remaining was heated to 130°. At 120° the solid began to melt and, after heating at 130°, a light brown, spongy mass had formed. After heating four hours at 130°, the material was cooled, then chipped loose and mixed with 250 g. of a 1:1 mixture of ice and concentrated hydrochloric acid. The yellow mixture which formed was filtered, the solid residue mixed with 100 g. of 1:1 mixture of ice and concentrated hydrochloric acid and the mixture stirred overnight. The next day the mixture was filtered and the residue extracted with 25 ml. of boiling ethanol. A light yellow residue remained which was dried at 110°. On drying, the material became black; yield 2.61 g. (44%). A 0.5-g. sample of the crude product was chromatographed over 30 g. of silicic acid and eluted with chloroform to give 0.5 g. of a light brown solid, m.p. 184–186°, reported[4] m.p. 187°.

Rearrangement with Solvent.—All runs were made with the same molar proportions and in the manner described for 1,4-bis-(2-hydroxy-5-methylphenyl)-butane-1,4-dione. For the rearrangement of the isophthalate and terephthalate esters heating was continued for 33 and 38 hr., respectively. Pertinent information is assembled in Table II.

1,4-Bis-(2-hydroxy-5-methylphenyl)-butane-1,4-dione.—Di-*p*-tolyl succinate (6 g., 0.02 mole), aluminum chloride (6.7 g., 0.05 mole) and chlorobenzene (50 ml.) were mixed in a 200-ml. flask equipped with a thermometer and a reflux condenser. The condenser was fitted with a calcium chloride tube leading to a water trough, which acted as a trap to absorb the hydrogen chloride evolved during the reaction. When the mixture was refluxed for six hours, a blackish residue had formed in the flask. After cooling, the mixture was added to 250 g. of a 1:1 mixture of ice and concentrated hydrochloric acid and stirred overnight. A clear yellow aqueous layer and a gray organic layer formed. The chlorobenzene was removed from the reaction mixture by steam distillation. A clear yellow aqueous solution containing some black solid remained in the flask. The mixture was cooled overnight, then filtered. The black solid which collected was then ground to a paste, mixed with water, and again filtered. The material gathered on the filter was air-dried, then extracted with two 25-ml. portions of boiling ethanol. A light greenish crystalline material remained; yield 2.9 g. (48.5%). A 0.5-g. sample of the crude product was chromatographed over 30 g. of silicic acid and eluted with chloroform to give 0.44 g. (43%) of a dark yellow crystalline material, m.p. 186–188°. A sample of the crude product was crystallized three times from ethanol to give white needles, m.p. 189°, reported[4] 187°.

2-Hydroxy-5-methylbenzoic Acid.—An attempted rearrangement of di-*p*-tolyl oxalate (2.7 g., 0.01 mole) was carried out as described above for the rearrangement of di-*p*-tolyl succinate. The temperature was increased from 60 to 120° during one hour, then held at 120° for two hours until the evolution of hydrogen chloride ceased. After the chlorobenzene was removed by steam distillation a dark oil remained in the distillation flask. This oil was extracted with 50 ml. of 10% sodium hydroxide. The hot alkali solution was made acidic with hydrochloric acid and upon cooling, 2-hydroxy-5-methylbenzoic acid separated as long white needles; yield 0.27 g. (17.7%), m.p. 150.5–151.5°, reported[20] m.p. 151°.

4-Hydroxy-6-methylcoumarin.—An attempted rearrangement of di-*p*-tolyl malonate (2.8 g., 0.01 mole) was carried out as described above for di-*p*-tolyl succinate. After the chlorobenzene was removed by steam distillation a light yellow solid remained in the distillation flask. This product was recrystallized from methanol to give long white needles; yield 0.66 g. (37.6%), m.p. 247–248° (dec. about 235–240°), reported 240°,[12a] 241° (dec. about 238°).[21]

Anal. Calcd. for $C_{10}H_8O_3$: C, 68.17; H, 4.58. Found: C, 68.20; H, 4.56.

1-Hydroxy-4-methylanthraquinone.—An attempted rearrangement of di-*p*-tolyl phthalate (3.5 g., 0.01 mole) was carried out as described above for di-*p*-tolyl succinate, except that the temperature was held at 100° for 16 hours. After the chlorobenzene was removed by steam distillation, a red-brown solid remained in the distillation flask. This solid was collected and recrystallized from glacial acetic acid to give 1-hydroxy-4-methylanthraquinone as red-brown needles; yield 0.53 g. (14%), m.p. 171–172°. A further recrystallization of a sample of this crude product from ethanol gave bright orange-yellow needles, m.p. 173°, reported[22] m.p. 175–176°.

