[CONTRIBUTION FROM THE RICHARD B. WETHERILL LABORATORY OF PURDUE UNIVERSITY]

Rates of Chlorination of Benzene, Toluene and the Xylenes. Partial Rate Factors for the Chlorination Reaction[1,2,3]

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The isomer distribution in the non-catalytic chlorination of toluene in acetic acid at 25° has been determined to be 59.78% *ortho*, 0.48% *meta* and 39.74% *para*. The relative rate of chlorination of benzene and toluene under these conditions is 1.00/344. These data establish the partial rate factors for the non-catalytic chlorination of toluene to be o_f = 617, m_f = 4.95 and p_f = 820. Excellent agreement is observed between the observed rates of chlorination of the isomeric xylenes and the rates calculated using these partial rate factors. Chlorination of *m*-xylene yields 23.0% 2- and 77.0% 4-chloro-1,3-dimethylbenzene. The small discrepancy with the calculated values, 27.3% 2- and 72.7% 4-, is attributed to the "double *ortho* effect" accompanying substitution in the 2- position.

In examining the partial rate factors for the halogenation of toluene, a large discrepancy was noted between two possible sets of partial rate factors for the chlorination reaction.[4] One set had been developed by Condon[5] and was based upon the isomer distribution observed in the catalyzed chlorination,[6] the relative rates of the uncatalyzed chlorination of benzene and toluene,[7] and an assumed value of m_f: $o_f = 600$, $m_f = 5.0$ and $p_f = 870$. The second set was obtained by solution of the simultaneous equations for the relative rates of chlorination of benzene, toluene, *o*- and *p*-xylene[7]: $o_f = 402$, $m_f = 8.2$ and $p_f = 1280$.

Excellent agreement had been realized previously in both the bromination[4] and the mercuration reactions[8] between partial rate factors based primarily upon the observed isomer distribution in toluene and those based upon relative rates. Consequently, a detailed study of the chlorination reaction appeared desirable in order to resolve the discrepancy.

Results

Bromination of aromatics in acetic acid solution exhibits complicated kinetics[9] and the reactivities are generally established by determining the time required for 10 or 20% reaction under identical conditions. Fortunately, the chlorination reaction does not exhibit these kinetic difficulties. Thus it has been observed that the chlorination of phenolic ethers and anilides[10] and the chlorination of a number of aromatic hydrocarbons[7,11,12] exhibit clean second-order kinetics.[13]

Accordingly, the relative reactivities were established by measuring the second-order rate constants for the reaction of chlorine with the aromatics in 99.87 mole % acetic acid. Light was carefully excluded to avoid reaction of the chlorine with the side chains. A number of check experiments indicated that such side-chain chlorination was less than 1-2% and could be neglected. Typical results are summarized in Table I.

TABLE I

SECOND-ORDER RATE CONSTANTS FOR THE REACTION OF CHLORINE WITH BENZENE AND METHYLBENZENES IN 99.87% ACETIC ACID AT 25.0°

	Concentration, *M*		Rate constant
Compound	[ArH]	[Cl_2]	$k_2 \times 10^4$, l. mole^{-1} sec.$^{-1}$
Benzene	0.1990	0.0893	0.0147 ± 0.0003
	.1990	.0885	.0158 ± .0005
Toluene	.1908	.0313	5.27 ± .04
	.1990	.0342	5.34 ± .17
o-Xylene	.1895	.0252	32.0 ± .5
	.2000	.0398	33.1 ± .4
	.1776	.0211	32.5 ± .2
p-Xylene	.1905	.0281	32.0 ± .1
m-Xylene	.0132	.0132	2870 ± 80
	.0130	.0120	2990 ± 100
	.00619[a]	.0167	2840 ± 110
	.00613[b]	.0166	2820 ± 40
	.0197[c]	.0197	2530 ± 100

[a] Solution contained benzene, 0.0646 *M*. [b] Benzene, 0.0993 *M*. [c] Benzene, 0.1974 *M*.

m-Xylene was very reactive and it was necessary to reduce both the chlorine concentration and the *m*-xylene concentration in order to reduce the rate of the reaction sufficiently to permit measurement. In the case of *o*-xylene it was demonstrated that a similar decrease in the chlorine concentration did not alter the rate constant significantly (Table I).

