fine coupling constants to calculated spin densities on contiguous carbon atoms. Values of $Q = 24$[23,33,34] have

$$a_H = Q_{CH}\rho_C$$

been used for aromatic nitriles and a value of 27 has been used in nitrogen heterocyclic nitriles. A value of $Q = 27$[19,24] was found to predict hydrogen coupling constants best in this study.

The following equations relate the cyano nitrogen coupling to the spin densities on nitrogen and carbon.

$$a_N(C\equiv N) = (16.1 \pm 0.7)\,\rho_N + (9.0 \pm 4.7)\,\rho_C \text{ (Jones)}[24]$$

$$a_N(C\equiv N) = \pm(23.1 \pm 1.4)\,\rho_N \mp (6.8 \pm 2.2)\,\rho_C$$

(Rieger and Fraenkel)[23]

The nitrogen couplings calculated from the former equation agree better with the observed values and are well within the established error limits of the equation.

The magnitude of the heterocyclic nitrogen coupling is presumed to depend on the spin densities on the nitrogen and on its neighboring carbon atoms. Q^C_{CN}

$$a_N = Q^N_N\,\rho_N + Q^C_{CN}\,\Sigma\rho_C$$

is small and frequently negligible. Values for Q^N_N and Q^C_{CN} in nitrogen heterocyclic anion radicals are 30.9 ± 2 and -2 ± 2, respectively.[35,36] For N-methylphenothyazyl cation radical the value for Q^N_N is 28.8 and Q^N_{CN} is neglected.[28] The latter values give a better fit to the observed heterocyclic nitrogen coupling constants for the neutral and anion radicals described in this work (Table I). For 9-cyanoacridine nitroxide, $a_N = 35.61\rho_N - 0.93\rho_O$ was used.[19]

(33) P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, **37**, 2811 (1962).
(34) E. W. Stone and A. H. Maki, *ibid.*, **38**, 1999 (1963).
(35) E. W. Stone and A. H. Maki, *ibid.*, **39**, 1635 (1963).
(36) P. J. Black and C. A. McDowell, *Mol. Phys.*, **12**, 233 (1967).

An equation similar to the McConnell expression has been employed for methyl proton coupling constants[23,33]

$$a^H_{CCH_3} = Q^H_{CCH_3}\rho_C$$

where $Q^H_{CCH_3} = 27.2$. The N-methyl proton coupling has been related to the spin density on nitrogen in N-methylphenothiazyl cation radical by a similar relationship[28]

$$a^H_{NCH_3} = Q^H_{NCH_3}\rho_N$$

with $Q^H_{NCH_3} = 27.2$ giving satisfactory results. A value of $Q^H_{NCH_3} = 27.2$ gave good results for the neutral radicals in Table I.

Conclusion

The formation of radicals or radical anions in the cyanide ion addition to compounds with electrophilic sites in air-saturated dipolar solvents appears to be a general reaction. Whether the radical produced is
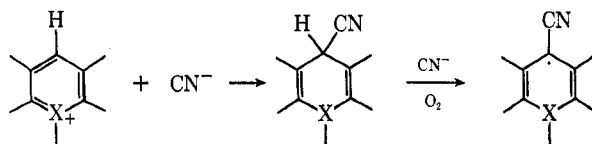
neutral or charged depends on the charge of the substrate; positively charged compounds produce neutral radicals and neutral compounds produce radical anions. The radical-producing reaction is probably facilitated by the acidifying effect of the cyanide group on the α proton.

Registry No.—N-Ethyl-9-thioacridone ketyl, 22027-35-6; N-methyl-9-t-butoxyacridanyl radical, 22027-36-7.

Alkylations of Benzene and *p*-Xylene with 1-Chloro-2-methylpropane, 1-Chloro-2-methylbutane, and 2-Chloro-3-methylbutane. Effects of Steric Hindrance and Catalyst Activity on Product Distribution[1a]

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Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712

Alkylation of *p*-xylene with isobutyl chloride (1-chloro-2-methylpropane) and aluminum chloride gave isobutyl- and *sec*-butyl-*p*-xylene in low yields; larger amounts of *t*-butyltoluene derivatives were formed. Alkylation of benzene with 1-chloro-2-methylbutane and 2-chloro-3-methylbutane, using aluminum chloride at 25°, gave 2-methyl-3-phenylbutane and *t*-pentylbenzene in the ratio 82:18. In reactions at 0°, the initial major product from both pentyl chlorides was *t*-pentylbenzene; the proportion of 2-methyl-3-phenylbutane increased with time until an 82:18 ratio was reached. Using nitromethane-modified aluminum chloride catalyst, the only monoalkylation product from either pentyl chloride was *t*-pentylbenzene. Alkylation of *p*-xylene with 1-chloro-2-methylbutane and aluminum chloride gave 2-methyl-3-*p*-xylylbutane as the only pentylxylene; 2-methyl-3-tolylbutane and *t*-pentyltoluene were also produced, in a ratio of 88:12. The data show that alkylations of benzene by the primary and secondary pentyl chlorides of the present study produce *t*-pentylbenzene initially, followed by isomerization to 2-methyl-3-phenylbutane when unmodified aluminum chloride catalyst is used. Mechanisms for the reactions are discussed—in particular, alternative possibilities for the production of 2-methyl-3-phenylbutane.