Anal. Calcd. for $C_{15}H_{10}O_3$: C, 75.62; H, 4.23. Found: C, 75.47; H, 4.20.

Infrared Spectra of Bis-(*o*-hydroxyketones).—The infrared spectra of all the bis-(*o*-hydroxyketones) and 1-hydroxy-4-methylanthraquinone were obtained as potassium bromide pellets. A Perkin–Elmer, model 21 spectrophotometer, was used. Important absorption bands are listed in Table II.

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(20) W. J. Pavaotović, *J. prakt. Chem.*, [2] **33**, 65 (1885).

(21) R. Anschütz, *Ann.*, **367**, 251 (1909).

(22) O. Fischer and A. Sapper, *J. prakt. Chem.*, **83**, 207 (1910).

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[CONTRIBUTION FROM SINCLAIR RESEARCH LABORATORIES, INC.]

The Alkylation of *p*-Xylene[1]

BY B. S. FRIEDMAN, F. L. MORRITZ, C. J. MORRISSEY AND R. KONCOS

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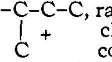
As reported by others, considerable steric hindrance is encountered in introducing a *t*-alkyl group *ortho* to a methyl group. While *p*-xylene can be *t*-butylated in low yield, attempts to accomplish the *t*-pentylation of *p*-xylene by reaction with isoamylenes in the presence of sulfuric acid, boron fluoride, ferric chloride or aluminum chloride–nitromethane result in formation of polymer or of small amounts of by-product *t*-butyl-*p*-xylene. With certain catalysts, *e.g.*, aluminum chloride or hydrogen fluoride, a secondary C_5-alkylate, 2-*p*-xylyl-3-methylbutane (II), is formed in good yield, but *t*-pentyl-*p*-xylene (I) was absent in all cases. Aluminum chloride–nitromethane also produces II in high yield when *t*-pentyl chloride is the alkylating agent. The evidence favors a mechanism involving formation of II *via* direct reaction with a secondary carbonium ion,  $\mathrm{C{-}\underset{\underset{C}{|}}{C}{}^{+}{-}C{-}C}$, rather than the mechanism postulating initial formation of I and subsequent isomerization to II. Aluminum chloride ± nitromethane produces sizeable amounts, and hydrogen fluoride somewhat less, of by-product condensation products of *p*-xylene. These consist of diphenylmethane derivatives, a major component being di-*p*-xylylmethane. A mechanism is presented for these condensation reactions.

p-Xylene is alkylated[2] readily with unbranched olefins, alcohols and alkyl halides but resists alkylation by the more branched members of these groups. This resistance is especially characteristic of reactions employing catalysts (*e. g.*, sulfuric acid and ferric chloride[3]) which strongly favor

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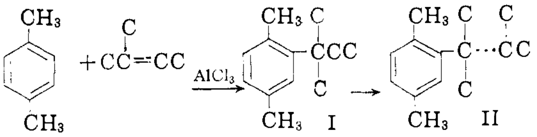
(1) Presented at the 131st Meeting of the American Chemical Society, Miami, Fla., April, 1957.

(2) See chapter on "The Alkylation of Aromatic Compounds by the Friedel-Crafts Method," by C. C. Price, "Organic Reactions," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1946.

(3) D. Nightingale and J. R. Janes, THIS JOURNAL, **66**, 154 (1944).

formation of, and reaction by, a tertiary carbonium ion. Such reactions must overcome the steric hindrance[4] encountered in introducing a *t*-alkyl group in a position *ortho* to a methyl group.[6a] Thus, Schneider,[5,7] Schlatter[6b] and also Corson, *et al.*,[7] suggested *t*-butylation as a method of separating *o*- and *m*-xylene from *p*-xylene.

Reaction with Isoamylenes and *t*-Pentyl Chloride.—*t*-Pentylation of *p*-xylene has not to our knowledge been accomplished *via* alkylation, and this suggested a method for evaluating the general applicability of the Schmerling, *et al.*,[8, 9] mechanism for the formation of secondary alkylates in the aluminum chloride catalyzed reaction of isoölefins with arenes. According to their mechanism the formation of the secondary alkylate, 2-*p*-xylyl-3-methylbutane (II) in the reaction shown would occur by initial formation of the tertiary alkylate, 2-*p*-xylyl-2-methylbutane (I), which would be subsequently isomerized to II by the catalyst.