It has been noted that the halogenation reaction is quite sensitive to changes in the polarity of the reaction medium.[10,14] To test the possible effect of the decrease in hydrocarbon concentration on the rate constant, the chlorination of *m*-xylene was examined in the presence of added benzene in several concentrations (Table I). With the possible exception of the highest concentration, the variations in the observed second-order rate constants resulting from this procedure are no greater than the experimental uncertainty. It was therefore concluded that in the concentration ranges utilized in the present experiments the effect of

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[1] Directive Effects in Aromatic Substitution. XVIII.

[2] Supported by the Petroleum Research Fund of the American Chemical Society.

[3] Based upon a thesis submitted by Leon M. Stock in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[4] H. C. Brown and L. M. Stock, THIS JOURNAL, **79**, 1421 (1957).

[5] F. E. Condon, *ibid.*, **70**, 1963 (1948).

[6] E. Wertyporoch, *Ann.*, **493**, 753 (1932).

[7] P. B. D. de la Mare and P. W. Robertson, *J. Chem. Soc.*, 279 (1943).

[8] H. C. Brown and C. W. McGary, Jr., THIS JOURNAL, **77**, 2310 (1955).

[9] See ref. 4 for pertinent references.

[10] A. E. Bradfield and B. Jones, *J. Chem. Soc.*, 1006 (1928), and subsequent papers in this series.

[11] K. Lauer and R. Oda, *Ber.*, **69**, 1061 (1936). See criticism of this study by de la Mare and Robertson, ref. 7.

[12] M. J. S. Dewar and T. Mole, *J. Chem. Soc.*, 342 (1957).

[13] It has been reported that hydrogen chloride, generated in the reaction, results in a small autocatalysis (ref. 7). However, this phenomenon was not observed in the present study.

[14] R. M. Keefer, A. Ottenberg and L. J. Andrews, THIS JOURNAL, **78**, 255 (1956).

changes in the hydrocarbon concentration could be neglected.

All previous studies of the isomer distribution in the chlorination of toluene have employed electrophilic catalysts and have been carried out generally in the absence of a solvent. Thus Wahl and co-workers observed 58% *o*- and 42% *p*-chlorotoluene with metallic iron as catalyst[15] while Wertyporoch noted 58% *o*- and 42% *p*- using antimony pentachloride and 55% *o*- and 45% *p*- with iodine as the catalyst.[6] The presence of "traces" of the *meta* isomer was reported in an early chlorination of toluene in the presence of molybdenum pentachloride.[16]

For purposes of the present investigation it was necessary to determine the isomer distribution under the identical conditions utilized for the rate measurements. Moreover, it was especially important to determine accurately the *meta* isomer formed in the reaction. Accordingly, the chlorination of toluene was carried out in the absence of catalyst by the slow addition of chlorine in acetic acid to a large excess of toluene in the same solvent. The product was isolated and analyzed by infrared. The results are summarized in Table II.

TABLE II

ISOMER DISTRIBUTION IN THE NON-CATALYTIC CHLORINATION OF TOLUENE IN ACETIC ACID AT 25°

Run	Procedure[a]	Product, mole % *ortho*	*meta*	*para*
1	A	60.32[b]		39.67[b]
2	A	60.58	0.45	38.98
3	B	59.77	.51	39.72
4	B	59.30	.52	40.18
5	B	59.21	.44	40.35
Mean		59.78 ± 0.42	0.48 ± 0.04	39.74 ± 0.42

[a] See Experimental Part. [b] These values were normalized with 0.048% *meta* to obtain the mean values.

Based upon our experience with analysis of synthetic mixtures, we believe that the values for the *ortho* and *para* isomers are probably accurate within the limits of uncertainty indicated in Table II. However, the limits of uncertainty for the *meta* isomer in the analysis of these synthetic mixtures appeared to be ±0.10. Consequently, the excellent agreement in the analytical results for this component may be somewhat fortuitous.

