzene (**21**). When this experiment was performed and the butylbenzene fraction of the reaction mixture was examined by gas chromatography and infrared spectrometry, it was found to consist of isobutylbenzene exclusively. Unmodified $AlCl_3$ was found to give the same result.

(18) L. Schmerling, R. W. Welch, and J. P. West, *J. Amer. Chem. Soc.*, **78**, 5406 (1956).

(19) A. A. Khalaf and R. M. Roberts, *J. Org. Chem.*, **31**, 926 (1966).

SCHEME II



14 **15** **16** **17** **18** **19** **20** **21**

In summary, on the basis of the results of the transalkylation reactions in which *tert*-pentyl groups were transferred between benzene and toluene, and the hydride exchange reactions of **10a** and **14**, we conclude that the rearrangement of **1a** to **2a**, induced by $AlCl_3$ (or by $AlCl_3$–CH_3NO_2 plus isopropyl chloride), takes place by a hydride abstraction process concerted with phenyl participation, producing a phenonium ion intermediate (**5a**).[20] The rearrangement is completed by a second hydride abstraction by the phenonium ion from the side chain of another molecule of hydrocarbon, so that a chain process is set up. Thus, we may now state that the formation of 2-methyl-3-phenylbutane in the aluminum chloride catalyzed reaction of benzene with *tert*-pentyl halides is the result of an initial rapid alkylation, followed by a slower rearrangement of *tert*-pentylbenzene to its isomer by a chain mechanism in which hydride exchange is concerted with phenyl participation.

Experimental Section[21]

Authentic Hydrocarbons.—*tert*-Pentylbenzene, 2-methyl-3-phenylbutane, 2-methyl-3-*p*-tolybutane, and 2-methyl-3-*m*-tolylbutane were available from previous work.[5] *p*-*tert*-Pentyltoluene was obtained by alkylating toluene with *tert*-pentyl alcohol in the presence of concentrated sulfuric acid, bp 212–215°, $n^{24}D$ 1.4885 [lit.[22] bp 86° (12 mm), $n^{20}D$ 1.4965]. Glpc

(20) Although the classical carbonium ions **7**, **8**, and **9** cannot be entirely ruled out as intermediates, there is no experimental evidence supporting them. It is interesting to note that, if one assumed **7a** to be an intermediate produced by hydride abstraction from **1a**, one might logically predict a 1,2-methyl shift to be more probable than a 1,2-phenyl shift on the basis that a tertiary benzyl cation (**9a**) would result from the former and only a tertiary alkyl cation (**8a**) from the latter process. The experimental results from the reaction of **14** indicate that phenyl participation represents a stronger driving force than the small difference in stability of cations such as **9a** (or **20**) and **8a** (or **17**), and indeed it appears that the formation of **7a** by a hydride abstraction that does not involve phenyl participation is unlikely.

(21) Microanalysis were performed by Chemalytics, Inc., Tempe, Ariz. The nmr spectra were determined on a Varian A-60 unless specified otherwise. A Beckman IR-5A spectrophotometer was used to record the ir spectra. The glpc analysis was carried out using a Varian Aerograph Hy-Fi Model 600-D instrument; the columns employed were either a 50 × 0.125 in. silicone oil DC 550 Hypak column operated at 150–160° with nitrogen carrier gas at 60 psi or a 16 ft × 0.125 in. DEGA (25%) column operated at 120–130° with nitrogen carrier gas at 22 psi. The identity and purity of starting materials and products were determined by glpc, ir, and nmr analysis.

(22) J. Colonge and L. Pichat, *Bull. Soc. Chim. Fr.*, 177 (1949).

analysis of the product indicated the presence of not more than 3% of the meta isomer.

Synthesis of 2-Chloro-3-methyl-3-phenylbutane. 3-Methyl-3-phenyl-2-butanone.—Phenyl-2-propanone (26.8 g, 0.2 mol) dissolved in 50 ml of dry dimethyl sulfoxide was added under nitrogen at room temperature over a period of 30 min to a stirred slurry of 50% sodium hydride (19.2 g, 0.4 mol) in 100 ml of dry dimethyl sulfoxide. After the addition, the reaction mixture was stirred for another hour at room temperature. Methyl iodide (56.8 g, 0.4 mol) was added dropwise at such a rate that the temperature was kept below 30°. The reaction mixture was then stirred at room temperature for 4 hr after which it was poured into 1000 ml of water and extracted with ether. The ether solution was washed several times with water and dried over anhydrous magnesium sulfate, and ether was removed using a rotatory evaporator. Distillation of the residue gave 21 g (70%) of 3-methyl-3-phenyl-2-butanone: bp 66–67° (0.7 mm), n^{25}D 1.5072 [lit.[23] bp 76–77° (15 mm), n^{25}D 1.5078]; nmr (CCl_4) δ 7.21 (s, 5, aromatic), 1.82 (s, 3, CH_3CO), and 1.42 ppm (s, 6, gem methyls).