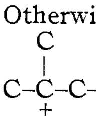
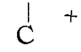


If, however, steric resistance prevents the formation of I, then this would rule out Schmerling's mechanism in the *p*-xylene amylation.

As shown in Table I, some catalysts which at room temperature promote only tertiary pentylation of benzene with isamylenes (*e. g.*, sulfuric acid, ferric chloride and boron fluoride) produced only negligible amounts of any pentyl derivatives of *p*-xylene (expts. 9, 10 and 16). However, hydrogen fluoride (expts. 6 and 7) yielded 34 to 40% of pentylxylene which was identified as the secondary alkylate, compound II. *t*-Pentyl groups could not be detected by infrared.

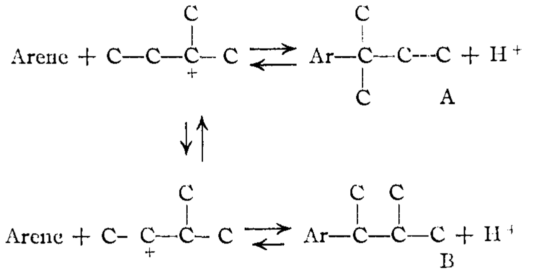
As reported previously,[10b] in the presence of aluminum chloride/nitromethane complex 2-methyl-2-butene yielded only 7% of pentylxylene and 8% of by-product *t*-butyl-*p*-xylene (expt. 14) whereas *t*-pentyl chloride yielded 46% pentyl-*p*-xylene, which has now been identified as compound II (expt. 15).

In contrast, the reaction of *t*-pentyl chloride with benzene in the presence of the aluminum chloride/nitromethane complex was not only more rapid as judged by liberation of hydrogen chloride, but the monoalkylate was substantially pure *t*-pentylbenzene (69% yield). Even though the reactants and products were in contact with the catalyst overnight, the *t*-pentyl group was isomerized extremely slowly, if at all. Therefore, if as postulated by the Schmerling mechanism, compound I had been formed initially in the reaction involving *p*-xylene it seems likely that it would have survived. Consequently, since none was isolated, compound I probably is not an intermediate in the formation of II from *p*-xylene and *t*-pentyl chloride in expt. 15.

It is noteworthy that catalysts such as aluminum chloride/nitromethane and hydrogen fluoride[10a] which effect only *t*-alkylation of benzene with *t*-pentyl chloride (room temperature) are able to bring about secondary alkylation in instances where steric hindrance greatly retards *t*-alkylation. Otherwise stated, when the more prevalent *t*-cation,  $\text{C--}\underset{+}{\overset{\text{C}}{\text{C}}}\text{--C--C}$, is prevented by steric effects from reacting (as with *p*-xylene), the more scarce secondary cation,  $\text{C--}\underset{\text{C}}{\text{C}}\text{--}\overset{}{\underset{+}{\text{C}}}\text{--C}$ with which it is in equilibrium, has an opportunity to become the predominant alkylating species.[11]

In the reaction of benzene with isoamylenes at 0°, uncomplexed aluminum chloride (promoted with hydrogen chloride) produces both *t*-alkylate and secondary alkylate, whereas with *p*-xylene the monoalkylate appeared to be exclusively the secondary alkylate, namely, compound II (expts. 12 and 13).

We can only conclude, therefore, that II is formed directly, *i.e.*, by alkylation of *p*-xylene with the secondary carbonium ion. Actually all that has been proven rigorously by the evidence presented so far is that the Schmerling, *et al.*, mechanism does not operate with hindered arenes. Of course, our mechanism may also operate with unhindered arenes; *i. e.*, the secondary alkylates also are formed here *via* alkylation with the secondary cation



$$\text{Arene} + \text{C--C--}\underset{+}{\overset{\text{C}}{\text{C}}}\text{--C} \rightleftarrows \text{Ar--}\underset{\text{C}}{\overset{\text{C}}{\text{C}}}\text{--C--C} + \text{H}^+ \quad \text{A}$$

$$\downarrow\uparrow$$

$$\text{Arene} + \text{C--}\underset{+}{\text{C}}\text{--}\overset{\text{C}}{\text{C}}\text{--C} \rightleftarrows \text{Ar--}\overset{\text{C}}{\text{C}}\text{--}\overset{\text{C}}{\text{C}}\text{--C} + \text{H}^+ \quad \text{B}$$