Fortunately, the *meta* partial rate factor and the mole per cent. *meta* isomer formed in the chlorination reaction may be estimated from independent data. First, solution of the set of simultaneous equations for the rates of chlorination of the three xylene leads to a value for m_f. This value indicated that the chlorination of toluene should result in the formation of 0.50 mole % *m*-chlorotoluene. Second, using the value of o_f from the rate and percentage *ortho* isomer in the chlorination of toluene, and the rate data for *p*-xylene, it is possible to calculate m_f. This value predicts a concentration of 0.49% for the *meta* isomer. Finally, it is possible to utilize the Selectivity Relationship[17]

$$\log p_f = 1.310 \log (p_f/m_f)$$

and the well established value for p_f. This procedure indicates that the product should contain 0.48 mole % *m*-chlorotoluene. In view of the excellent agreement between these different approaches, it would appear that considerable confidence may be placed in the experimental value of 0.48 mole %.

It was of interest to examine also the isomer distribution in the chlorination of *m*-xylene. The hydrocarbon was chlorinated using procedures identical with those adopted for toluene. The product was isolated, distilled and analyzed by infrared spectroscopy. The results are summarized in Table III.

TABLE III

ISOMER DISTRIBUTION IN THE NON-CATALYTIC CHLORINATION OF *m*-XYLENE IN ACETIC ACID AT 25°

Run	Procedure[a]	Product, mole % 2-Chloro	4-Chloro	Recovery %
1	B	22.0	78.0	97.5
2	B	24.1	75.9	88.8
Mean		23.0 ± 1.0	77.0 ± 1.0	

[a] See Experimental Part.

Discussion

For convenience in following the discussion, the average values of the second-order rate constants are summarized in Table IV, together with the available literature values.

The second-order rate constant for the chlorination of benzene, 14.8 × 10^{-7} (24°) l.mole^{-1}sec.$^{-1}$, obtained by de la Mare and Robertson,[7] is in serious disagreement with that reported by Lauer and Oda,[11] 4.2 × 10^{-5} (30°) l.mole^{-1} sec.$^{-1}$. However, the present value, 15.4 × 10^{-7} l.mole^{-1}sec.$^{-1}$ supports the lower value of the former workers.[18]

The relative rate data for toluene and *p*-xylene are in excellent agreement with the earlier values of de la Mare and Robertson.[7] However, our value for *o*-xylene is less than half of the earlier value. Some confidence may be placed in the present value on the basis that it leads to a consistent set of partial rate factors, whereas the higher value results in serious discrepancies.[19]

The relative rate of chlorination of *m*-xylene has not been reported previously. The reaction is exceedingly fast. Even utilizing very low concentrations of the reactants results in a relatively fast reaction with a half-life of approximately 3 minutes. As a result, the uncertainty in this value may be somewhat greater than in the case of the other, less reactive hydrocarbons.

Utilizing the relative rates of chlorination of benzene and toluene and the observed isomer distribution in toluene, we can calculate the partial rate factors. These are listed in Table V. The

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(15) A. Wahl, G. Norman and G. Vermeylen, *Bull. soc. chim.*, [4] **31**, 570 (1922).

(16) B. Aronheim and G. Dietrich, *Ber.*, **8**, 1401 (1875); J. S. Reese, *Chem. Revs.*, **14**, 55 (1934).

(17) H. C. Brown and C. R. Smoot, THIS JOURNAL, **78**, 6255 (1956).

(18) Dewar and Mole (ref. 12) have reported a value of 6 ± 1 × 10^{-7} l. mole^{-1} sec.$^{-1}$ for this reaction. However, they utilized solutions relatively concentrated in the hydrocarbon, 0.6 *M*, and the lower rate constant may result from the decrease in the polarity of the reaction medium (ref. 10, 14).

