EXPERIMENTAL

Butyllithium solution was prepared under conditions as dry and air-free as possible. In a 1-l. flask fitted with condenser, stirrer, graduated dropping funnel, batch thermometer, argon inlet, and water bath, 33.20 g. of Foote's 52.5% lithium dispersion (2.500 g.-atoms) was dispersed in 500 ml. of sulfuric acid-washed, sodium-dried heptane (Phillips' 99%) in a gentle current of argon. In the course of 55 min. 115.7 g. (1.250 moles) of 1-chlorobutane (n^{20}_{D} 1.4019) was added dropwise, the batch temperature varying between 35 and 43°. The slurry was stirred for another 30 min. at 35°, then quickly discharged into a baked, argon-filled, 28-oz. beverage bottle (capped under a slight positive pressure of argon). After the whole had settled for 100 hr. 512 ml. of colorless butyllithium solution was forced with argon pressure into a second baked, lamp nitrogen-filled, 28-oz. beverage bottle (capped under slight positive pressure of lamp nitrogen).[2]

One gallon of anhydrous ether (Baker and Adamson) was treated with 25 g. of sodium ribbon; then it was confined under argon for 50 days. Benzyl chloride (Baker and Adamson, reagent) was distilled in vacuum over phosphorus pentoxide, then stored over anhydrous calcium chloride under argon.

Exactly 1.00 ml. of clear butyllithium solution titrated 8.87 ml. of 0.19850N hydrochloric acid to the faintest Methyl Orange change.

Three 60-ml. bottles with serum caps were baked at 110°, then flushed with argon (using #19 and #20 hypodermic needles) until cool. Exactly 1.5 ml. of benzyl chloride and 10, 20, and 30 ml. of dry ether (from hypodermic syringes and needles baked at 110° and cooled over phosphorus pentoxide) were charged through the serum cap, respectively. After mixing, 1.00 ml. of colorless butyllithium solution was charged to each bottle through the serum cap. After reacting for 2 min., 5 ml. of water was added to each. Each was titrated with 0.19850N hydrochloric acid, first against phenolphthalein then Methyl Orange (faintest change). The titrations against Methyl Orange were 0.40, 0.43, and 0.46 ml., respectively.

The above experiment was repeated using lamp nitrogen instead of argon as the flushing agent. The titrations were 0.34, 0.37, and 0.40 ml., respectively.

Ten milliliters of sodium-dried ether contained enough oxygen, moisture, and ethanol to destroy butyllithium equivalent to 0.03 ml. of 0.19850N hydrochloric acid.

One milliliter of ball-milled lithium butoxide dispersion in dry heptane (titn., 4.07 ml. of 0.19850N hydrochloric acid) was treated with 1.8 ml. of dry benzyl chloride and 10 ml. of dry ether at 45–50° for 2 min. After dilution with water the titration remained unchanged.

CALCULATIONS AND CONCLUSIONS

Taking the best figure from a determination in lamp nitrogen, 8.87 ml. (total titn.) − 0.34 ml. (titn. after BzCl) + 0.03 ml. (ether corr.) × 100%/8.87 ml. (total titn.) or 96.5% of the base in the colorless butyllithium solution was destroyed by benzyl chloride. Since lithium butoxide is unaffected by benzyl chloride in ether in 2 min. at 45–50°, it is reasonable to believe that 96.5% of the total base in the clear butyllithium solution was carbon-bound lithium. One could assume that if butyllithium free from lithium butoxide and hydroxide could be prepared, benzyl chloride in absolutely dry and oxygen-free ether would destroy all of the alkalinity in it. The author feels that the method of Gilman and Haubein for assay of alkyllithium is most reliable.

Acknowledgment. The author is indebted to Dr. F. W. Stavely of the Firestone Research Laboratories for his interest in this work and to Mr. Harold A. Kerry of the American Potash and Chemical Corporation for much valuable advice.