In this connection we have experimental evidence (to be published later) which firmly supports the above postulates of (1) a rapid alkylation–dealkylation equilibrium involving A and of (2) the stability of B once formed. Nevertheless while we believe the above is a more plausible mechanism for unhindered arenes, we have not ruled out the applicability of the Schmerling, *et al.*, mechanism. Indeed both mechanisms could be operating concurrently as in the aluminum-chloride catalyzed alkylation of toluene with isoamylene, a reaction which results (to be published later) in a mixture of (a) *ortho*, (b) *meta* and (c) *para* secondary alkylates and (d) *meta* and (e) *para* tertiary alkylates. The *o-t* alkylate was not

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[4] H. C. Brown and K. L. Nelson, THIS JOURNAL, **75**, 24 (1953).

[5] A. Schneider, U. S. Patent 2,648,713; *C. A.*, **48**, P8258e (1954).

[6] (a) M. J. Schlatter and R. D. Clark, THIS JOURNAL, **75**, 361 (1953); (b) M. J. Schlatter, *ibid.*, **76**, 4952 (1954).

[7] B. B. Corson, W. J. Heintzelman, R. C. Odioso, H. E. Tiofenthal and F. J. Pavlik, *Ind. Eng. Chem.*, **48**, 1180 (1956).

[8] L. Schmerling and J. P. West, THIS JOURNAL, **76**, 1917 (1954).

[9] L. Schmerling, R. W. Welch and J. P. Luvisi, *ibid.*, **79**, 2636 (1957).

[10] (a) B. S. Friedman and F. L. Morritz, *ibid.*, **78**, 2000 (1956); (b) **78**, 3430 (1956).

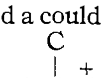
[11] G. Baddeley, *Quart. Revs.*, **8**, 355 (1954), see esp. p. 366.

TABLE I

ALKYLATION OF *p*-XYLENE

Expt. no.	Method[m]	Moles *p*-xylene	Alkylating agent[b]	Catalyst	G.	Promoter	Temp., °C.	Duration min.[a]	Products identified Yield[c]	Identity
1[l]	A	5	Isobutylene	$AlCl_3$[d]	27	*t*-BuCl 5 cc.	25	36/9	11%	*t*-Butyl-*p*-xylene
2	A	5	Isobutylene	$AlCl_3$	27	*t*-BuCl 5 cc.	25	27/7	0.2m	Toluene
									.023m	Pseudocumene
									.03m	*t*-Butyltoluenes (*m*-, *p*-)
									.25m	Compound III
									.1m	Largely 210 mol. wt. (type IV)
3	A	2[e]	Isobutylene	H_2SO_4 (92%)	1212	None	4	24/30	7%	*t*-Butyl-*p*-xylene
4	C	5	*t*-BuCl	$AlCl_3$	7	None	25	255/180[k]	0.063m	*t*-Butyltoluenes (*m*-, *p*-)
									.089m	3,5-Di-*t*-butyltoluene
									.15m	Compound III
									.07m	Largely 210 mol. wt. (type IV)
5	B	5	*t*-BuCl	$AlCl_3$[d]	27	None	25	26/250[k]	.11m	*t*-Butyltoluenes (*m*-, *p*-)
									.11m	*t*-Butyl-*p*-xylene
									.12m	Compound III
6	D	2	3-Methyl-1-butene	HF	110	None	23–25	56/30	34%	Pentylxylene, II
7	D	1.7	2-Methyl-2-butene	HF	114	None	24–28	90/5	40%	Pentylxylene, II
									0.02m	Compound III
8	B	2[f]		HF	85	None	0	28/30	Low yield contam. with polymer	
9	D[g]	3[e]		BF_3	..	None	15	30/10	Low yield contam. with polymer	
10	B	3		$FeCl_3$	50	HCl	25	45/15	Very low yield	
11	C	5	*t*-Pentyl chloride	$FeCl_3$	32	None	85	50/10	Low yield of C_{12}- and C_{13}- alkylbenzenes	
12	A	2[h]	3-Methyl-1-butene	$AlCl_3$	13	HCl	0	21/5	0.19m	Isopentane
									41%	Pentylxylene, II
									Some	Compound III
13	A	2.4[i]		$AlCl_3$	13	HCl	0	30/5	0.31m	Isopentane
									26%	Pentylxylene, II
									0.14m	Compound III
14[l]	B	5	2-Methyl-2-butene	$AlCl_3$[d]	27	*t*-$C_5H_{11}Cl$[j]	25	25/10	Considerable polymer	
									8%	*t*-Butyl-*p*-xylene
									7%	Pentylxylene, II
15	B	5	*t*-Pentyl-chloride	$AlCl_3$[d]	27	None	21–24	30/90[k]	46%	Pentylxylene, II
									0.07m	Compound III
16	A	2[i]	3-Methyl-1-butene	H_2SO_4 (96%)	184	None	0	35/30	Low yield contam. with polymer	
17	E	2	2-Ethyl-propanol-2	H_2SO_4 (93%)	1182	None	0–7	60/30	Considerable polymer	
									11%	Mixt. of C_{14}-, C_{15}-, etc., poly-alkylbenzenes