(19) In preliminary experiments utilizing *o*-xylene of 99.5 mole % purity we observed an initial rapid depletion in the chlorine concentration. It was suspected that the phenomenon was due to the highly reactive *m*-xylene present as an impurity. Utilization of a sample of *o*-xylene of 99.99 mole % purity avoided this difficulty. It is possible that the high value for *o*-xylene observed by de la Mare and Robertson is due to this cause.

TABLE IV

OBSERVED AND CALCULATED RELATIVE RATES OF CHLORINATION OF BENZENE AND THE METHYLBENZENES IN ACETIC ACID AT 25°

Compound	Rate constants[a] $k_2 \times 10^4$, mole^{-1} sec.$^{-1}$	Relative rates, k/k° Obsd.	Lit.[b]	Calcd.[c]
Benzene	0.0154	1.00	1.00	1.00
Toluene	5.30	344	350	344
o-Xylene	32.3	2.10×10^3	4.6×10^3	2.37×10^3
m-Xylene	2850	1.85×10^5		2.32×10^5
p-Xylene	32.0	2.08×10^3	2.2×10^3	2.04×10^3
Hemimellitene				8.37×10^5
Pseudocumene				7.34×10^5
Mesitylene				1.56×10^8
Prehnitene				4.13×10^6
Isodurene				5.15×10^8
Durene				3.11×10^6
Pentamethylbenzene				1.27×10^9

[a] Mean values based on data in Table I together with additional determinations. [b] Ref. 7. Benzene and toluene were compared in 80% acetic acid and the remaining compounds in 99% acetic acid by measurement of the 10 and 20% reaction time at 24°. [c] Based on o_f 617, m_f 4.95, p_f 820.

agreement with Condon's estimated values[5] ($o_f = 600$, $m_f = 5.0$, $p_f = 870$) is remarkably close. A set of partial rate factors can also be calculated from the observed rates of chlorination of benzene, toluene, *o*- and *p*-xylene. In a similar manner it is possible to derive a set of partial rate factors from the relative reactivity data for the three xylenes. Finally, the partial rate factors can be based upon p_f and the Selectivity Relationships for toluene. The results of these different approaches to the partial rate factors are summarized in Table V.

TABLE V

PARTIAL RATE FACTORS FOR THE CHLORINATION OF TOLUENE IN ACETIC ACID AT 25°

Source	Partial rate factors o_f	m_f	p_f	Selectivity factor, S_f[a]
Isomer distribution and k_T/k_B	617	4.95	820	2.219
Relative rates: k_B, k_T, k_{p-Xy}, k_{o-Xy}	681	4.58	694	2.180
Relative rates: k_B, k_{p-Xy}, k_{o-Xy}, k_{m-Xy}	604	5.17	615	2.076
Selectivity relationship	529	4.87	820	2.224

[a] Log (p_f/m_f). Ref. 17.

Considering the possible effects of experimental uncertainties in these different approaches to the partial rate factors, the agreement in the values may be considered excellent. Since the values based upon the isomer distribution in toluene and the toluene/benzene relative rate involve a direct calculation without any additional assumptions, we shall adopt this set for the chlorination reaction. The Hammett reaction constant, ρ, may then be calculated to be -9.80.

Utilizing these partial rate factors, o_f 617, m_f 4.95 and p_f 820, it is possible to calculate the rates of chlorination of all of the methylbenzenes (Table IV). In the case of three xylenes the observed chlorination rates agree with those calculated from the partial rate factors with an average deviation of 10%. Unfortunately, the rates of chlorination of the higher methylbenzenes are far too fast to measure by the present procedure and experimental values for their rates could not be obtained for comparison. However, earlier studies have revealed good agreement between the observed and calculated rates for the mercuration[3] and the bromination of all of the methylbenzenes.[4] The measure of the agreement is indicated by Figs. 1 and 2. On this basis, considerable confidence may be placed in the calculated values for the chlorination of the higher methylbenzenes.[20]

