views of Hughes and Ingold.[1,12] In a recent paper[13] they reported a study of nucleophilic displacements on *t*-butyl halides in Finkelstein's reaction but did not apply their observation to solvolysis reactions.

Our results differ from those of Gelles, Hughes and Ingold[1] who used water, phenol and methanol in nitromethane solution to react with *t*-butyl bromide. In the concentration ranges studied they found evidence for electrophilic catalysis only. The two highest concentrations of water used did show evidence of a higher order reaction, however. The only explanation that we can offer for this discrepancy is that the concentrations they used were so low that the reagents could not compete with either the solvent or added pyridine as the nucleophile. The reaction with pyridine alone was a significant part of the total rate even though it was not sensitive to pyridine concentration. The work of Hawthorne and Cram[14] indicates that a reaction of this type may not necessarily be very sensitive to the nucleophile.

Further work is contemplated to determine the importance of gross dielectric constant, the entropy effect and variations in the substrate and products.

Acknowledgments.—The authors wish to express their appreciation to E. S. Lewis and M. F. Hawthorne for their constructive criticism and helpful suggestions.

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[12] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 308–418.

[13] P. B. D. de la Mare, L. Fowden, E. D. Hughes, C. K. Ingold and J. D. H. Mackie, *J. Chem. Soc.*, 3200 (1955).

[14] M. F. Hawthorne and D. J. Cram, THIS JOURNAL, **76**, 3451, (1954).

RUSTON, LOUISIANA

[CONTRIBUTIONS FROM SINCLAIR RESEARCH LABORATORIES, INC.]

t-Butylation of Aromatics with Isoamylene[1]

BY B. S. FRIEDMAN AND FRED L. MORRITZ[2]

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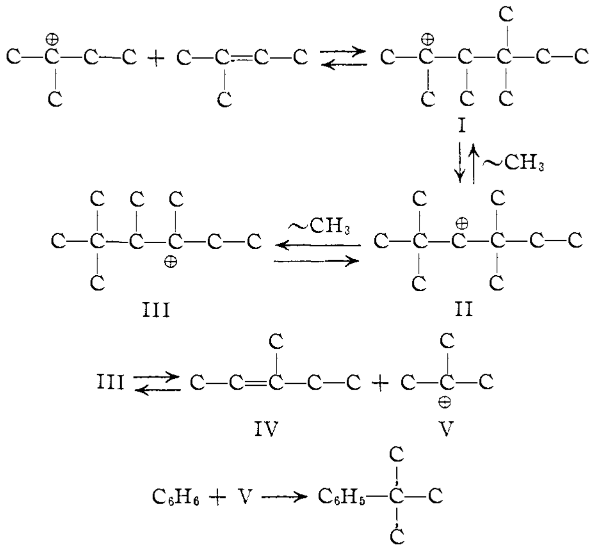
It has been found that *t*-butyl derivatives are frequently produced, often in yields up to 25%, during the reaction of aromatics with isoamylene. The C_4-fragment probably arises from the dimerization of the C_5-olefin followed by rearrangement and scission of the resulting C_{10}-olefin to yield C_4- and C_6-fragments. Conditions which favor this reaction are described.

During the course of an investigation of the alkylation of benzene with isoamylene[3] it was noted that under certain conditions *t*-butylbenzene is formed as one of the important products of reaction.

It is proposed that *t*-butylbenzene is formed by the mechanism



The first-formed *t*-amyl cation reacts with a molecule of olefin to form a decyl cation I which by a series of methyl shifts forms the tertiary carbonium ion III. If one prefers not to envision the formation of a secondary carbonium ion from a tertiary (*e.g.*, II from I), one can postulate a 1,3-methyl shift to form III directly. Cation III then decomposes by β-scission to form a hexene, IV, and the *t*-butyl cation, V. The cation V reacts with a molecule of benzene to form *t*-butylbenzene.

