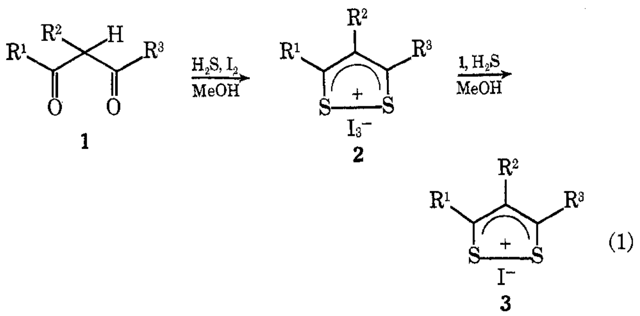

a, $R^1 = R^3 = Me$; $R^2 = H$
b, $R^1 = Me$; $R^2 = H$; $R^3 = C_6H_5$
c, $R^1 = R^2 = R^3 = Me$
d, $R^1 = R^2 = R^3 = H$

as its triiodide salt (**2**). This intermediate has been characterized by analysis for the 3,5-dimethyl-1,2-dithiolium ion (**2a**) only, but appears to form with the other 1,2-dithiolium ions studied. Further reaction with H_2S results in complete conversion of this intermediate to the iodide salt (**3a–c**). Bromine has been successfully used as oxidant to form the 3,5-dimethyl-1,2-dithiolium bromide (**4**). No attempt has been made to utilize chlorine as the oxidant.

Two further cations prepared in this work, *viz.*, the 3,4,5-trimethyl- (**3c**) and 3-methyl-5-phenyl-1,2-dithiolium ions (**3b**), suggest that the method may be widely applicable for the preparation of trisubstituted and aryl-substituted cations. The parent compound, 1,2-dithiolium iodide (**3d**), is not obtained from this reaction utilizing malondialdehyde tetraethyl acetal as the "β-dicarbonyl." However, this dithiolium salt has been obtained in reasonable yield from the same reaction in the presence of anhydrous HCl.[9]

Experimental Section

H_2S gas was dried by passage through anhydrous $CaCl_2$ towers. Nmr spectra were obtained at 100 MHz on approximately 0.5 *M* solutions of the salts in trifluoroacetic acid. All chemical shift values (δ, parts per million) are reported relative to internal TMS.

3,5-Dimethyl-1,2-dithiolium Iodide (3a). Method A.—Iodine (25 g) was dissolved in MeOH (AR, 150 ml) containing acetylacetone (10 g), and H_2S was passed through the stirred mixture at room temperature. The ensuing reaction was quite exothermic although cooling was not utilized. Large yellow-green crystals of the triiodide separated initially, but on continued treatment with H_2S they dissolved and were replaced by the dithiolium iodide. The crude product was collected, washed with MeOH, CS_2, and Et_2O, and recrystallized from glacial acetic acid (12 g), mp 148–150° (reported[6] mp 146–150°), nmr CH_3, 3.12 (6), H, 8.21 (1).

Anal. Calcd for $C_5H_7IS_2$: C, 23.3; H, 2.7; I, 49.2; S, 24.8. Found: C, 23.1; H, 2.8; I, 49.3; S, 24.8.

Method B.—H_2S was bubbled into a vigorously stirred solution of acetylacetone (50 g) and iodine (100 g) in MeOH (200 ml). After 2 hr the triiodide salt had crystallized out. The reaction mixture was brought to reflux and H_2S was passed for a further 2 hr. At this stage, the hot solution was decanted from the sulfur (~5 g) and diethyl ether (500 ml) was added. On cooling the solution deposited 60 g of the pure crystalline, yellow iodide salt, yield 60%.

Anal. Calcd for $C_5H_7IS_2$: C, 23.3; H, 2.7; I, 49.2; S, 24.8. Found: C, 23.5; H, 2.7; I, 48.8; S, 24.7.