The alkylation of benzene with either *t*-butyl or isobutyl chloride and aluminum chloride catalyst gives only *t*-butylbenzene.[2] Alkylation of *o*-xylene with

(1) (a) Paper XXII in the series "New Friedel-Crafts Chemistry." Presented in part at the Tetrasectional American Chemical Society Meeting, Bartlesville, Okla., March 15, 1969; (b) Robert A. Welch Predoctoral Fellow, 1963–1966, NASA Trainee, 1966–1967.
(2) R. M. Roberts and D. Shiengthong, *J. Amer. Chem. Soc.*, **82**, 732 (1960).

t-butyl alcohol and boron trifluoride gives 1,2-dimethyl-4-*t*-butylbenzene.[3]
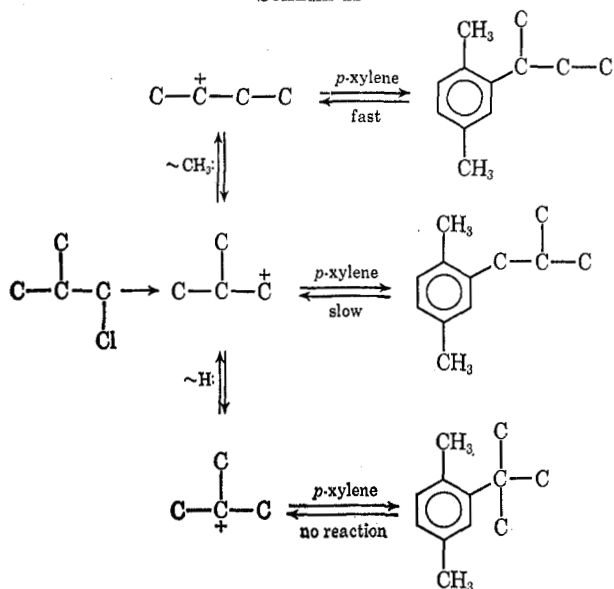
Similar alkylations of *p*-xylene, where substitution *ortho* to a methyl group must occur, are, however, quite different. Considerable steric hindrance must be overcome to accomplish introduction of a tertiary group

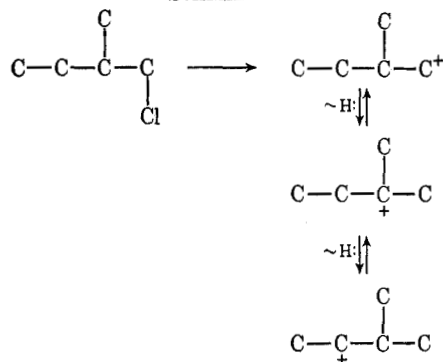(3) D. V. Nightingale and J. R. Janes, *ibid.*, **66**, 154 (1944).

SCHEME I
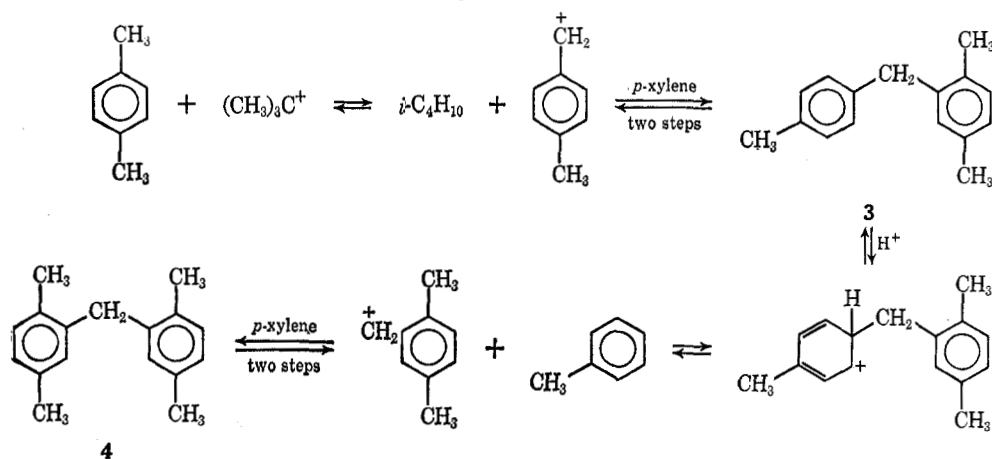
SCHEME II

SCHEME III

adjacent to a methyl group.[4,5] This hindrance is probably felt mainly during collapse of the intermediate σ complex to product,[6] since in the σ complex the tertiary carbon is situated out of the plane of the ring, but in the collapse to product it becomes planar, and considerable steric influence from groups adjacent to the point of attachment is encountered. The steric effect is powerful enough to enable separation of *o*- and *m*-xylene from *p*-xylene by tertiary butylation.[7-9]

