TABLE III

S-BENZYLISOTHIURONIUM SALTS OF ISOMERIC ALKYLBENZENESULFONATES

$\overset{R'}{RCH}C_6H_4SO_3Na$					Nitrogen, %		Sulfur, %	
Orientation	R	R′	M.P.[a]	M.P. (Ref. 1b)	Calcd.	Found	Calcd.	Found
p	C_7H_{15}	H	125.6–125.8	125.6–126.0	...	...	...	...
o	C_7H_{15}	H	98–99[b]	105.5–106	...	...	...	...
p	C_9H_{19}	H	94.2–95.3	...	6.03	6.20	13.78	13.23
o	C_9H_{19}	H	113–114	...	6.03	5.94	13.78	13.95
p	$C_{11}H_{23}$	H	117–118	117–118	...	...	...	...
o	$C_{11}H_{23}$	H	101–103	101–103	...	...	...	...
p	C_9H_{19}	CH_3	104.0–104.4	...	5.85	5.66	13.37	13.98
o	C_9H_{19}	CH_3	108.6–109	...	5.85	5.72	13.37	13.46
p	$C_{11}H_{23}$	CH_3	105.9–106.2	105–106	5.53	5.43	12.63	12.93
o	$C_{11}H_{23}$	CH_3	86–86.5	...	5.53	5.38	12.63	12.90
p	$C_{13}H_{27}$	CH_3	106–106.9	...	5.24	5.06	11.97	12.05
o	$C_{13}H_{27}$	CH_3	113.7–115	...	5.24	5.15	11.97	12.07
p	$C_{15}H_{31}$	CH_3	109–109.4[c]	...	4.98	4.91	11.38	11.48
o	$C_{15}H_{31}$	CH_3	92.2–93.2	...	4.98	4.60	11.38	11.24

[a] All melting points were taken after drying at least six hours over phosphorus pentoxide at 78 (2 mm.). [b] On resolidification of the melt, the melting point was 106–106.8. [c] *p*-Toluidine derivative had a melting point of 119.1–119.5. *Anal.* Calcd. for $C_{30}H_{49}NO_3S$: N, 2.78; S, 6.35. Found: N, 2.73; S, 6.36.

of purity a phase solubility analysis[4] was conducted with I. The results of the analysis show conclusively that the compound isolated is essentially a single component with a 5.5% solubility in water at 46.5°. The *S*-benzylisothiuronium derivative of I, which is presumably the *para* isomer, melted at 126–128°.

Anal. Calcd. for $C_{26}H_{40}N_2O_3S_2$: N, 5.60; S, 13.62. Found: N, 5.63; S, 13.40.

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[4] W. J. Mader, *Organic Analysis*, Interscience Publishers Inc., New York, Vol. II., 253 (1954).

[CONTRIBUTION FROM THE BENZOL PRODUCTS CO.]

Isomer Distribution of Some Chloromethylated Alkylbenzenes

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Some alkylbenzenes were chloromethylated and the isomer contents of the resulting products examined by infrared spectrometry and gas-liquid chromatography. *meta*-Substitution occurred and in increasing amounts for ethyl-, methyl-, *i*-propy, and *t*-butylbenzenes.

Ingold,[1] in commenting upon the data of Le Févre,[2] stated that it was inconceivable that no *meta* compounds were formed when ethyl- and *i*-propylbenzenes were mononitrated. It was later found[3] that not inconsiderable quantities of the *meta* isomers actually did result and that there was increasing *meta* substitution in the series methyl-, ethyl-, *i*-propyl-, *t*-butylbenzenes. H. C. Brown[4] recently reported analogous behavior for acetylation and benzoylation.

Nazarov and Semenovskii[6] determined the isomer distribution of chloromethylated ethyl-, *i*-propyl-, and *t*-butylbenzenes by oxidation to the corresponding dicarboxylic acids. No *meta* substituted compounds were recovered, but it is apparent that small quantities could have escaped detection by their semiquantitative oxidation technique. We decided to investigate the isomeric products of the chloromethylation reaction by hydrogenolysis and subsequent examination by means

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[1] C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, Cornell University Press, Ithaca, New York, 1953, p. 257.