3,5-Dimethyl-1,2-dithiolium Triiodide (2a).—A sample of the 3,5-dimethyl-1,2-dithiolium triiodide intermediate formed in the preparation of the iodide salt was isolated and twice recrystallized from MeOH, mp 118–120° (reported[6] mp 118–125°), nmr CH_3, 3.12 (6), H, 8.19 (1).

Anal. Calcd for $C_5H_7I_3S_2$: C, 11.7; H, 1.4; I, 74.4; S, 12.5. Found: C, 12.0; H, 1.4; I, 72.9; S, 11.9.

3,5-Dimethyl-1,2-dithiolium Bromide (4a).—Acetylacetone (6 ml) was carefully added to a solution of bromine (24 g) in methanol (100 ml) at 0°. H_2S was bubbled into this vigorously stirred mixture. After 5 min the remainder of the acetylacetone (9 ml) was added, almost completely discharging the color of the bromine. H_2S was bubbled into the solution at room temperature until the solution turned deep red (~4 hr). Stirring was continued overnight. The solution was separated from a small quantity of sulfur, and diethyl ether (300 ml) was slowly added with stirring. The crystals were collected and washed. The compound was recrystallized by dissolving the crude product in a quantity of warm methanol, filtering, and adding a fourfold excess of diethyl ether. On cooling, the solution deposited crystals (8 g, 25%) which were collected, washed, and dried, mp slowly decomposes above 160°, nmr CH_3, 3.12 (6), H, 8.19 (1).

Anal. Calcd for $C_5H_7BrS_2$: C, 28.5; H, 3.4; Br, 37.8; S, 30.4. Found: C, 28.5; H, 3.4; Br, 38.0; S, 30.6.

3-Methyl-5-phenyl-1,2-dithiolium Iodide (3b).—A solution of benzoylacetone (40 g) and iodine (51 g) in MeOH (150 ml) was stirred vigorously while H_2S was passed through at room temperature. Initially, sulfur was deposited and finally the dithiolium iodide crystallized from the solution. Addition of diethyl ether to the reaction mixture led to further recrystallization of the required compound, which was twice recrystallized from methanol (16 g), mp 127–132°, nmr CH_3, 3.18 (3), C_6H_5, 7.5–8.1 (5), H, 8.58 (1).

Anal. Calcd for $C_{10}H_9IS_2$: C, 37.6; H, 2.8; I, 39.7; S, 20.0. Found: C, 37.7; H, 2.9; I, 39.7; S, 20.2.

3,4,5-Trimethyl-1,2-dithiolium Iodide (3c).—H_2S was bubbled into a methanolic solution (150 ml) of α-methylacetylacetone (19 g) and iodine (46 g) for approximately 0.5 hr, when large crystals separated (presumed to be 3,4,5-trimethyl-1,2-dithiolium triiodide). On continued bubbling of H_2S (~2 hr) the large crystals were replaced by smaller yellow crystals. When the red coloration of the iodine was completely discharged the product was collected, washed, and recrystallized from MeOH as pale yellow crystals (15 g), mp 217–218°, nmr 3-CH_3 and 5-CH_3, 3.00 (6), 4-CH_3, 2.52 (3).

Anal. Calcd for $C_6H_9IS_2$: C, 26.5; H, 3.3; I, 46.6; S, 23.6. Found: C, 26.4; H, 3.3; I, 46.8; S, 23.7.

Registry No.—**1a**, 123-54-6; **1b**, 93-91-4; **1c**, 815-57-6; **2a**, 22372-84-5; **3a**, 22251-86-1; **3b**, 37344-00-6; **3c**, 39703-73-6; **4a**, 20365-60-0; iodine, 7553-56-2; bromine, 7726-95-6.

Acknowledgment.—One of the authors (A. R. H.) wishes to thank the CSIRO for a Postgraduate Studentship.

Comparisons of the Reactions of Chlorine and Alkyl Hypochlorites with Aromatics in Nitromethane

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A few years ago Norman and Harvey[2] investigated the reactions of *tert*-butyl hypochlorite with several aromatic hydrocarbons. They found that these reac-

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[9] G. A. Heath, A. R. Hendrickson, R. L. Martin, and A. F. Masters, unpublished results.