Friedman[10] and Schmerling[11] showed that the principal products from the reaction of *t*-butyl chloride and *p*-xylene with aluminum chloride catalyst were *m*- and *p*-*t*-butyltoluene (1), 3,5-di-*t*-butyltoluene (2), 2-(*p*-methylbenzyl)-*p*-xylene (3), and di-*p*-xylylmethane (4). The formation of 3 and 4 was explained in terms of Scheme I. Compounds 1 and 2 may arise

from *t*-butylation of the toluene produced, as outlined in Scheme I.

One object of the present research was to investigate the alkylation of *p*-xylene with isobutyl chloride (1-chloro-2-methylpropane). A system such as outlined in Scheme II might result. It seemed possible that steric resistance to tertiary butylation might allow alkylation by a primary or secondary carbon atom to occur, resulting in formation of isobutyl- or *sec*-butyl-*p*-xylene.

Moreover, in extending this idea to the pentyl system, an interesting new possibility is presented. Rearrangement of the primary alkyl chloride 1-chloro-2-methylbutane, the next higher homolog of isobutyl chloride, may possibly provide a secondary alkylating agent, as well as the expected tertiary carbonium ion (Scheme III).

The alkylation of benzene with *t*-pentyl chloride using trace amounts of aluminum chloride[12] or aluminum chloride modified by nitromethane[10] gave only *t*-pentylbenzene. Larger quantities of AlCl₃ gave a mixture of *t*-pentylbenzene (10) and 2-methyl-3-phenylbutane (14).[12,13] The latter result was attributed to initial alkylation to produce 10, followed by rearrangement to 14. When steric hindrance was introduced, as in the alkylation of *p*-xylene with *t*-pentyl chloride and AlCl₃,[11] with 3-methyl-1-butene and AlCl₃ with HCl promotion,[10] or with *t*-pentyl chloride and AlCl₃/CH₃NO₂,[10] the only monoalkylation product found was 2-methyl-3-*p*-xylylbutane. These results were interpreted as indicating that, when the *t*-pentyl

(4) H. C. Brown and K. L. Nelson, *J. Amer. Chem. Soc.*, **75**, 24 (1953).
(5) M. J. Schlatter and R. D. Clark, *ibid.*, **75**, 361 (1953).
(6) K. L. Nelson and H. C. Brown in "The Chemistry of Petroleum Hydrocarbons," B. J. Brooks, S. S. Kurtz, C. E. Boord, and L. Schmerling, Ed., Reinhold Publishing Corp., New York, N. Y., 1955, p 501.
(7) A. Schneider, U. S. Patent 2,648,713 (1953); *Chem. Abstr.*, **48**, 8258 (1954).
(8) M. J. Schlatter, *J. Amer. Chem. Soc.*, **76**, 4952 (1954).
(9) B. B. Carson, *et al.*, *Ind. Eng. Chem.*, **48**, 1180 (1956).
(10) B. S. Friedman, F. L. Morritz, C. J. Morrissey, and R. Koncos, *J. Amer. Chem. Soc.*, **80**, 5867 (1958).
(11) L. Schmerling, J. P. Luvisi, and R. J. Welch, *ibid.*, **81**, 2718 (1959).

(12) B. S. Friedman and F. L. Morritz, *ibid.*, **78**, 2000 (1956).
(13) L. Schmerling and J. P. West, *ibid.*, **76**, 1917 (1954).