The following evidence can be presented for this mechanism. When benzene was allowed to react with 2-methyl-2-butene in the presence of a small amount of aluminum chloride which was added gradually during the course of the reaction, *t*-butylbenzene was formed in 25% yield. An 11% yield of pentylbenzene also was formed. Spectrometric analysis of the higher boiling products indicated the presence of both hexylbenzene (probably derived from IV) and decylbenzene (reaction of benzene with I, II or III). Disubstitution was essentially absent. When the dimer of 2-methyl-2-butene (formed in the presence of sulfuric acid) was used to alkylate benzene (aluminum chloride catalyst), a 17% yield of *t*-butylbenzene was formed as well as 39% of pentylbenzene.

The formation of several of the intermediate cations mentioned in the above mechanism is amply documented. The action of sulfuric acid on methylisopropylcarbinol has been shown[4,5] to yield 3,4,5,5-tetramethyl-2-hexene (which corresponds to cation III). Whitmore and Mosher[4] obtained 45% of this decene and in addition 3% of 3-methyl-2-pentene (IV above) and 1% of diisobutylene (easily yields cation V). These authors state,

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[1] Presented in part at the 128th Meeting of the American Chemical Society, Minneapolis, Minn., September, 1955.

[2] Armour Research Foundation, Illinois Institute of Technology, Chicago, Ill.

[3] B. S. Friedman and F. L. Morritz, THIS JOURNAL, **78**, 2000 (1956).

[4] F. C. Whitmore and W. A. Mosher, *ibid.*, **63**, 1120 (1941).

[5] N. L. Drake, G. M. Kline and W. G. Rose, *ibid.*, **56**, 2076 (1934).

"The 3,4,5,5-tetramethyl-2-hexene . . . is relatively easy to depolymerize. The products of the splitting process would be 3-methyl-2-pentene and isobutene. The first is found and the second is polymerized with itself to yield the diisobutylenes and copolymerized with trimethylethylene to yield 2,3,4,4-tetramethyl-1-pentene (2%)." 3,4,5,5-Tetramethyl-2-hexene is formed[6] in 30% yield by treating 2-methylbutanol-2 with sulfuric acid.

The best yield of *t*-butylbenzene was obtained, in runs employing aluminum chloride, when a small amount of this catalyst was added gradually to a mixture of olefin and benzene. Apparently, these operating conditions are favorable for the initial formation of dimer and less so for alkylation. The dimer undergoes subsequent rearrangement and fragmentation to form the *t*-butyl cation. Finally, sufficient catalyst is present to ensure eventual reaction of the olefinic monomer, dimer and the various fragments with the benzene present.

It is interesting to note that in no case where *t*-pentyl chloride was used to alkylate benzene (or chlorobenzene or *p*-xylene) were *t*-butyl derivatives found among the products. This may be attributed to two factors: (1) the formation of olefin from *t*-pentyl cation and the subsequent dimerization are both slow compared to the alkylation step, and/or (2) the alkylation may proceed *via* an S_N2 concerted molecular nucleophilic displacement[7] rather than through an S_E attack involving carbonium ions. It is noteworthy in this respect that disproportionation of *t*-pentyl chloride to *t*-butyl chloride (or ion) does occur[8] in the condensation of *t*-pentyl chloride with ethylene in the presence of aluminum chloride at −5°.

It would be expected that less reactive aromatics would yield a greater amount of *t*-butyl derivatives, since the rate of alkylation would be retarded while the competing dimerization–cleavage reactions would proceed unimpeded. This appears to be the case. When chlorobenzene was treated with 2-methyl-2-butene in the presence of aluminum chloride at 24°, 12% *t*-butyl chlorobenzene was formed. Under essentially these same conditions benzene gave only 5% *t*-butylbenzene. However, here again, no *t*-butylation occurs if the alkylation of chlorobenzene is conducted with *t*-pentyl chloride instead of the corresponding olefin; the product consists chiefly of pentyl derivatives.