3-Methyl-3-phenyl-2-butanol.—Reduction of 3-methyl-3-phenyl-2-butanone with sodium borohydride in refluxing methanol following standard procedures gave 3-methyl-3-phenyl-2-butanol in 94% yield: bp 80–81° (0.9 mm), n^{25}D 1.5195; nmr (CCl_4) δ 7.2 (m, 5, aromatic), 3.73 (quartet, 1, sec-CH, J = 6.5 Hz), 2.16 (s, 1, -OH), 1.26 and 1.25 (two overlapping singlets, 6, gem diastereomeric methyls), and 0.91 ppm (d, 3, CH_3, J = 6.5 Hz). *Anal.* Calcd for $C_{11}H_{16}O$: C, 80.42; H, 9.82. Found: C, 80.23; H, 10.08.

2-Chloro-3-methyl-3-phenylbutane.—A solution of thionyl chloride (13 g, 0.11 mol) in pyridine (8.69 g, 0.11 mol) was added to a stirred, cooled solution of 3-methyl-3-phenyl-2-butanol (16 g, 0.1 mol) at such a rate that the temperature did not exceed 5°. After addition was complete, the mixture was heated at 40° for 2 hr. The reaction mixture was diluted with water and extracted with ether, and the ether layer was washed with water, dilute sodium bicarbonate, and finally with water, and then dried over anhydrous magnesium sulfate. Careful vacuum distillation gave 12 g (66%) of the title compound: bp 80° (1.2 mm); nmr (CCl_4) δ 7.17 (s, 5, aromatic), 2.99 (quartet, 1, CHCl, J = 7 Hz), 1.51 (s, 3, first diastereomeric gem CH_3), 1.43 (s, 3, second diastereomeric gem CH_3), and 1.47 ppm (doublet with lower field signal overlapping the first diastereomeric gem methyl, 3, CH_3, J = 7 Hz). These overlapping signals were resolved when the sample was analyzed on the HA-100. *Anal.* Calcd for $C_{11}H_{15}Cl$: Cl, 19.41. Found: Cl, 19.31.

General Transalkylation Procedure.—Reactions were carried out in stoppered flasks with magnetic stirring. The hydrocarbons were placed into the flask and the catalyst ($AlCl_3$ or $AlCl_3$–CH_3NO_2) was added in one portion to the stirred solution. Samples were withdrawn at intervals and quenched with water, and the organic material was extracted with ether. The dried ether extracts were analyzed by glpc. All reactions were carried out at room temperature (~25°). Other reaction conditions are summarized in Tables I and II.

The isomer distributions were established using glpc. Results in Tables Iand II are given in normalized mole % of total monopentylarenes.

Reaction of Neophyl Chloride (1-Chloro-2-methyl-2-phenylpropane) with $AlCl_3$ in Methylcyclopentane.—Neophenyl chloride (1.68 g, 0.01 mol) was added all at once to a stirred slurry of $AlCl_3$ (0.133 g, 0.001 mol) in 10 ml of methylcyclopentane. The reaction m xture was stirred for 0.5 hr and then decomposed with water, and the products extracted with ether. The ether layer was washed, dried, and distilled. Among other fractions, this gave 0.1 g of a cut, bp 57–58° (2.15 mm). This was found by vpc and ir to contain isobutylbenzene with no detectable amounts of *sec*-butylbenzene.

Reaction of Neophyl Chloride with $AlCl_3$–CH_3NO_2 in Methylcyclopentane.—The same procedure and amounts of reagents s described above were used except that the catalyst was $AlCl_3$ dissolved in 1.5 g of CH_3NO_2 and the reaction time was extended to 1.5 hr. After processing and distillation of the product, a fraction with bp 55–56° (2.0 mm) was found by glpc and ir to contain isobutylbenzene with no detectable amounts of the secondary isomer.

Reaction of 2-Chloro-3-methyl-3-phenylbutane with $AlCl_3$–CH_3NO_2 in Methylcyclohexane.—2-Chloro-3-methyl-3-phenylbutane (1.82 g, 0.01 mol) was added all at once to a rapidly stirred solution of $AlCl_3$ (0.133 g, 0.001 mol) and CH_3NO_2 (0.61 g, 0.01 mol) in methylcyclohexane (3.92 g, 0.04 mol). Samples were withdrawn after various time intervals, decomposed, and analyzed by glpc for monopentylbenzenes. The following proportions of *tert*-pentylbenzene to 2-methyl-3-phenylbutane were found after the times given: 5 min, 56:44; 15 min, 40:60; 2 hr, 40:60; 6 hr, 41:59; 26 hr, 35:65; 48 hr, 33:67.

Treatment of *p-tert*-Pentyltoluene and 2-Methyl-3-*p*-tolylbutane with $AlCl_3$–CH_3NO_2.—The reaction procedure was similar to that described above for transalkylation; a molar ratio of hydrocarbon–$AlCl_3$–CH_3NO_2 of 3.3:1:6 was used.

Starting with *p-tert*-pentyltoluene, the following proportions of *p*- to *m-tert*-pentyltoluene were found after the times given: 1 hr, 94:6; 2 hr, 78:22; 5 hr, 54:46; 24 hr, 30:70. Toluene, as well as two other products with higher retention times than monopentyltoluenes, were also produced and amounted to about 20% of the total aromatics after 24 hr.

Similar treatment of 2-methyl-3-*p*-tolylbutane resulted in no change even after 24 hr.

Registry No.—**1a**, 2049-95-8; **1b**, 4237-70-1; **2a**, 4481-30-5; 3-methyl-3-phenyl-2-butanol, 2977-31-3; **10a**, 25975-92-2.

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