TABLE I

ALKYLATIONS OF p-XYLENE WITH BUTYL CHLORIDES

Method[a]	Chloride	Mol ratio[b]	Time, hr	Yield of products, %[c]		
				Isobutyl- and sec-butyl-p-xylene	m- and p-t-butyl-toluene	3,5-Di-t-butyl-toluene
A	Isobutyl	4:1:0.1	1	3	6	10
A	Isobutyl	4:1:0.1	6	3[d]	8	10
A	Isobutyl	8:1:0.1	3	3	15	8
B	Isobutyl	4:1:0.1	6	4[e]	18	2
A	t-Butyl	8:1:0.1	3	0	15	7
C	sec-Butyl	2:1:0.05	2	50[f]	0	0

[a] Method A: AlCl₃ was added to a stirred solution of p-xylene, butyl chloride, and hexane at 0°. Method B: isobutyl chloride was added dropwise to a stirred mixture of p-xylene, AlCl₃, and hexane at 0°. Method C: p-xylene was cooled to 15° and AlCl₃ was added; sec-butyl chloride was added dropwise as the temperature was rapidly lowered to 5°. [b] p-Xylene/butyl chloride/AlCl₃. [c] Determined by glpc, based on the butyl chloride used. [d] 65% sec-butyl-p-xylene, 35% isobutyl-p-xylene (nmr). [e] 60% sec-butyl-p-xylene, 40% isobutyl-p-xylene (nmr). [f] 100% sec-butyl-p-xylene (nmr).

cation is prevented from reacting with p-xylene by steric effects, the sec-pentyl cation

$$C-C-\overset{C}{\overset{|}{C}}-C$$
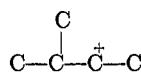
in equilibrium with it, although it is in low concentration, has the opportunity of becoming the predominant—if not the only—alkylating species.[10,14,15] Although this seems to be a very reasonable explanation for the formation of 2-methyl-3-p-xylylbutane, the possibility remains that the mechanism proposed earlier[13] for the formation of 2-methyl-3-phenylbutane is correct in cases where steric hindrance does not preclude attachment of t-pentyl groups to the aromatic ring.

We wish now to present new data obtained from alkylations of benzene and p-xylene with 1-chloro-2-methylpropane, 1-chloro-2-methylbutane, and 2-chloro-3-methylbutane, and to puruse further the question as to the stage, or stages, at which rearrangement occurs in Friedel–Crafts alkylations with pentyl halides.

Results and Discussion

Alkylations with Butyl Chlorides.—Alkylations of p-xylene with isobutyl chloride (1-chloro-2-methylpropane) and t-butyl chloride gave very similar results, with one outstanding exception. A comparison of the third and fifth experiments of Table I shows that alkylation with isobutyl chloride gave a mixture (3%) of isobutyl- and sec-butyl-p-xylene, while alkylation with t-butyl chloride gave neither of these products in detectable amounts. The reactions of both isobutyl chloride and t-butyl chloride gave m- and p-t-butyltoluene and 3,5-di-t-butyltoluene in the same amounts, within the limits of precision of the gas chromatographic analysis.

These alkylations with isobutyl chloride were carried out at 0° with small amounts of catalyst to ensure that any electrophilic attack on the p-xylene would occur in a sterically hindered position *ortho* to a methyl group, i.e., with no possibility of methyl reorientation having preceded alkylation.[16] As mentioned above, low yields

of isobutyl- and sec-butyl-p-xylene were detected. These products were not present in reaction mixtures from t-butyl chloride and p-xylene, nor were any isobutyl- or sec-butylbenzene found as products of the alkylation of benzene by either isobutyl chloride or t-butyl chloride.[1] Thus, the expectation was realized that, owing to the steric hindrance encountered by the bulky t-butyl cation, the isobutyl and sec-butyl cations[17]—with much smaller steric requirements—had an opportunity to alkylate the p-xylene ring.

Analysis by nmr of the butyl-p-xylene mixtures isolated in the second and fourth experiments of Table I showed them to be composed of a nearly 2:1 ratio of sec-butyl- to isobutyl-p-xylene. This apparently represents direct competitive alkylation by the secondary and primary alkylating agents, since interconversion of sec-butyl- and isobutyl-p-xylene does not occur under the conditions of the alkylation.[18] This is borne out by the results of the sixth experiment, in which alkylation with sec-butyl chloride gave only sec-butyl-p-xylene.

Alkylations with Pentyl Chlorides.—The alkylation of benzene with 1-chloro-2-methylbutane closely paralleled the previously reported alkylation with t-pentyl chloride.[13] The reaction carried out at 25° (Table II, first experiment) gave 80% 2-methyl-3-phenylbutane (**14**) and 20% t-pentylbenzene (**10**) after 0.25 hr, and this ratio changed only slightly (to 83:17) over a 4-hr reaction time. This is very similar to the 85:15 distribution found by Schmerling and West[13] and apparently represents an equilibrium composition of the two pentylbenzenes.[19] When the alkylation was carried out at a lower temperature, the initial reaction mixture (0.25 hr) contained **10** as the major alkylation product, and the proportion of **14** increased until an equilibrium ratio (82:18) was reached after 4 hr. When the catalyst was modified by the addition of nitromethane (Table II, third experiment), the exclusive initial monoalkylation product was t-pentylbenzene (**10**), with a change to only 4% 2-methyl-3-phenyl-

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

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

(16) Absence of methyl reorientation under alkylation conditions was demonstrated by transalkylations between alkylxylenes and benzene. The alkylbenzene and xylene so produced could be characterized unambiguously. See Experimental Section.