Firestone Tire and Rubber Co.
Chemical and Physical Research Laboratories
Akron 17, Ohio

---

[2] Lamp nitrogen is almost completely dry and free from oxygen while commercial argon is not. However, lamp nitrogen reacts fairly rapidly with lithium dust at room conditions to yield lithium nitride, but it has no effect upon butyllithium over a period of 8 months.

A Study of Reaction Variables in Aromatic Chlorination by Antimony Pentachloride[1]

Peter Kovacic and Allen K. Sparks[2]

Received August 4, 1960

Our previous investigations[3] on aromatic chlorination by antimony pentachloride have been concerned primarily with the reaction mechanism. This report presents a study of reaction variables in the chlorination of aromatic compounds, particularly chlorobenzene, by antimony pentachloride. The aspects dealt with include solvent and catalytic effects, mode of addition, temperature, and time. In addition, the practicality of chlorination by this method was investigated.

The presence of nitrobenzene as a solvent in the chlorobenzene reaction, while ineffective in altering the isomer distribution significantly, necessitated the use of more drastic conditions to effect chlorination. Pyridine inhibited the reaction completely. These effects are attributed to the formation of addition compounds from antimony pentachloride and the solvents, resulting in deactivation of the metal halide. In fact, solid separated initially from solution in both cases, in accord with reports that antimony pentachloride forms complexes with pyridine[4] and nitrobenzene.[5] With titanium tetrachloride solvent, it is not known whether the increased temperature required for reaction is due to complexing or to a concentration influence.

---

[1] Part IX of a series on "Reactions of Metal Halides with Organic Compounds"; from the Ph.D. thesis of A. K. Sparks, Case Institute of Technology, 1960.

[2] Allied Chemical Corporation Fellow, 1958–1960.

[3] (a) P. Kovacic and N. O. Brace, *J. Am. Chem. Soc.*, **76**, 5491 (1954); (b) P. Kovacic and A. K. Sparks, *J. Am. Chem. Soc.*, **82**, 5740 (1960).

[4] J. C. Hutton and H. W. Webb, *J. Chem. Soc.*, 1518 (1931).

[5] T. Maki and M. Yokote, *J. Soc. Chem. Ind., Japan*, **39** (suppl.), 442 (1936); *Chem. Abstr.*, **31**, 4499 (1937).

TABLE I

SOLVENT AND CATALYTIC EFFECTS

Solvent or Catalyst	Mole	C_6H_5Cl, Mole	$SbCl_5$, Mole	Time, hr.	Temp.	Dichlorobenzene Yield, %	*o*	*m*	*p*
—	—	2	0.5	2	41–59	82	15	1	84
$TiCl_4$	1	1	.25	3.1	80–92[a]	66	20	1	79
$C_6H_5NO_2$	1	1	.25	6.2	70–102[a]	76	16	1	83
C_5H_5N	1	1	.25	2.5	124	0	—	—	—
$TiCl_4$	0.5	0.5	.125	2.0	82–84	68[b]	—	—	—
$C_6H_5NO_2$	.5	.5	.125	2.0	82–84	67[b]	—	—	—
$AlCl_3$	.01	2	.5	1.2	24–38	81	16	1	83
$CuCl_2$	.02	2	.5	2.6	42–50[a]	93	16	1	83

[a] Hydrogen chloride was first detected at the lower temperature. [b] Isomer distribution not determined.

In an investigation of possible catalytic effects, no alteration in the isomer distribution of the chlorinated aromatic compound resulted from the concomitant use of small amounts of aluminum chloride or cupric chloride.

The mechanism which has been proposed[3b] for aromatic chlorination by antimony pentachloride is consistent with the observed solvent and catalytic effects.

The mode of addition significantly affects the *ortho/para* ratio, as shown by a decrease from 0.18 for dichlorobenzene from the usual method to 0.065 when chlorobenzene is added to antimony pentachloride. This is probably due to further chlorination of dichlorobenzene during the "reverse addition," entailing a difference in the rates of reaction for the various isomers. The *ortho* isomer is reported[6] to be more reactive than the *para* toward electrophilic reagents.