[1] Bethany Nazarene College.

[2] D. R. Harvey and R. O. C. Norman, *J. Chem. Soc.*, 3604 (1961).

tions were very slow[3] and that the hypochlorite and chlorine gave nearly identical ratios of aromatic substitution products. On the basis of their observations, these researchers came to the conclusion that *tert*-butyl hypochlorite reacts by initially decomposing to atomic chlorine. The chlorine radicals can then react directly with the aromatics (toluene to give benzyl chloride) or combine to form molecular chlorine which subsequently reacts with the aromatic (anisole).[4]

We have recently reported[5] that there are significant differences between the reactions of alkyl hypochlorites with aromatics in nitromethane and in the other solvents.[2] In nitromethane the reactions are far more rapid, and in certain cases there is a competition between chlorination of the aromatic and nitromethane[6] (formation of chloronitromethane). We have continued to study both of these reactions and wish to present information here on the aromatic substitution reaction.

Results and Discussion

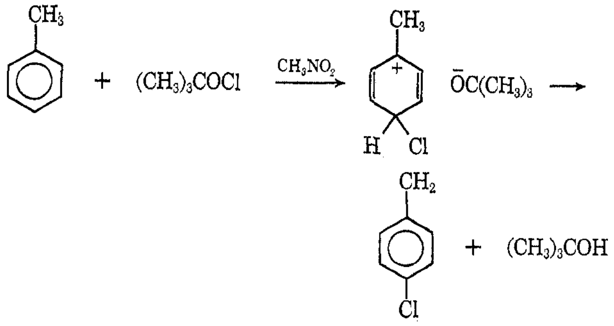
The data in Table I indicate that all three hypochlorites give significantly different ratios of substitution products with toluene and *m*-xylene than chlorine does. These results suggest that the hypochlorites and chlorine do not involve the same chlorinating agent, and that there is a direct reaction between the hypochlorite and the aromatic. The probable reaction pathway for *tert*-butyl hypochlorite is illustrated in the following equations with toluene (showing para attack).

TABLE I

CHLORINATION OF AROMATICS WITH HYPOCHLORITES AND CHLORINE

Aromatic	Chlorinating agent	Orientation 2	Orientation 4
Toluene	DEMC hypochlorite[a]	32	68
Toluene	*tert*-Butyl hypochlorite	32	68
Toluene	Methyl hypochlorite	34	66
Toluene	Chlorine	45	55
m-Xylene	DEMC hypochlorite	11	89
m-Xylene	*tert*-Butyl hypochlorite	10	90
m-Xylene	Methyl hypochlorite	12	88
m-Xylene	Chlorine	18	82
Anisole	*tert*-Butyl hypochlorite	8	92
Anisole	Methyl hypochlorite	8	92
Anisole	Chlorine	10	90

[a] DEMC hypochlorite equals diethylmethylcarbinyl hypochlorite.



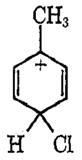
Since the reactions of the hypochlorites with toluene and *m*-xylene are relatively slow in comparison to those with chlorine (see Table II), the preference for the 4 position probably results from the greater stability of resonance structure **1** compared to **2** (illustrated with toluene).[7] Anisole, on the other hand, reacts extremely rapidly with the hypochlorites and with chlorine. In this case, since the transition state is reactant-like, the substitution ratio should be a reflection of the relative electron densities in the 2 and 4 positions in the ground state, and should result in the attack occurring primarily at the 4 position.[8]

TABLE II

RELATIVE REACTIVITIES OF CHLORINE AND HYPOCHLORITES WITH SEVERAL AROMATICS

Aromatic	Relative reactivities[a] *t*-BuOCl	MeOCl	Cl_2
Toluene	1.00	2.24	47.6
p-Xylene	1.48	2.75	296
o-Xylene	2.42	4.05	405
m-Xylene	2.81	32.9	*b*
Naphthalene	15.8	5497	*b*
Anisole	115	*b*	*b*

[a] See the Experimental Section for a discussion of the procedure for determining the relative rates. [b] Reactions were too rapid to be followed under our reaction conditions.