(17) There is serious doubt that isobutyl cations, or any other primary carbonium ions, exist as such in the alkylating media, but for the sake of simplicity they will be referred to and represented in this way throughout the paper.

(18) R. M. Roberts, Y. W. Han, C. H. Schmid, and D. A. Davis, *J. Amer. Chem. Soc.*, **81**, 640 (1959). The equilibrium concentration of sec-butyl- and isobutylbenzene (1:2)[19] is the inverse of the ratio of the sec-butyl- and isobutyl-p-xylene found (2:1).

(19) There is probably not a true thermodynamic equilibrium between the two arenes, but this composition represents the relative stability of the two arenes to the various competing reactions that occur during a considerable time period in the presence of aluminum chloride.

TABLE II

ALKYLATIONS OF BENZENE WITH PENTYL CHLORIDES[a]

Pentyl chloride	Temp, °C	Time, hr	Yield, %[b]	Yield of products,[c] %	
				t-Pentylbenzene	2-Methyl-3-phenylbutane
1-Chloro-2-methylbutane	25	0.25		20	80
		1.0		19	81
		4.0	65	17	83
	0–5	0.25		56	44
		1.0		26	74
		4.0	69	18	82
	25[d]	0.25		100	0
		5.0		97	3
		11		96	4
		23	42	96	4
2-Chloro-3-methylbutane	0–5	0.25		43	57
		1.0		20	80
		4.0		18	82
	25[d,e]	0.25		100	0
		5.0		100	0
		11		100	0
		24		98	2

[a] Mole ratio, benzene/phenyl chloride/AlCl₃ = 5:1:0.1. [b] Combined yield of pentyl benzene isomers. [c] Relative percentages of pentylbenzene isomers, by glpc. [d] Catalyst modified by nitromethane; mol ratio, benzene/pentyl chloride/AlCl₃/CH₃NO₂ = 5:1: 0.1:1. [e] This experiment was performed by Dr. A. A.Khalaf.

butane (14) occurring after 23 hr at 25°. No 2-methyl-butylbenzene (7) was produced with either catalyst.

Alkylations with 2-chloro-3-methylbutane, which would give 14 directly, were also investigated, with the results shown in Table II. It may be seen that the products were very similar to those from 1-chloro-2-methylbutane. With AlCl₃ catalyst at 0°, almost equal amounts of t-pentylbenzene (10) and 2-methyl-3-phenylbutane (14) were produced initially, with a subsequent change to the equilibrium composition (82% 14, 18% 10). With nitromethane-modified catalyst, the exclusive monoalkylation product was t-pentylbenzene (10), and no significant change occurred during a 24-hr period.

The results of the alkylation of p-xylene with 1-chloro-2-methylbutane (Table III) closely paralleled those

TABLE III

ALKYLATION OF p-XYLENE
WITH 1-CHLORO-2-METHYLBUTANE[a] AT 0°

Time, hr	3-Methyl-2-p-xylylbutane	t-Pentyltoluene (meta/para)	2-Methyl-3-tolylbutane (meta/para)
0.25	80		12 (64:36)
1.0	66		25 (59:41)
3.0	40	6 (60:40)	47 (51:49)
6.0	31		53

[a] Mol ratio of p-xylene/pentyl chloride/AlCl₃ = 4:1:0.1. [b] Determined by glpc and nmr analysis.

reported for alkylation with t-pentyl chloride.[10,13] The only monoalkylation product from the primary chloride was the same as from the tertiary chloride, 2-methyl-3-p-xylylbutane. No t-pentyl-p-xylene was formed because of steric hindrance. The 3-methyl-2-butyl cation, which is produced by isomerization of the original primary chloride, has a much smaller steric requirement than the t-pentyl cation and alkylates p-xylene readily. No alkylation product corresponding to the original primary chloride was detected.

Examination of the pentyltoluenes produced in this reaction[20] yielded an interesting result: the amounts of 2-methyl-3-tolylbutane (47%) and t-pentyltoluene (6%) were in a ratio (88:12) similar to that of 2-methyl-3-phenylbutane and t-pentylbenzene (82:18) produced by alkylation of benzene with the same pentyl chloride (Table II).