[2] R. J. W. Le Févre, *J. Chem. Soc.*, 1501 (1934).

[3] H. C. Brown and W. H. Bonner, *J. Am. Chem. Soc.*, 76, 605 (1954).

[4] H. C. Brown and G. Marino, *J. Am. Chem. Soc.*, 81, 5611 (1959).

[6] I. N. Nazarov and A. V. Semenovskii, *Izvest. Akad. Nauk. S.S.S.R. Otdel. Khim. Nauk.*, 100–111 (1957) [*Chem. Abstr.*, 51, 10400 (1957)].

TABLE I

ISOMER DISTRIBUTIONS OF CHLOROMETHYLATED ALKYLBENZENES

Chloromethyl Benzene	% *meta*		% *para*		% *ortho*	
	IR	GLC	IR	GLC	IR	GLC
Methyl[a]	1.1	—	54.0	55[b]	45.0	45.4
Ethyl	1.9	—	69.2	70.0[b]	29.0	30.0
i-Propyl	3.2	3.4	84.0	84.4	12.0	12.2
t-Butyl	5.8	6.4	94.0	93.6	*ca.* 0.1	

[a] H. C. Brown and K. L. Nelson[9] reported 1.3% *m*-, 64.0% *p*-, and 34.7% *o*-. C. D. Shacklett and H. A. Smith[10] reported 3.0% *m*-, 54% *p*-, and 43% *o*-. [b] Includes *meta*.

of infrared spectrometry and gas-liquid chromatography.

The results of this study (Table I) show that *meta* substitution does indeed occur and in increasing amounts for ethyl-, methyl-, *i*-propyl-, and *t*-butylbenzenes. This increase is probably due to a combination of inductive effects[7] and dispersion forces.[8] The amount of *meta*-*t*-butylbenzyl chloride found agrees well with the value expected based on Brown's "Selectivity Factor."[5] Benzoylation (S_f 2.1)[12] yields 5.4% *meta*[4] and chloromethylation (S_f 1.99)[12] is reported here to form 6.1% of the *meta* isomer. The quantity of *meta* compound increases with decreasing selectivity of the entering group. The insignificant quantity of *ortho* substitution formed by the chloromethylation of *t*-butylbenzene indicates that the steric requirements of the chloromethyl group is rather large. A comparison among the amounts of *ortho* isomers resulting from the benzoylation, bromination, and chloromethylation reactions leads to the conclusion that

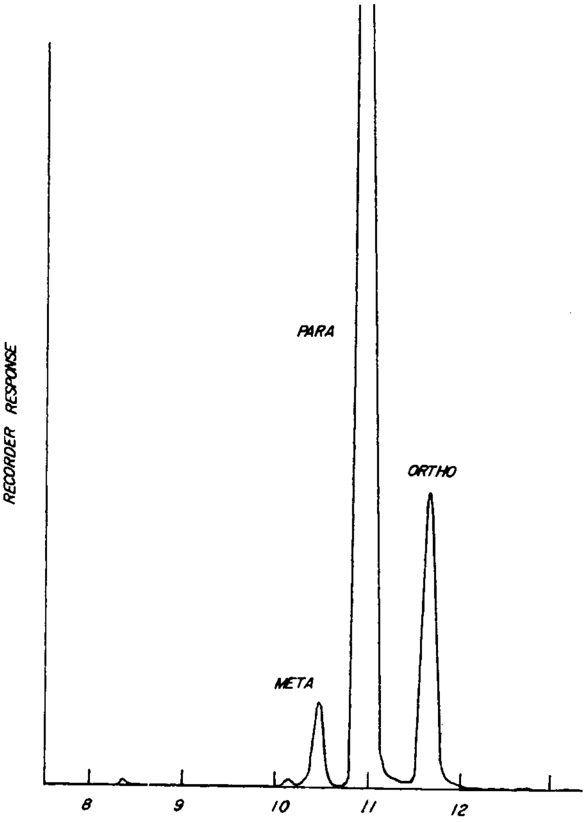

Fig. 1. Gas-liquid chromatogram of the isomeric *i*-propyltoluenes: 100 ft. by 0.01 in. stainless steel Ucon 50 HB 2000 capillary column, 135° column temp., 20 p.s.i. helium, 0.2 μl sample