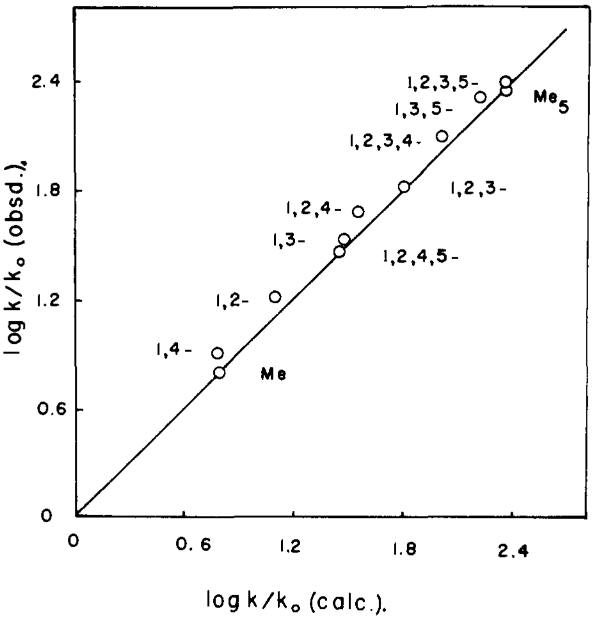

Fig. 1.—Observed and calculated relative rates of mercuration of the methylbenzenes.

The partial rate factors also permit a calculation of the isomer distributions to be expected in the chlorination reaction. The values are summarized in Table VI.

Experimental determination of the isomer distribution in the chlorination of *m*-xylene indicated the formation of 23.0% 2-chloro-1,3-dimethylbenzene and 77.0% 4-chloro-1,3-dimethylbenzene.

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[20] The zinc chloride-catalyzed bromination and the iodine chloride iodination of the methylbenzenes have also been examined: L. J. Andrews and R. M. Keefer, THIS JOURNAL, **78**, 4549, 5623 (1956). However, in these cases the agreement between the observed and calculated relative rates is somewhat less satisfactory.

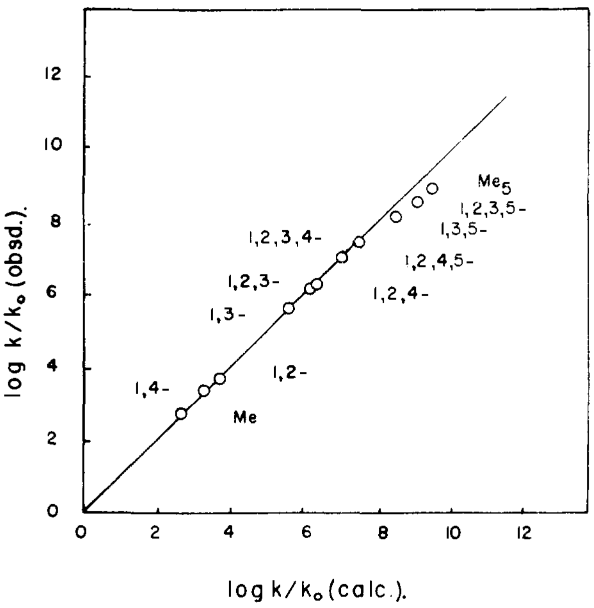

Fig. 2.—Observed and calculated relative rates of bromination of the methylbenzenes.

This is in reasonable agreement with the calculated values: 27.3% 2- and 72.7% 4-. The somewhat lower value observed experimentally for the 2- isomer may be due to a slightly retarded rate of substitution in the 2-position where the chlorine atom must substitute *ortho* to two methyl groups. It was pointed out previously that retarded substitution rates may be anticipated for such "double-*ortho*" positions.[8,20]

TABLE VI

CALCULATED ISOMER DISTRIBUTION IN THE CHLORINATION OF THE METHYLBENZENES IN ACETIC ACID AT 25°

Compound	Mole % monochloro isomer in products 2-	3-	4-	5-	6-
Toluene	59.7	0.5	39.8		
o-Xylene		42.9	57.1		
m-Xylene	27.3		72.7	0.002	
Hemimellitene			99.7	0.3	
Pseudocumene		42.8	56.9		0.3

The partial rate data define a point which fits precisely on the Selectivity Graph for the substitution reactions of toluene.[21] It may be concluded that the chlorination reaction clearly follows all other electrophilic substitution reactions previously examined in obeying the Selectivity Relationship.