The Mechanism of Isomerization of t-Pentylbenzene to 2-Methyl-3-phenylbutane.—The results from alkylations of benzene with the pentyl chlorides can best be discussed in terms of Scheme IV, which is an extension and elaboration of Scheme III. Treatment of 1-chloro-2-methylbutane (5) and 2-chloro-3-methyl-butane (12) with AlCl₃ gives the corresponding carbonium ions 6 and 13 (or their equivalent complexes with the catalyst[17]), and these rapidly isomerize by 1,2-hydride shifts to the tertiary carbonium ion 9. This ion (9) is also produced directly from t-pentyl chloride (8), of course. Regardless of which of the three pentyl chlorides is used as starting material, and of whether AlCl₃ or a milder catalyst is used, 9 rapidly alkylates benzene to produce t-pentylbenzene (10). Under suitable experimental conditions, 10 will be the observed product or a major product. "Suitable" conditions include a very small amount of AlCl₃[12] or a milder catalyst such as BF₃,[11] ZrCl₄,[11] or AlCl₃–CH₃NO₂, as in the present work. At a low temperature and with a short reaction time, the use of even unmodified AlCl₃ with 5 and 12 gives 10.

There are two plausible explanations for the subsequent isomerization of t-pentylbenzene (10) to 2-methyl-3-phenylbutane (14). The first of these involves a dealkylation–realkylation mechanism that is essentially a revision and elaboration of the Friedman[10]–Baddeley[14]–Gould[15] mechanism. Although 10 is formed more rapidly than 14, it is also dealkylated more readily and, if equilibrium is reached, 14 may become the major product. The rapid initial formation

(20) These derivatives are produced by alkylation of toluene, which results from the transaralkylation reactions depicted in Scheme I. They were not reported by Friedman[10] or Schmerling.[11]

SCHEME IV
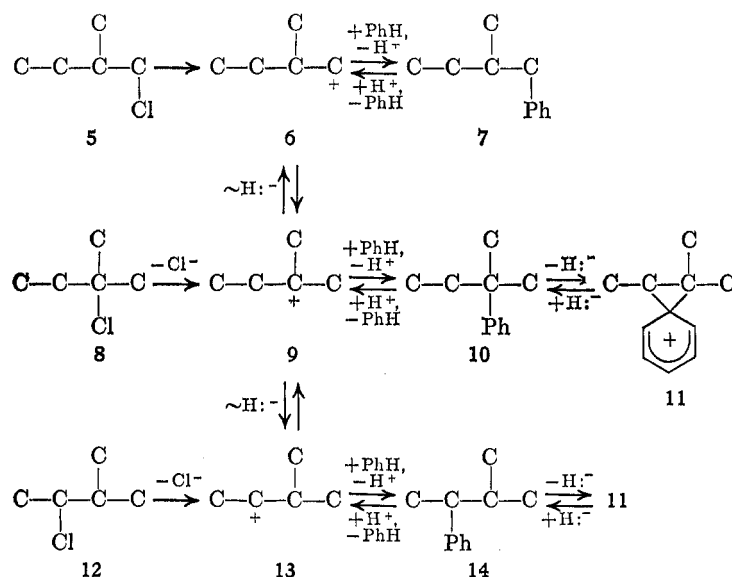
of **10**, followed by a slower isomerization of **10** to **14**, may thus represent another example of kinetic control *vs.* equilibrium control of products. The experiments in which **10** is found to be the sole or major product exhibit kinetic control, whereas those in which **14** is the major product exhibit equilibrium control. The failure of **10** to rearrange when weak alkylation catalysts are employed ($AlCl_3-CH_3NO_2$, $FeCl_3$, BF_3, $ZrCl_4$) must be ascribed to the fact that the rate of dealkylation-realkylation is so low that equilibrium is not established.

An alternative explanation for the isomerization of **10** to **14** is the one originally proposed by Schmerling and West.[13] According to this explanation, **10** rearranges to **14** *via* the intermediate phenonium ion **11**. Rearrangement by $AlCl_3$ and nonrearrangement by $AlCl_3-CH_3NO_2$ and other mild catalysts is attributed to the ability of $AlCl_3$ to abstract hydride ions, and thus produce **11**, whereas the other catalysts lack this ability.[21]

There is evidence that mechanisms of both of these types operate, and the possibility that both are involved in the rearrangement of **10** to **14** should be considered. In the reactions of *t*-pentyl chloride and 1-chloro-2-methylbutane with *p*-xylene, which yield 2-methyl-3-*p*-xylylbutane as the only pentylxylene, intermediate formation of *t*-pentylxylene is prohibited by steric hindrance. The rearranged product, then, must arise from isomerization of **6** and **9** to **13** before alkylation. Another essential step of the dealkylation-realkylation mechanism for rearrangement of **10** to **14** is the dealkylation of **10** to produce benzene and **9**. This type of reaction is assumed to be involved in the transalkylations of *t*-alkylarenes[22] and in the formation of alkanes from *t*-alkylarenes heated with aluminum chloride.[28] These data taken together give some credibility to the route **10** → **9** → **13** → **14**.