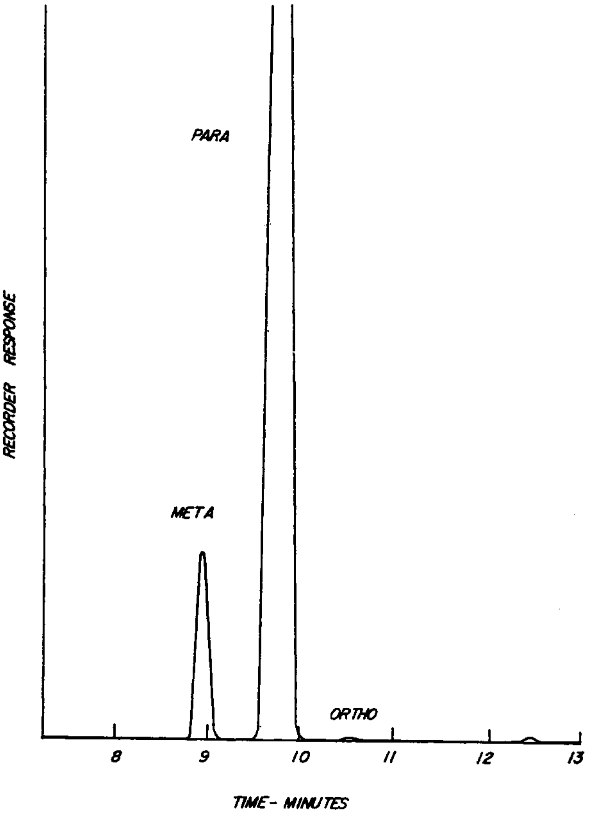

Fig. 2. Gas-liquid chromatogram of the isomeric *t*-butyltoluenes: 100 ft. by 0.01 in. stainless steel Ucon 50 HB 2000 capillary column, 135° column temp., 30 p.s.i. helium, 0.2 μl sample

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(7) H. C. Brown and M. Dubeck, *J. Am. Chem. Soc.*, 81, 5608 (1959).

(8) T. L. Brown, *J. Am. Chem. Soc.*, 81, 3229 (1959).

(5) H. C. Brown and C. R. Smott, *J. Am. Chem. Soc.*, 78, 6255 (1956).

(12) L. M. Stock and H. C. Brown, *J. Am. Chem. Soc.*, 81, 3323 (1959).

(9) H. C. Brown and K. L. Nelson, *J. Am. Chem. Soc.*, 75, 6292 (1953).

(10) C. D. Shacklett and H. A. Smith, *J. Am. Chem. Soc.*, 73, 766 (1951).

the chloromethyl group lies between the larger benzoyl group and bromine.

The disparity between the quantities of *ortho* and *para* isomers found in the chloromethylation of toluene as reported by H. C. Brown[9] and this work may result because the former's reaction was carried out in glacial acetic acid. Rather good agreement with Shacklett and Smith[10] has been obtained by us. Rapp and Kornev[11] recently reported nearly equal amounts of *ortho* and *para* chloromethyl toluenes arising from the chloromethylation reaction.