Experimental Part

Materials.—Samples of all of the aromatic hydrocarbons were available from previous studies[4,8] with purities of 99.5% or better.

The *o*-, *m*- and *p*-chlorotoluenes utilized as infrared standards were commercial materials, purified by fractionation. *p*-Chlorotoluene was further purified by fractional crystallization. The mole % purities were established by analysis of the cooling curves. The products utilized exhibited the following physical properties and purities (in mole %): *o*-chlorotoluene, b.p. 158° at 747 mm., $n^{20}D$ 1.5258, f.p. −35.59°, 99.6%; *m*-chlorotoluene, b.p. 162° at 738 mm., $n^{20}D$ 1.5218, f.p. −48.89, 99.7%; *p*-chlorotoluene, $n^{20}D$ 1.5208, f.p. 7.20°, 99.7%.

The isomeric chloro-*m*-xylenes were prepared from the corresponding xylidines in concentrated hydrochloric acid solutions.[22] However, this technique did not result in increased yields over those realized with the Sandmeyer procedure for these compounds.[23] The 2-chloro-1,3-dimethylbenzene was obtained in 30% yield, while the 4-chloro-1,3-dimethylbenzene was obtained in 40% yield. These compounds were purified by two steam distillations from aqueous sodium hydroxide, extraction with ether, followed by fractionation. The following properties and purities (in mole %) were observed: 2-chloro-1,3-dimethylbenzene, b.p. 183.9° at 750 mm., f.p. −34.96°, $n^{20}D$ 1.5268, 99.6%; 4-chloro-1,3-dimethylbenzene, b.p. 185.1° at 740 mm., f.p. −32.49°, $n^{20}D$ 1.5235, 99.1%.

Carbon disulfide and acetic acid were purified by procedures previously described.[4] Chlorine (Matheson, 99.5%) was used directly, after drying by passage through sulfuric acid. The acetic acid used in the kinetic experiments was purified by distillation followed by a low temperature sublimation, f.p. 16.585°, 99.87 mole % purity. The acetic acid in the isomer distribution studies was used after fractionation, but without sublimation, f.p. 16.25°, 99.3 mole % purity.

Kinetic Measurements.—It was established that the rate of the dark reaction of chlorine with acetic acid was slow at 70°, $k_1 = 7.0 \times 10^{-4}$ sec.$^{-1}$, and negligible at 25° compared to the rate of reaction with the aromatics. Consequently, no correction for this side reaction was necessary.

All rate measurements were performed in black flasks with a long narrow neck in an enclosed constant temperature-bath at 25.00 ± 0.03°. Experiments were initiated by mixing thoroughly acetic acid solutions of known concentrations of aromatic and chlorine. An aliquot was withdrawn to establish zero time, thereby minimizing the effects of initial losses due to the volatility of the chlorine and the effect of trace impurities in the aromatic. Analyses for unreacted chlorine were made iodimetrically. The kinetic experiments were carried out to 75–80% completion, except in the case of benzene which had proceeded to 10% reaction only in five days. (In the latter case, a small correction, 0.001 *M* Cl_2, established in blank experiments was applied to compensate for small losses in chlorine during the removal of aliquots over the extended reaction time.)

The specific second-order rate constants were calculated for each point taken, 5 to 7 for each kinetic study. The second-order rate constants are reported in Table IV. Rate data for a typical determination are reported in Table VII.