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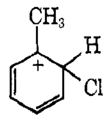

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We anticipated that the bulky hypochlorites (*tert*-butyl and diethylmethylcarbinyl) when compared to

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(3) The reactions in carbon tetrachloride, dioxane, acetonitrile, and *tert*-butyl alcohol took approximately 2 days; reactions in acid solution were considerably more rapid (15 min). Nitromethane was not employed as a solvent.

(4) Chlorinations in acid solution with *tert*-butyl hypochlorite were assumed to involve the chlorinium ion intermediate.

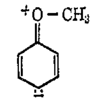
(5) V. L. Heasley, G. E. Heasley, M. R. McConnell, K. A. Martin, D. M. Ingle, and P. D. Davis, *Tetrahedron Lett.*, 4819 (1971).

(6) As described earlier,[5] the presence of the aromatic is essential as a catalyst in the reaction of the hypochlorite with nitromethane. The extent of chlorination of nitromethane varies with the particular aromatic, as described in the Experimental Section.

We are continuing to investigate this complex reaction. Preliminary work suggests that in the case of the xylenes the ratio of chloronitromethane to chloroaromatic is influenced by the presence of traces of acid, base, and water in the solvent. We are assuming that the ratios of chloroaromatics are not affected by the competing reaction between the hypochlorites and nitromethane.

(7) Norman and Radda [*J. Chem. Soc.*, 3610 (1961)] present a detailed discussion on the comparison of the transition states of slow and rapid aromatic substitution reactions. In our case, since the reactions of the hypochlorites with toluene and *m*-xylene are much slower than those wtih chlorine, these reactions (hypochlorites) involve a product-like (cyclohexadienyl intermediate) transition state; **1** makes a greater contribution to this transition state than **2**. Since chlorine reacts extremely rapidly with these aromatics in nitromethane, the transition state should be reactant-like, and hence influenced primarily by the relative electron densities in the ground state. Therefore, since the electron densities are significant in the 2 position in the ground state in the cases of toluene and *m*-xylene because of the inductive effects of the methyl groups, considerable attack occurs at the 2 position.

(8) With anisole the electron density in the ground state is decreased in the 2 position by the inductive effect of the oxygen, and is increased in the 4 position by the following resonance structure.



methyl hypochlorites might show preference for the less hindered 4 position in *m*-xylene. Apparently this is not the case.[9] (All of the substitution products from *m*-xylene and the hypochlorites are within experimental error of each other.)

The relative rate data (Table II) provide additional proof for the fact that the hypochlorites are not reacting *via* chlorine. If chlorine were involved, all of the aromatics should react at the same rate, since the rate-limiting step would certainly be the decomposition of the hypochlorites, as illustrated in the following equations.

$$\mathrm{ROCl} \xrightarrow[\text{slow}]{} \mathrm{Cl}\cdot(\mathrm{Cl_2}) \xrightarrow[\text{fast}]{\mathrm{ArH}} \text{product}$$

The rates of reaction do fall in the expected order if the basicities of the leaving anions ($\mathrm{Cl^-}$, $\mathrm{OCH_3^-}$, and O-*t*-Bu$^-$) and the reactivities of the aromatics are considered, and if the suggestion of a direct reaction between the hypochlorites and the aromatics is accepted.

Experimental Section

Materials.—All solvents and reagents were obtained commercially in high purity unless otherwise indicated. The hypochlorites were prepared as described by Walling and McGuinness.[10] Their structures were confirmed by ir and uv analysis. A detailed discussion of the synthesis and physical properties of 2-chloro-1,3-dimethylbenzene and 4-chloro-1,3-dimethylbenzene has been reported.[11]

Reaction Conditions.—To a well-stirred solution of nitromethane (n = 0.98) and the aromatic (n = 0.02) in an ice bath was added instantly a dichloromethane–hypochlorite (or chlorine) solution. (Final volume was about 28 ml.) Sufficient halogenating agent was added to react with approximately 30% of the aromatic. The molarities of the dichloromethane–halogenating agent solutions in the cases of toluene and *m*-xylene were, respectively, 1.40 and 1.00. Our studies indicate that the molarity of the halogenating agent solution seemed to have no effect on the substitution ratio.