On the other hand, the rearrangement of isobutylbenzene to *sec*-butylbenzene[18,21] cannot be explained in

terms of dealkylation-realkylation.[24] This rearrangement probably follows a course analogous to the sequence **14** → **11** → **10**.[21,25]

The data in the literature and in this paper do not allow a clear choice between the two alternative mechanisms for the rearrangement of **10** to **14**. Results from additional experiments which we believe do provide the basis for this choice are being reported separately.[26] The present work does indicate quite clearly that the initial alkylation product from benzene and *t*-pentyl chloride, 1-chloro-2-methylbutane, and 2-chloro-3-methylbutane is *t*-pentylbenzene. When mild catalysts and conditions are employed, the initial product is stable. When stronger catalysts and/or conditions are employed, *t*-pentylbenzene is isomerized to 2-methyl-3-phenylbutane.

Experimental Section

The structure and purity of all starting materials and products were checked by glpc, ir, and nmr analyses.[27]

A. Synthesis of Alkyl Chlorides.—The method described by Vogel[28] was used for the preparation of the primary and secondary halides from the alcohols. A Carbowax 20M column (6 ft × 0.25 in.) was used for glpc analysis.

B. Synthesis of Authentic Hydrocarbons.—A silicone gum rubber (SE-30) column (6 or 12 ft × 0.25 in.) was used for glpc analysis of the butylxylenes, and a silicone oil DC-550 Hypak column (50 ft × 0.125 in.) was used for glpc analysis of the pentylarenes.

2-Methyl-3-*m*-tolylbutane.—Reaction of *m*-bromotoluene, magnesium turnings, and methyl isopropyl ketone in anhydrous ether gave the carbinol. The crude carbinol was hydrogenated,

(21) C. D. Nenitzescu, I. Necsoiu, A. Glatz, and M. Zalman, *Chem. Ber.*, **92**, 10 (1959).

(22) (a) R. H. Allen, *J. Amer. Chem. Soc.*, **82**, 4856 (1960); (b) G. A. Olah, S. H. Flood, and M. E. Moffatt, *ibid.*, **86**, 1060 (1964).

(23) (a) R. M. Roberts, E. K. Baylis, and G. J. Fonken, *ibid.*, **85**, 3454 (1963); (b) V. N. Ipatieff and H. Pines, *ibid.*, **59**, 56 (1937).

(24) R. M. Roberts, *Chem. Eng. News*, **43**, 104 (1965).

(25) Another similar mechanism involving diphenylbutane intermediates has been suggested as an additional or alternative mechanism for the iso-butylbenzene–*sec*-butylbenzene interconversion; *cf.* R. M. Roberts, A. A. Khalaf, and R. N. Greene, *J. Amer. Chem. Soc.*, **86**, 2846 (1964).

(26) A. A. Khalaf and R. M. Roberts, paper in preparation.

(27) Infrared spectra were recorded on a Beckman IR-5A instrument. Nmr data were obtained using a Varian A-60 spectrometer with TMS as internal standard. Analytical gas chromatography (glpc) was performed with either a Beckman GC-2A or a Wilkens Aerograph A-600 instrument; preparative glpc separations were made with a Wilkens A-700 (Autoprep) instrument. Details of columns are given in the individual experimental descriptions.

(28) A. I. Vogel, "A Textbook of Practical Organic Chemistry," 3rd ed, Longmans, Green and Co., New York, N. Y., 1956, p 384.

using the procedure described above, to 2-methyl-3-*m*-tolylbutane, bp 126–134° (100–120 mm).

Anal. Calcd for C₁₂H₁₈: C, 88.89; H, 11.11. Found: C, 88.38; H, 11.32.

2-Methyl-3-*p*-tolylbutane.—The method was exactly the same as that described for 2-methyl-3-*m*-tolylbutane, except that *p*-bromotoluene was used in place of *m*-bromotoluene. The 2-methyl-3-*p*-tolylbutane thus obtained boiled at 132–144° (100–110 mm).

Anal. Calcd for C₁₂H₁₈: C, 88.89; H, 11.11. Found: C, 88.36; H, 11.42.

2-Methyl-3-phenylbutane.—Reaction of bromobenzene, magnesium turnings, and methyl isopropyl ketone in anhydrous ether gave methylisopropylphenylcarbinol. Hydrogenation with 5% palladium on charcoal catalyst plus a few drops of 70% perchloric acid in glacial acetic acid solvent gave 2-methyl-3-phenylbutane, bp 185–189° (lit.[29] bp 188–189°).