TABLE VII

RATE DATA FOR THE REACTION OF CHLORINE WITH TOLUENE IN 99.87% ACETIC ACID AT 25.00°

Time, sec. × 10^{-2}	Toluene, *M* $a - x$	Chlorine, *M* $b - x$	Rate constant, $k_2 \times 10^4$ l. mole^{-1} sec.$^{-1}$
0.0	0.1908	0.0313	
27.9	.1833	.0238	5.24
76.9	.1745	.0150	5.29
96.9	.1719	.0123	5.34
140	.1682	.0086	5.21
191	.1650	.0055	5.24

Examination of several reaction mixtures for non-aromatic organic chlorides indicated the presence of a maximum of 1–2% of the chlorine in this form. This side reaction was therefore neglected.

Isomer Distribution in Toluene.—Two different procedures were followed. Procedure A: Toluene, 0.471 mole, was added to a solution of chlorine, 0.09 mole, in acetic acid and the total volume adjusted to 500 ml. Samples were taken immediately to establish the chlorine concentration. The reaction was allowed to proceed to completion in the dark (10–18 hours).

Procedure B: Approximately 0.1 mole of chlorine in 240 ml. of acetic acid was added dropwise to a stirred solution of toluene, 0.471 mole, in 250 ml. of acetic acid over a 5–6 hour

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[21] See Fig. 1, ref. 4.

[22] H. C. Beyerman and G. L. G. Wielaert, *Rec. trav. chim.*, **71**, 1213 (1952).

[23] G. Stapleton and A. I. White, *J. Am. Pharm. Assoc.*, **43**, 193 (1954).

interval in the dark and the reaction allowed to proceed to completion.

The resulting solutions of toluene and chlorotoluene in acetic acid were then transferred to a continuous liquid-liquid extractor, 1500 ml. of water added, and the mixture subjected to extraction for 16–20 hours with carbon disulfide. The resulting extract was concentrated by the distillation of the carbon disulfide in a small column, and the residual carbon disulfide and toluene were removed by fractionation in a Todd micro column. Yields of monochlorotoluene of 78–81% were realized. The column was washed down with carbon disulfide and the combined washings and product were utilized for infrared analysis of the *o*- and *p*-chlorotoluenes in dilute (0.25 M) carbon disulfide solution, using the wave lengths 9.48 μ for *o*- and 12.44 μ for *p*-.

Small quantities of benzyl chloride interfered with the analysis for the *meta* isomer. To ensure the absence of benzyl chloride, 2,4,6-collidine (b.p. 169° at 750 mm.) was added to the reaction product and the material distilled through the Todd micro column. The fraction collected included a trace of toluene and an excess of the collidine. The base was extracted with hydrochloric acid and the chlorotoluene fraction was dried over calcium hydride.

The resulting product was analyzed for *ortho* and *para* isomers as before. No significant change in the isomer distribution was observed as a consequence of these manipulations. The product was analyzed for the *meta* isomer using the wave length of 12.98 μ and a differential infrared technique with *o*- and *p*-chlorotoluene in the reference cell.

The characteristic bands for the dichlorinated toluenes were absent from spectra obtained in concentrated carbon disulfide solutions and as the pure chlorotoluenes. Consequently, the reaction had proceeded to the monochlorotoluene stage and no further.

These procedures were extensively tested through the recovery of synthetic mixtures of the chlorotoluenes and toluene from acetic acid solutions. In these experiments we realized average recoveries of 95% and analyses for *o*- and *p*-chlorotoluene which agree with the synthetic composition with an average error of 1–1.5%. The precision of the analyses for the much smaller content of the *meta* isomer was considerably lower, with a mean error of 15% indicated. The results of these analyses are summarized in Table VIII.

TABLE VIII

THE ANALYSIS OF SYNTHETIC MIXTURES OF THE CHLOROTOLUENES ISOLATED FROM ACETIC ACID SOLUTIONS

Run	Mole % chlorotoluene Known *ortho*	Known *meta*	Known *para*	Found *ortho*	Found *meta*	Found *para*	Recovery,[a] %
1[b]	63.93	1.21	34.86	64.30	1.45	34.25	95.5
2[b]	64.18	0.72	35.10	64.57	0.66	34.77	95.2
3[b]	64.02	.83	35.15	64.45	.75	34.80	95.8
4[b]	61.55	.53	37.92	62.20	.45	37.35	100.5
5[b]	60.13	..	39.87	61.49	..	38.51	93.5
4[a,c,d]	...	..	...	62.25	0.36	37.39	...
6[c]	60.23	1.12	38.65	59.50	1.28	39.22	90.1
7[c]	59.65	0.52	39.83	59.17	0.41	40.42	...
8[c]	58.59	0.71	40.70	60.22	0.69	39.09	...