[a] First figure gives time for addition; second figure, additional stirring. [b] One mole employed. [c] % based on product theoretically obtainable from alkylating agent used; m = moles obtained. [d] 100 g. of nitromethane. [e] 100 g. of *n*-heptane as solvent. [f] 68 g. of *n*-heptane as solvent. [g] Saturate 1.5 moles of *p*-xylene plus *n*-heptane with boron fluoride, then add mixture of 1 mole of olefin and 0.5 mole of *p*-xylene while passing slow stream of boron fluoride through liquid reactants. [h] 200 g. of *n*-heptane as solvent. [i] 168 g. of cyclohexane as solvent. [j] Added with olefin plus aromatic. [k] Then allowed to stand overnight. [l] Reported previously, ref. 10b. [m] Procedure employed: (A) olefin added to mixture of aromatic hydrocarbon, catalyst and promoter; (B) add mixture of one mole alkylating agent and one mole aromatic to a stirred mixture comprising the balance of the aromatic, the catalyst and the solvent (where employed); (C) catalyst added in portions during the course of the reaction to a stirred mixture of the aromatic and alkyl halide; (D) same as "B" only in autoclave (Magnedash); (E) add mixture of aromatic and alcohol to stirred acid; to work up product add benzene and let settle one hour at 0° before separating the layers.

present. Compound a could have been formed only via alkylation with  $\mathrm{C{-}\overset{\overset{C}{|}\;+}{C}{-}C}$, but b and c may have been formed either this way or *via* isomerization of d and e in the sense of Schmerling, *et al.*, mechanism.

Reaction with 2-Methylpropene and *t*-Butyl Chloride.—As reported previously,[10b,12] *t*-butylation in a position *ortho* to a methyl group is apparently possible. Thus the reaction (expt. 14) of *p*-xylene with 2-methyl-2-butene in the presence of aluminum chloride/nitromethane complex yielded 7% *t*-butyl-*p*-xylene (*via* polymerization–scission–alkylation)[10b] as well as 8% of the pentyl derivative (not *t*-amyl). When the C_5-olefin was replaced with 2-methylpropene, *t*-butyl-*p*-xylene was produced in 11% yield (expt. 1).

In the absence of nitromethane, aluminum chloride at 25° effects considerable displacement of

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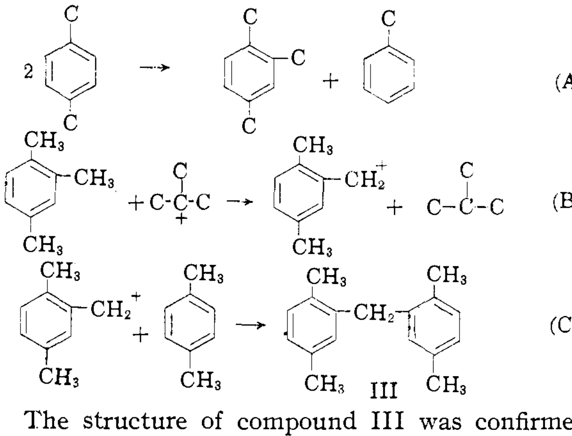
(12) M. J. Schlatter, Division of Petroleum Chemistry, Symposium on Chemicals for Petroleum, American Chemical Society, Dallas, Texas, April 8–13, 1956, Preprints p. 77.