C. Test for Methyl Reorientation by Transalkylation.—Benzene (74 mmol), isobutyl-*p*-xylene (18.5 mmol), and aluminum chloride (18.5 mmol) were stirred at 25° for 21 hr. After the reaction mixture was quenched and the organic products were worked up in the usual way, the butylbenzene and xylene fractions were isolated by preparative gas chromatography and shown to consist of isobutylbenzene (100%) and *p*-xylene (95%) and *m*-xylene (5%). This experiment was typical of several which were performed.

D. Alkylations. 1. *p*-Xylene with Butyl Chlorides.—These alkylations were carried out using one of the three methods described in Table I. The reaction vessel generally consisted of a three-necked flask fitted with thermometer, condenser with CaCl₂ drying tube, and dropping funnel; it was equipped for stirring with a Teflon-covered magnet. The reaction mixtures were hydrolyzed by pouring into a stirred ice–hydrochloric acid–ether mixture. The organic layer was separated, washed with saturated NaHCO₃ solution and brine, and dried over CaCl₂. Most of the solvent was removed on a rotary evaporator, and the remaining liquid was subjected to the required analysis. The results are presented in Table I.

In the first five experiments of Table I, the products were isolated by preparative glpc (Bentone-34 column, 10 ft × 0.25 in.). The *m*- and *p*-*t*-butyltoluene mixture and the 3,5-di-*t*-butyltoluene were identified by their nmr spectra. The isobutyl- and *sec*-butyl-*p*-xylene appeared as one peak upon glpc analysis. They were identified and analyzed by means of the nmr spectrum of the binary mixture. A quantitative analysis of this isomer mixture could be obtained by comparing the ratios of the nmr signals in the region δ 1.02–1.25 (characteristic of the *s*-butyl isomer) and in the region δ 6.60–7.00 (aromatic protons) from the reaction products with the corresponding ratios obtained from mixtures of known compositions prepared from standards.[30]

The high-boiling residue of the fourth experiment was analyzed by glpc (Carbowax 1000 column, 3 ft × 0.25 in.) and determined to be 2-(*p*-methylbenzyl)-*p*-xylene (9.6% yield) and di-*p*-xylylmethane (28% yield) by comparison with the properties of the alkylation products from the tertiary butylation of *p*-xylene reported by Friedman[10] and by Schmerling.[11]

In the last experiment of Table I, the *sec*-butyl-*p*-xylene was isolated by distillation. It was identified by comparison of glpc retention time and nmr spectrum with those of authentic *sec*-butyl-*p*-xylene.

2. Benzene with Pentyl Chlorides.—The pentyl chloride and benzene were stirred at the desired temperature in a flask fitted with magnetic stirrer, condenser with CaCl₂ drying tube, thermometer, and rubber septum to allow aliquots to be withdrawn by hypodermic syringe. The AlCl₃ was then added and 0.25-ml aliquots were withdrawn at intervals by syringe and quenched with water. The organic layer was analyzed directly by glpc (silicone oil DC-550 Hypak column, 50 ft × 0.125 in.) to determine the pentylbenzene distribution. Finally, the entire reaction mixture was quenched with water. It was worked up in the usual manner, distilled, and analyzed by glpc to determine the yield of pentylbenzenes. The results are given in Table II.

3. *p*-Xylene with 1-Chloro-2-methylbutane.—The same reaction vessel was used as described above. The AlCl₃ was added to the *p*-xylene. This mixture was then cooled and the 1-chloro-2-methylbutane was quickly added dropwise. As before, 0.25-ml aliquots were withdrawn by syringe, quenched with water, and analyzed by glpc (silicone oil DC-550 Hypak column, 50 ft × 0.125 in.). The *t*-pentyltoluene and 2-tolyl-3-methylbutane were isolated as a mixture by preparative glpc. The nmr spectrum of the mixture confirmed that both products were present. The results are summarized in Table III.

A considerable quantity of liquid was collected which boiled at 285–320°. This was apparently a mixture of 2-(*p*-methylbenzyl)-*p*-xylene and di-*p*-xylylmethane, which were reported as products of the tertiary pentylation of *p*-xylene.[10,11]

Registry No.—Benzene, 71-43-2; *p*-xylene, 106-42-3; isobutyl chloride, 513-36-0; 1-chloro-2-methylbutane, 616-13-7; 2-chloro-3-methylbutane, 631-65-2; *t*-butyl chloride, 507-20-0; *sec*-butyl chloride, 78-86-4; 2-methyl-3-*m*-tolylbutane, 22040-30-8; 2-methyl-3-*p*-tolylbutane, 22040-31-9.

(29) A. Klages, *Ber.*, **36**, 3691 (1903).

(30) The pertinent nmr spectra are recorded in the Ph.D. dissertation of S. E. McGuire, The University of Texas at Austin, 1967.