The reaction of *p*-xylene with 2-methyl-2-butene in the presence of aluminum chloride–nitromethane complex at 25° yielded 8% of *t*-butyl-*p*-xylene (identical to the C_{12}-aromatic obtained in this same reaction employing isobutylene), and only 7% pentylxylene. *t*-Butylation in this case can be attributed to the modified catalyst used[9] and to the fact that the alkylation step is slowed since every open position is *ortho* to a methyl substituent. As far as can be ascertained, *t*-pentylxylene was not formed. This and other data to be reported later indicate greater resistance of *p*-xylene to *t*-pentylation than to *t*-butylation.

As anticipated from the results with benzene and chlorobenzene, the reaction of *t*-pentyl chloride with *p*-xylene produced no *t*-butyl-*p*-xylene. The reaction required a considerable time for completion (as judged by evolution of hydrogen chloride), and this procedure probably accounts for the high yield (46%) of pentylxylene. *t*-Pentylxylene was not detected in the product.

TABLE I

FORMATION OF *t*-BUTYL AROMATICS[a]

Procedure[3]	Catalyst, g.		Promoter	Temp., °C.	Duration min.	Mono-alkylate[n] % *t*-Bu	% Pentyl
1	$AlCl_3$	27	HCl	−40	49	1	39
1	$AlCl_3$	27	HCl	21	34	5	42
1	$AlCl_3$	27	HCl	0	180	1	45
2	$AlCl_3$	3.5	[b]	22	96	25	11[k]
2[c]	$AlCl_3$	3.5	[b]	25	82	20[m]	46[m]
2[d]	$AlCl_3$	3.5		24	150	0	71
2	H_2SO_4[e]	185		0	67	2	4[f]
3	$AlBr_3$	27	HBr	25	1 sec.	17	22
1	$AlBr_3$	27	HBr	25	25	13	21
4	HF	100		100	34	2	32
4	BF_3	1 mole		28	29	6	10
4	BF_3	1 mole		119	30	6	11
4	HF BF_3	100 27		0	18	7	51
1[g]	$AlCl_3$[h]	27	[b]	25	35	8	7[l]
1[i]	$AlCl_3$	27	HCl	24	60	12[m]	8[m]
1[j]	$AlCl_3$	27	HCl	25	60	17	39
1[i,d]	$AlCl_3$	27		24	63	<1	63
1[d,g]	$AlCl_3$[h]	27		23	1080	<1	46

[a] Except where noted, 5 moles benzene reacted with 1 mole of 2-methyl-2-butene. [b] Five grams of *t*-pentyl chloride was added. [c] Five moles of toluene used as aromatic. [d] One mole of *t*-pentyl chloride used as alkylating agent. [e] 96% H_2SO_4. [f] Admixed with polymer. [g] Five moles of *p*-xylene used as aromatic. [h] 100 g. of CH_3NO_2 added. [i] Five moles of chlorobenzene used as aromatic. [j] Three-quarters mole of diisoamylene and 15 moles of benzene. [k] Mass spectrometer analysis shows hexylbenzene and decylbenzene are also present. [l] Further results with *p*-xylene will be reported in a future communication. [m] Mixture of *meta* and *para* isomers. [n] Yield based on alkylating agent charged.

On the other hand, when toluene, a more reactive aromatic, was alkylated with 2-methyl-2-butene in such manner that a small amount of catalyst was added gradually to the reaction medium, the yield of *t*-butyl derivatives[10] was not materially less than that formed from benzene. However, the yield of pentyltoluene was considerably larger (46 *vs.* 11%).

This study is being extended to other types of aromatic compounds.

Acknowledgment is due Dr. F. L. Voelz, Mr. F. L. Boys and Mr. R. Wertzler for the infrared analyses, and Mr. J. F. Kinder for the mass spectrometric analyses.