[a] Chlorotoluenes recovered from solutions of acetic acid based on analysis of pot composition. [b] Analysis performed on pot residues. [c] Analyses performed on isolated chlorotoluene fraction after distillation from 2,4,6-collidine. [d] The results of the subsequent distillation of run 4 from 2,4,6-collidine.

Isomer Distribution in *m*-Xylene.—Two chlorinations were carried out under the conditions of procedure B and the isolation and extraction were achieved in a manner similar to that utilized for the *o*- and *p*-chlorotoluenes. Since *m*-xylene possesses a very strong band at 13.07 μ, the only suitable wave length for 2-chloro-1,3-dimethylbenzene, it was necessary to remove the *m*-xylene by fractionation from the reaction product prior to the infrared analysis. Analysis for 4-chloro-1,3-dimethylbenzene was based on the absorption band at 12.45 μ. The procedure was tested on a synthetic mixture containing 5 ml. of *m*-xylene, 7.48 g. (74.7%) of 4- and 2.53 (25.3%) of 2-chloro-1,3-dimethylbenzene. After recovery from acetic acid, the analysis indicated 7.24 g. (72.0%) 4- and 2.81 g. (28.0%) 2-chloro-1,3-dimethylbenzene. The isomer distribution and recoveries in the actual chlorination experiments are summarized in Table III.

Acknowledgment.—We are indebted to Mrs. Barbara Polister and Miss Margee Haley for the infrared spectra and to the Petroleum Research Fund of the American Chemical Society for the financial support which made this study possible.

LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

Organoboron Compounds. II. Preparation and Properties of Some Trialkylboroxines[1-3]

BY PATRICK A. MCCUSKER, EUGENE C. ASHBY AND HENRY S. MAKOWSKI

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An azeotropic distillation process has been found to be convenient for the quantitative dehydration of large laboratory quantities of organoboronic acids. A number of new or heretofore unpurified trialkylboroxines have been prepared, purified and characterized. The trialkylboroxines have been found to undergo disproportionation to a very slight extent above 200° into boric oxide and trialkylboranes but to be completely stable on distillation at lower temperatures.

For the preparation of a series of alkyldichloroboranes a variety of trialkylboroxines was required. The preparation, purification and characterization of a number of trialkylboroxines from the corresponding alkylboronic acids are reported in the present paper. A direct procedure for the preparation of trialkylboroxines without isolation of the boronic acids is also described.

Experimental

***n*-Butyl-, *sec*-Butyl-, *t*-Butyl-, *n*-Amyl-, Cyclohexyl- and *n*-Hexylboronic Acids.**—These were prepared in three- or four-mole quantities by the method of Snyder, Kuck and Johnson,[4] as previously described.[1]

Methylboronic Acid.—Some modifications of the standard procedure[4] were required for the preparation of methylboronic acid. This preparation is therefore described in detail. A 3-liter, 3-neck flask was equipped with a condenser, high speed Tru-bore stirrer, a 2-liter dropping funnel with delivery tube bent to deliver solution to the center of the flask and a bridge-bubbler system to supply and maintain a nitrogen atmosphere. A solid carbon dioxide trap to

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(1) Paper I, P. A. McCusker and L. J. Glunz, THIS JOURNAL, **77**, 4253 (1955).

(2) The authors acknowledge with thanks helpful discussions with Professor G. F. Hennion.

(3) Trialkylboroxines are also known as trialkylboroxols, alkylboron oxides and alkylboronic acid anhydrides.

(4) H. R. Snyder, J. A. Kuck and J. R. Johnson, THIS JOURNAL, **60**, 105 (1938).