ring-attached methyl groups. Fractionation of the product from the reaction of *p*-xylene with 2-methylpropene (expt. 2) yielded 0.2 ml. of toluene, a small amount of 1,2,4-trimethylbenzene, some *t*-butyl toluene, but no *t*-butyl-*p*-xylene. A large amount (0.25 mole) of a product boiling at about 318° also was isolated. This material solidified upon standing (m.p. 62–62.5° after recrystallization). The high refractive index (n^{20}_D 1.565) suggested a diphenyl derivative (III) formed most probably *via*



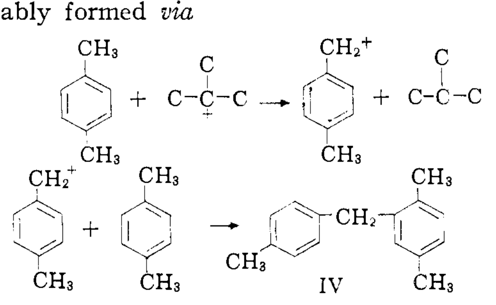
The structure of compound III was confirmed by comparison to synthetic di-*p*-xylylmethane.

Baddeley[13] proposed a similar mechanism for the formation of polymethylanthracenes when mesitylene is treated with pivaloyl chloride.[13b]

Baddeley[13a] proposed a similar mechanism for the formation of polymethylanthracenes when mesitylene is treated with pivaloyl chloride.[13b]

Steps B and C above resemble the hydrogen transfer reactions reported[14] for the alkylation of *p*-ethyltoluene and *p*-propyltoluene with methylcyclohexene in the presence of hydrogen fluoride or sulfuric acid. These reactions involved the α-methylene groups of the ethyl or propyl side chain rather than the methyl side chain, the products consisting of 1-*p*-tolyl-1-(2-methyl-5-ethylphenyl)-ethane and 1-*p*-tolyl-1-(2-methyl-5-propylphenyl)-propane, respectively.

In addition to compound III, about 0.1 mole of a lower boiling product was separated which also appears to be a diphenylmethane (IV) containing one less methyl group than compound III, and probably formed *via*



Compound IV is probably 2-(*p*-methylbenzyl)-*p*-xylene, but this structure was not established.[15]

The reaction of *p*-xylene with one mole of *t*-butyl chloride catalyzed by aluminum chloride (7 g. added during course of over 4 hours) was very slow as judged by evolution of hydrogen chloride (expt. 4). After 12.5 hours of additional contact, the product contained a small amount of *m*- and *p*-*t*-butyltoluene and di-*t*-butyltoluene, 0.15 mole of compound III, 0.07 mole of a C_{16}-diphenylmethane (IV), but no *t*-butyl-*p*-xylene.

Since nitromethane effectively prevents formation of high-boilers such as compound III from 2-methylpropene (expt. 1), it was of interest to perform the reaction of *t*-butyl chloride with *p*-xylene in the presence of the aluminum chloride/nitromethane complex (expt. 5). Evolution of hydrogen chloride was very slow (0.043 mole in 2 hours, 0.108 during next 2 hours) and the reactants were therefore allowed to stand 14 hours (total of 0.682 mole of hydrogen chloride liberated). Fractionation of the product yielded not only *t*-butyltoluene and *t*-butyl-*p*-xylene (0.11 mole each) but also 0.12 mole of compound III. Thus, under the proper conditions, *e. g.*, slow but continuous availability of *t*-carbonium ions, aluminum chloride complexed with nitromethane is also capable of promoting the required reactions leading to III, namely, disproportionation of xylene[16] and hydride abstraction from ring-attached methyl groups (see also expt. 15).

Miscellaneous Alkylations Producing Compound III.—Compound III is present also in the product resulting from the reaction of isoamylenes (expts. 12 and 13) with *p*-xylene in the presence of uncomplexed aluminum chloride. However, hydrogen fluoride produces only a minor amount of compound III (expts. 6, 7 and 8) and none was isolated from products obtained in reactions catalyzed by boron fluoride, ferric chloride or sulfuric acid (expts. 9, 10, 11, 16 and 17).

Experimental

Materials.—The olefins were pure grade (99%⁺) purchased from Phillips Petroleum Co. and used as received. *t*-Pentyl chloride, *t*-butyl chloride and 2-ethylpropanol-2 were purchased from Eastman Kodak Co. and from Mathieson, Coleman and Bell, and found to be pure by infrared examination. The *p*-xylene consisted of Phillips 98% and 99% grade further purified by recrystallization from *n*-pentane; it then contained 0.0% *o*-xylene, 0.17–0.26% *m*-xylene and 0.0–0.15% ethylbenzene.