Increased temperatures produced an increase in the *ortho/para* ratio, as would be expected. It is noteworthy that at mild temperatures prolonging the reaction time resulted in essentially a quantitative yield of dichlorobenzene.

TABLE II

VARIATION OF TIME, TEMPERATURE, AND ORDER OF ADDITION[a]

Time, hr.	Temp.	Dichlorobenzene Yield, %	B.P.	*o*	*m*	*p*
2	41–59	82	170–172	15	1	84
51[b]	25–59	99	171–173	16	1	83
1.3	102–128	81	171–172.6	22	1	77
1.3[c]	23–35	57[d]	170–173	6	1	93

[a] Chlorobenzene (2 moles) and antimony pentachloride (0.5 mole). [b] 3 hr. at 34–59° and the remainder at room temperature. [c] Chlorobenzene was added to antimony pentachloride during 1 hr. of reaction time. [d] Trichlorobenzene (10 g.), b.p. 193–210°, was also obtained.

Since aromatic chlorination by antimony pentachloride produces an isomer distribution different[3] from that obtained by the usual method (chlorine gas-catalyst), the practicality of the antimony pentachloride method was investigated and shown to be promising. By direct distillation of the reaction mixture, by-product antimony trichloride was separated from the chlorinated aromatic product, then treated with chlorine, and the regenerated antimony pentachloride was recycled satisfactorily.

EXPERIMENTAL[7]

Materials. Chlorobenzene (Matheson Coleman and Bell) was dried over sodium sulfate. Commercial toluene was distilled, b.p. 109.4–109.6°, through a 60-cm., helix-packed column. Commercial nitrobenzene was distilled, b.p. 93° (17 mm.), through a 12-in. column. The other materials were commercial products which were used directly.

General procedure. The method is previously described.[3b] In some cases, in place of steam distillation, extraction with dilute hydrochloric acid was used, followed by fractional distillation of the organic phase.

Antimony pentachloride-toluene-aluminum chloride. Toluene (2 moles), containing anhydrous aluminum chloride (0.05 mole), was allowed to react with antimony pentachloride (0.5 mole) at 14–27° according to the general procedure. Fractionation of the steam-volatile material yielded 44 g. of chlorotoluene[8] (*ortho*, 51%; *meta*, 2%; *para*, 47%), and 1.4 g. of dichlorotoluene, b.p. 194–195° (infrared spectrum used in identification).

Antimony pentachloride and chlorobenzene. Regeneration of antimony pentachloride. After the reaction of antimony pentachloride (0.5 mole) with chlorobenzene (2 moles) at 34–59° for 3 hr., the mixture was allowed to stand at room temperature for an additional 48 hr. Direct distillation[9] yielded 71.2 g. (99%) of dichlorobenzene (*o/m/p* = 16/1/83). Treatment of the residual antimony trichloride with chlorine gas effected the regeneration of antimony pentachloride which was allowed to react with chlorobenzene at 30–37° for 3 hr., yielding 65 g. of dichlorobenzene (83% *para* by m.p.-f.p. determination).

Analytical methods—The infrared and melting point-freezing point methods of analysis have been described.[3]

Acknowledgment. We are grateful to the National Science Foundation for support of part of this work.

DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING
CASE INSTITUTE OF TECHNOLOGY
CLEVELAND 6, OHIO

---

[6] E. H. Huntress, *Organic Chlorine Compounds*, Wiley Inc., New York, 1948, p. 119.

[7] Boiling points are uncorrected.

[8] A similar isomer distribution (*o/m/p* = 47/2/51) is obtained[3b] in the absence of aluminum chloride.

[9] Direct distillation has also been used[3b] with the reaction mixture from fluorobenzene.