EXPERIMENTAL

A Perkin-Elmer Model 21 Infrared Spectrometer was used for the qualitative and quantitative examination of the alkyltoluenes. The gas-liquid chromatographic work was performed on a Perkin-Elmer Fractometer 154B equipped with a $^1/_4$-in. × 10-foot silicone oil (Dow Corning 550) column and thermal conductivity cells. In addition, a Barber-Coleman capillary column chromatograph was employed with a 100-foot Ucon 2000 capillary column and an ionization gauge detector. The packed column instrument effectively separated the *ortho* and *para* isomers but failed to resolve the *meta* from the *para*. Of many columns examined, only 7,8-benzoquinoline was somewhat effective for the separation of the isomeric xylenes. The capillary column coupled with ionization gauge nicely resolved all of the isomers (Figs. 1, 2). The chromatographic assays were obtained by the normalization technique and practically no area correction factors were necessary when using the Perkin-Elmer instrument. The infrared analytical wave lengths selected were as follows:

Alkyltoluene	*ortho*	*meta*	*para*
Methyl	13.46 μ	13.02 μ	12.55 μ
Ethyl, *i*-propyl, *t*-butyl	13.18–13.25	12.74–12.76	12.25–12.27

Known mixtures bracketing the values obtained by gas-liquid chromatography were prepared and standard curves drawn. *i*-Octane solutions were used for determining the major components and neat spectra recorded for the minor constituents.

The alkylbenzenes used as starting materials were of commercial quality and ranged between 95 and 98% pure. The chloromethylation reaction was carried out according to the method of Shacklett and Smith[10] and yielded products with analyses (alkaline hydrolysis) of over 99%. A.P.I. alkyltoluenes were used for the infrared standard curves.

The chloromethyl derivatives were transformed into the analogous alkyltoluenes by shaking 30 ml. of 50% ethanolic solution with 0.3 g. of 10% palladium–barium sulfate catalyst for 1 hr. at 50 p.s.i. hydrogen in a Parr hydrogenation apparatus. About 90% of the theoretical amount of hydrogen was absorbed. In all instances between 5 and 8% (determined by GLC) of unchanged chloromethylated material was found in the reduced product. A second reduction was carried out after filtering, driving off the hydrochloric acid and adding fresh catalyst. This sufficed to eliminate the unchanged residue. There was no difference in the isomer ratios of the alkyltoluenes when the first and second reductions were compared, indicating that the isomers of a particular alkyl chloromethyl benzene were hydrogenolyzed at the same rate. The analyses were carried out subsequent to filtering of the solutions, neutralizing with sodium carbonate and stripping off the alcohol.

Acknowledgment. The author expresses his appreciation to Professor H. C. Brown of Purdue University for some helpful comments concerning this investigation.

We are indebted to Dr. M. J. Schlatter of the California Research Corp. for supplying purified samples of the isomeric *i*-propyltoluenes.

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[11] L. B. Rapp and K. A. Kornev, *Ukrain. Khim. Zhur.*, **25**, 351–353 (1959) [*Chem. Abstr.*, **54**, 1368 (1960)].

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, CASE INSTITUTE OF TECHNOLOGY]

Solvent and Catalytic Effects in the Reaction of Ferric Chloride with Aromatic Compounds[1]

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A large number of metal halides were investigated for their influence as solvents or catalysts upon the reaction of anhydrous ferric chloride with simple aromatic compounds. Yield and isomer distribution of products, and rate of the various reactions which occur were affected by certain of the metal halides. The significance of the results is discussed.

It has been reported[2] that compounds of the Friedel-Crafts catalyst type, present either in small amounts or as solvents, decrease the temperature at which reaction occurs ("initiation temperature") and alter the isomer distribution in the chlorination of chlorobenzene by ferric chloride. Moreover, nitrobenzene, a solvent which would be expected to coordinate strongly with ferric chloride, retarded the reaction. These effects were interpreted as evidence for a polar mechanism. Catalytic influences in the ferric chloride–benzene system are treated elsewhere.[3]

Our intention in the present work was to make

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[1] Paper V in the series, "Reactions of Metal Halides with Organic Compounds"; an abstract of a portion of the Ph.D. thesis of C. Wu, Case Institute of Technology, 1960.

[2] P. Kovacic and N. O. Brace, *J. Am. Chem. Soc.*, **76**, 5491 (1954).

[3] P. Kovacic and C. Wu, forthcoming publication.