Experimental

Alkylation Procedures.—The procedures used are those previously described.[3]

Alkylation of Chlorobenzene with 2-Methyl-2-butene. Four moles of chlorobenzene and 0.1 mole of aluminum chloride were saturated with anhydrous hydrogen chloride. A mixture of 1 mole of chlorobenzene and 1 mole of 2-methyl-2-butene was then added with stirring at 24°. The product, worked up as in procedure 1[3] and fractionated, yielded the following plateau cuts: (a) 24 g., b.p. 210–212° (760 mm.)

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(6) G. C. Johnson, THIS JOURNAL, **69**, 146 (1947).

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

(8) L. Schmerling, *ibid.*, **67**, 1152 (1945).

(9) In the absence of nitromethane these reactants produce negligible yields of *t*-butyl derivatives.

(10) Infrared analysis indicates approximately 50% *meta* and 50% *para*.

(210–212 (730 mm.),[13] $n^{20}D$ 1.5088–96 ($n^{18}D$ 1.5125[13]), Cl 20.7; mol. wt.[11] 168 (182), calcd. for *t*-butylchlorobenzene 21.03%, 168; infrared indicates mixture of *meta* and *para*, no *ortho;* (b) 17 g., b. p. 220–222; $n^{20}D$ 1.5084–1.5100, Cl 18.9%, mol. wt. 182 (168); calcd. for amylchlorobenzene 19.42%, 182. (c) 17 g., b.p. 251–254°, $n^{20}D$ 1.5190–1.5237, Cl 15.3%, calcd. for di-butyl 15.11%; for butylbutenyl[12] 15.24%.

Identification.—*t*-Butylbenzene, *m*- and *p*-*t*-butyltoluenes, and the various pentylbenzenes were identified by physical properties and by reference to available standards and infrared spectra. No attempt was made to identify the polyalkylated derivatives.

***t*-Butyl-*p*-xylene.**—This compound was prepared in 11% yield by alkylation of *p*-xylene (5 moles) with isobutylene (1 mole) in the presence of nitromethane–aluminum chloride (100 g./28 g.) complex at 25°. The product was worked up as in procedure 1,[3] and fractionated to separate the *t*-butyl derivative, b.p. 217°, $n^{20}D$ 1.5000, d^{20}_4 0.8738. (Burgoyne, *et al.*,[14] reported 213–217° (735 mm.), $n^{28.5}D$ 1.5003, $d^{29.5}_{29.5}$ 0.8757, for this compound prepared in 5.2% yield *via* the reaction of *t*-butyl chloride with the Grignard reagent prepared from 2-bromo-*p*-xylene.) The infrared spectrum confirmed 1,2,4-trisubstitution and presence of a *t*-butyl side chain, and was identical to that for the C_{12}-aromatic obtained from *p*-xylene and 2-methyl-2-butene. These data do not eliminate the 1,3-dimethyl-4-*t*-butyl isomer which might form by isomerization of *p*- to *m*-xylene followed by alkylation. However, the formation of this isomer is not considered probable in view of the complete absence of (1) *m*-xylene in the recovered xylene, and of (2) the 1,3-dimethyl-5-*t*-butyl isomer in the product. Furthermore, dealkylation of this material over silica alumina[15] (Socony–Vacuum "Chrome Bead") at 375°, 1.8 vol. per vol. of catalyst per hour, yielded a liquid product consisting of 85% *p*-xylene, 4 ± 2% *m*-xylene, and only traces of *o*-xylene and toluene. The gas evolved contained 78% isobutylene and 14.4% isobutane. Under the same conditions with pure *p*-xylene as the feed, the product contained 90% *p*-, 4 ± 2% *m*-, no *o*-xylene and 6 ± 2% toluene.

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[11] Mass spectrograph parent mass main peaks (minor peaks) based on Cl^{35} isotope.

[12] This fraction rapidly discolors potassium permanganate solution, indicating olefinic bonds.