Yields.—The yields of chloroanisoles with chlorine, methyl hypochlorite, and *tert*-butyl hypochlorite were, respectively, 96, 77, and 73%. The vpc analysis procedure (ortho and para isomers were resolved) has been previously described.[12]

Toluene reacted with the halogenating agents (listed as with anisole) to give the following yields of chlorotoluenes, respectively, 58, 51, and 54%. (The yield of chlorotoluenes with diethylmethylcarbinyl hypochlorite was not determined.) Traces of chloronitromethane were formed in the cases of anisole and toluene with the hypochlorites.[6] The yields of the chlorotoluenes were determined by vpc analysis (isomers were unresolved) under the following conditions: column temperature, composition and dimensions, 67°, 1.5% dinonyl phthalate on 60–80 mesh Chromosorb W, and 4 ft × 0.25 in. The retention times of the chlorotoluenes and the internal standard (*p*-chlorobromobenzene) were, respectively, 5.4 and 9.5 min at a flow rate (He) of 60 ml/min.

m-Xylene reacted with chlorine, methyl, *tert*-butyl, and diethylmethylcarbinyl hypochlorites to give the following yields of chloro *m*-xylenes, respectively, 83, 51, 38, and 31%. (The yields of chloronitromethane with the hypochlorites are, respectively, 5, 55, and 38%). The yields of chloro-*m*-xylenes were determined by vpc analysis (peaks were unresolved) under the following conditions: column temperature, composition and dimensions, 67°, 15% diethylene glycol succinate on 60–80 mesh Chromosorb W, and 5 ft × 0.25 in. The retention times of the chloro-*m*-xylenes and the internal standard (*p*-chlorobromobenzene) were, respectively, 5.4 and 9.5 min, at a flow rate (He) of 60 ml/min.

Determination of Substitution Ratios—The ratios of 2- and 4-chlorotoluenes were determined by an ir analysis procedure which has been described previously,[11] and by vpc analysis. The accuracy of the vpc analysis procedure was confirmed by repeated analysis of mixtures of chlorotoluenes of known composition. The ir and vpc analyses were in very close agreement (1–3%). The vpc analysis conditions for determination of the substitution ratio for the chlorotoluenes are as follows: column temperature, composition and dimensions, 39°, 1.5% dinonyl phthalate on 80–100 mesh Chromosorb W, and 8 ft × 0.125 in. The retention times for 2- and 4-chlorotoluene are, respectively, 13.5 and 15.1 min.

The substitution ratios for the 2-chloro- and 4-chloro-1,3-dimethylbenzenes were determined by ir analysis, as described previously,[11] with the exception that we isolated the individual chloro-*m*-xylenes by preparative gas chromatography. Since *m*-xylene interferes with the ir analysis, we confirmed by vpc analysis that each collected sample contained none of the starting aromatic.

The data on the substitution ratios (Table I) are accurate to ±2%.

Relative Rate Determinations.[13]—The relative rates of reaction of the hypochlorites and chlorine with the aromatics (Table II) were determined in the following manner. To a stirred solution (20 ml) of nitromethane (n = 0.98) and the appropriate aromatic (n = 0.02) at 0–0.5° was added instantly 2 ml of a 1.25 M solution of the halogenating agent in dichloromethane. Periodically, samples were removed and titrated iodometrically. The half-life for each aromatic was determined graphically.

The reciprocal of each half-life (in seconds) was then calculated and made relative to the value for *tert*-butyl hypochlorite and toluene. (Half-life of these reactants was 19,500 sec.)