Isolation of Products.—After reaction, the mixture was permitted to stand for about 5 to 10 minutes (50 to 60 minutes for sulfuric acid alkylates). The upper layer was separated from the catalyst layer, washed with water, stirred several hours with water at about 85 to 95°, dried, stirred with sodium sand at 130–150° for several hours and distilled. The material volatilizing during the water and sodium treatments was collected, dried and analyzed. The distillation fractions were analyzed by infrared[17] and mass spectrometry.[17]

Identification.—Toluene, pseudocumene, *m*- and *p*-*t*-butyltoluenes, 3,5-di-*t*-butyltoluene and *t*-butyl-*p*-xylene were identified by physical properties and by reference to readily available standards, mass spectrometry (m. s.) and

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(13) (a) See p. 374 of ref. 11; (b) D. V. Nightingale, R. L. Sublett, R. A. Carpenter and H. D. Radford, *J. Org. Chem.*, **16**, 655 (1951).

(14) H. Pines, D. R. Strehlau and V. N. Ipatieff, This Journal, **71**, 3534 (1949).

(15) After this paper had been submitted for publication, L. Schmerling, J. P. Luvisi and R. W. Welch proposed (paper presented before Chicago Catalysis Club, May 17, 1958) what seems to be a more probable mechanism for the formation of III, namely, cleavage of IV, experimentally confirmed, to yield toluene plus the 2,5-dimethylbenzyl cation required for step c.

(16) Not required in mechanism proposed by Schmerling, *et al.*[15]

(17) The authors are indebted to F. L. Voelz and F. L. Boys of the Spectrochemical Laboratory of Sinclair Research Laboratories, Inc., for these analyses.

infrared spectra. Standards for compounds I, II and III were synthesized or obtained as follows:

2-*p*-Xylyl-2-methylbutane (I).—To the Grignard prepared from 2 moles of 2-bromo-*p*-xylene (Eastman Kodak Co.) and 48.6 g. of magnesium turnings in 620 ml. ether was added 2 moles of acetone (Reagent grade, M., C. and B.) in 155 ml. of ether. Additional ether (280 ml.) was added to ease the stirring; the addition took 4 hours. The mixture was allowed to stand overnight and then hydrolyzed with aqueous ammonium chloride. Fractionation *in vacuo* yielded 2-*p*-xylylpropanol-2 (b.p. 93° (2.5 mm.), n^{20}D 1.5248–1.5254).

Treatment of the carbinol in *n*-pentane solution with hydrogen chloride gas at 0° for 1.75 hours produced the corresponding chloride derivative which was isolated by separation of the organic layer and then evaporation *in vacuo* at room temperature by means of a water aspirator to remove the solvent and excess hydrogen chloride. The chloride was added in ether solution with stirring to an ether solution of the Grignard reagent prepared from ethyl bromide. The addition required 4 hours. Stirring under reflux was continued for 3.5 days. Hydrolysis and fractionation produced I (over-all yield, 8%), b.p. 230°, n^{20}D 1.5083).

Anal. Calcd. for $C_{13}H_{20}$: C, 88.56; H, 11.44; mol. wt., 176. Found: C, 87.8; H, 11.75; mol. wt., 176 (by m.s.).

2-*p*-Xylyl-3-methylbutane (II).—2-*p*-xylyl-3-methylbutanol-2 (b.p. 92° (1 mm.), n^{20}D 1.5187) was prepared by the addition of the Grignard of 2-bromo-*p*-xylene to 3-methylbutanone-2.

The carbinol was dehydrated by treatment with a crystal or two of iodine at 140–150° to form what was probably 2-*p*-xylyl-3-methylbutene-1 (b.p. 218°, n^{20}D 1.5099–1.5113; strong band at 11.14 μ indicative of a $R_2C{=}CH_2$ olefin). This olefin was hydrogenated in pentane at 10 p.s.i.g. in the presence of Adams platinum catalyst to yield II, b.p. 221°, n^{20}D 1.4985.

Anal. Calcd. for $C_{13}H_{20}$: C, 88.56; H, 11.44; mol. wt., 176. Found: C, 88.33; H, 11.59; mol. wt., 176 (by m.s.).