[13] For *p*-*t*-butylchlorobenzene; I. P. Tsukervanik, *J. Gen. Chem.*, (*U.S.S.R.*), **8**, 1512 (1938).

[14] E. E. Burgoyne, T. J. Klose and D. K. Watson, *J. Org. Chem.*, **20**, 1508 (1955).

[15] M. J. Schlatter, paper presented before the Division of Petroleum Chemistry of the American Chemical Society, Symposium on Petrochemicals in the Postwar Years, at the Chicago Meeting, September, 1953.

HARVEY, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

The Room Temperature Polymerization of Propylene Oxide

BY LEON E. ST. PIERRE[1a] AND CHARLES C. PRICE[1b]

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Polymerization of propylene oxide proceeds readily at room temperature in the presence of powdered potassium hydroxide. The polymer has a molecular weight of 3000–5000 and has a high proportion of unsaturated end-groups, apparently largely of an allyl ether type, with some propenyl type in the primary polymer. The polymerization appears to be a specific surface-catalyzed reaction and a chain-type reaction, not a slow stepwise build-up, since polymer formed at low conversion is substantially the same molecular weight as at higher conversion. Non-oxidative degradation of the polymer has been shown to be catalyzed by toluenesulfonic acid at 270°. The products are volatile, and the presence of propionaldehyde and dimethyldioxane was established. Degradation with evolution of hydrogen and other gases was observed by electron irradiation.

The present work on the preparation of polypropylene oxide[2] through the polymerization of propylene oxide was undertaken with the hope that a polymer network based on high molecular weight material of this structure might have useful elastomeric properties. Earlier work, using bases at elevated temperatures (100–200°) and pressures,[3a,b] had been found to produce polymer of relatively low molecular weight, in the neighborhood of 1000 to 2000. Other work reported since the completion of this investigation,[4] however, discloses that the polymerization of propylene oxide by the use of ferric chloride or ferric hydroxide catalysis at 50–150° yields high molecular weight polymer, which is partially rubbery and partially solid. This claim was made earlier by Staudinger although he did not specify the polymerization procedure.

During the course of our work, it was accidentally discovered that propylene oxide could be polymerized readily by powdered potassium hydroxide at room temperature and atmospheric pressure, which led us to a study of catalysis and temperature effects on this polymerization. Propylene oxide was stirred at room temperature with about 10% by weight of a great variety of inorganic and organic bases. Of those studied, only powdered potassium hydroxide gave a reasonably fast polymerization under these conditions. In Table I are listed some of the catalysts used and their catalytic effects. In all cases where heterogeneity existed the catalysts were powdered and then continuously stirred during polymerization. The reactions were all carried out at room temperature and the presence of a non-volatile residue, after heating a portion of the liquid phase on a steam-bath, was taken to be a positive criterion of polymerization.

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[1] (a) General Tire and Rubber Co. Fellow, 1951–1953. Research Laboratories, General Electric Co., Schenectady, N. Y. (b) John Harrison Laboratory of Chemistry, University of Pennsylvania, Philadelphia 4, Pa. Presented at the 128th Meeting of the American Chemical Society, Minneapolis, Minn., September 12, 1955.

[2] First reported by P. A. Levene and A. Walti, *J. Biol. Chem.*, **75**, 325 (1927).

[3] (a) U. S. Patent 2,425,845, August 19, 1947, W. J. Toussaint and H. R. Fife (to Union Carbide and Carbon Corp.); (b) Makoto Okawara, *J. Chem. Soc. Japan, Ind. Chem. Sec.*, **55**, 335 (1952).

[4] U. S. Patents 2,706,181 and 2,706,182, April 12, 1955, M. E. Pruitt and J. M. Bagett (to Dow Chemical Co.).

[5] H. Staudinger, "Die hochmolekularen organischen Verbindungen," Berlin, J. Springer, 1932, p. 295.