Di-*p*-xylylmethane (III).—The compound boiling at 318° was found identical by melting point (62–62.5°), mixed melting point (62°), as well as by infrared and mass spectrometry, with a sample synthesized by Welch and Smith[18] from *p*-xylene with formaldehyde.[19]

C_{16}-Diphenylmethane Derivatives.—The material boiling 302–308° (n^{20} 1.5491–1.5620) showed a strong mass spectrograph parent mass peak at 210 and secondary peaks at 196 characteristic of 2,5,4′-trimethyldiphenylmethane.[20] However, the identity of the components in this mixture was not established.

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[18] C. M. Welch and H. A. Smith, THIS JOURNAL, **73**, 4391 (1951).

[19] We are grateful to Dr. H. A. Smith for making this sample available to us.

[20] Sample supplied to us through the courtesy of Professor G. W. Wheland and Dr. George Kurhajec of the University of Chicago.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The $BF_3 \cdot N_2O_5$ Complex. Its Use as a Nitrating Agent[1]

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Boron trifluoride reacts with dinitrogen pentoxide to form a stable, colorless complex, $BF_3 \cdot N_2O_5$. Physical and chemical properties suggest that the structure is best represented as $(F_3B \leftarrow ONO_2)^-(NO_2)^+$. The complex is an excellent nitrating agent in the aromatic series and is of some utility in the nitration of aliphatics.

It has been reported that boron trifluoride forms a 1:1 addition complex with dinitrogen tetroxide,[2] which is an excellent nitrating agent. More recently it has been found that boron trifluoride also forms a 1:1 addition complex with dinitrogen trioxide,[3] which is a weak nitrating agent and a powerful diazotizing agent for aromatic amines. It has now been found that dinitrogen pentoxide also forms a 1:1 complex with boron trifluoride. The complex is a colorless, stable liquid in the presense of polychlorinated alkanes and a white solid in nitroalkanes. It is insoluble in all substances tested except those with which it reacts. The complex decomposes at about 75° in inert solvents as evidenced by the evolution of brown NO_2 fumes. These properties together with the chemical properties described below suggest that the complex is ionic and is formed as illustrated in equation 1.

$$BF_3 + O_2N{-}O{-}NO_2 \longrightarrow (F_3B \leftarrow ONO_2)^-(NO_2)^+ \quad (1)$$

The $BF_3 \cdot N_2O_5$ complex reacts rapidly with substances with which BF_3 and N_2O_5 react separately, including water, alcohols, ethers, amines and pyridine. Also, the complex affords a ready means for introducing the NO_2 group into aromatic nuclei; thus, nitrobenzene reacts with a two-mole ratio of the complex in carbon tetrachloride to give an 86% yield of *m*-dinitrobenzene after 18 hours at 75°. Yields of 80–90% have been reported[4] using excess fuming HNO_3 and concentrated H_2SO_4 mixtures at about 100°. Benzoic acid reacts with a three-mole ratio of the complex in carbon tetrachloride in 36 hours at 70° to form 3,5-dinitrobenzoic acid (70% yield) and *m*-nitrobenzoic acid (9.3% yield). The results compare favorably with results obtained using other nitrating agents. Yields of 54–60% of 3,5-dinitrobenzoic acid have been reported[5,6] using an excess of mixtures of fuming nitric acid and concentrated sulfuric acid at above 100°. Other nitration results are shown in Table I.

An attempt was made to nitrate 2,6-di-*t*-butylphenol using a 1:1 mole ratio of the reactants in carbon tetrachloride at room temperature for five hours. The only product isolated was 2,2′,6,6′-tetra-*t*-butyl-4,4′-biphenylquinone, in 50% yield. In addition to this there was considerable tar formation. The fact that the only pure product obtained was the above-mentioned biphenylquinone indicates that the complex is also a strong oxidizing agent.

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[1] From the M. S. Thesis of James L. Dever, Purdue University, January, 1958.

[2] G. B. Bachman, H. Feuer, B. R. Bluestein and C. M. Vogt, THIS JOURNAL, **77**, 6188 (1955).

[3] G. B. Bachman and T. Hokama, *ibid.*, **79**, 4370 (1957).

[4] E. E. Royals, "Advanced Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1954, p. 456.

[5] R. Q. Brewster and B. Wiliams, *Org. Syntheses*, **22**, 48 (1942).

[6] R. Phillips, *ibid.*, **22**, 49 (1942).