Studies on the Decomposition of the Hypochlorites.—We determined that the hypochlorites do not decompose to chlorine in nitromethane by the following procedure. Methyl and *tert*-butyl hypochlorite were allowed to stand in nitromethane for 12 hr at ice-bath temperatures. 1-Hexene was then added to these hypochlorite–nitromethane solutions. Only traces of 1,2-dichlorohexane were formed in either case; chloronitromethane was the product. Previous studies of ours[5] have shown that alkyl hypochlorites and 1-hexene in nitromethane gives chloronitromethane; chlorine, 1-hexene, and nitromethane give 1,2-dichlorohexane.

Comparisons of Our Substitution Ratios with Those of Previous Studies.—Stock and Hinoe[14] reported the following product composition (%) for the chlorination of toluene in nitromethane: 2-chlorotoluene (34) and 4-chlorotoluene (66). Using their exact conditions we were unable to obtain their result, although we repeated the reaction several times. In fact, we found that the product composition was not influenced by the method of addition of chlorine, or whether the chloride was dissolved in nitromethane, dichloromethane, or carbon tetrachloride. In all cases we obtained the composition reported in Table I.

Apparently the chlorinations of anisole of *m*-xylene in nitromethane have not been investigated; the chlorination of anisole in 2-nitropropane has been reported[14] to give less than 1% of the ortho isomer.

There have been no previous studies on the reactions of alkyl hypochlorites with aromatics in nitromethane.

Registry No.—Toluene, 108-88-3; *m*-xylene, 108-38-3; anisole, 100-66-3; diethylmethylcarbinyl hypo-

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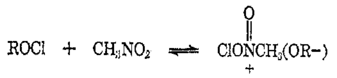
[9] It is conceivable that the "active" chlorinating agent in these reactions is the product of a reaction between the hypochlorites and nitromethane, as shown in the following equation.



$$\mathrm{ROCl} + \mathrm{CH_3NO_2} \rightleftharpoons \mathrm{ClO\overset{\overset{\displaystyle O}{\|}}{\underset{+}{N}}CH_3(OR^-)}$$

This seems doubtful, however, in the light of the reactivities in Table II. Also, we have carried out ir studies on t-BuOCl–$\mathrm{CH_3NO_2}$ solutions and have observed that there were no detectable decreases in the t-BuOCl absorption bands, nor were any "new" bands formed. We recognize that this does not rule out the possibility of the existence of a trace amount (in equilibrium) of another halogenating agent, but it makes it very unlikely.

[10] C. Walling and J. A. McGuinness, *J. Amer. Chem. Soc.*, **91**, 2053 (1969).

[11] H. C. Brown and L. M. Stock, *J. Amer. Chem. Soc.*, **79**, 5175 (1957).

[12] F. S. Broun and L. P. Hager, *J. Amer. Chem. Soc.*, **89**, 719 (1967).

[13] The relative rate data indicate how rapidly the halogenating agent is consumed. In certain cases there is concomitant chlorination of the solvent (chloronitromethane formation) and the aromatic. The reaction of the halogenating agent and the solvent becomes significant in the following cases (% chloronitromethane): methyl hypochlorite and naphthalene (100); *tert*-butyl hypochlorite with naphthalene (100); *m*-xylene (55); *o*- and *p*-xylene (*ca.* 25%).

[14] L. M. Stock and A. Hinoe, *Tetrahedron Lett.*, **No. 13**, 9 (1960).

chlorite, 39835-22-8; *tert*-butyl hypochlorite, 507-40-4; methyl hypochlorite, 593-78-2; chlorine, 7782-50-5; *p*-xylene, 106-42-3; *o*-xylene, 95-47-6; naphthalene, 91-20-3.

Acknowledgment.—Support for this work was provided by the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Research Corporation, and the Union Oil Co. of California Foundation, Brea, Calif.

Preparation and Characterization of Dichlorocyclopentadienylborane and Attempted Preparation of 1-Chloro-2,3,4,5,6-pentacarba-*nido*-hexaborane Cation

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The properties and structure of dialkylcyclopentadienylboranes have been reported by Grundke and Paetzold.[1] We wish to report a dichloro analog which appears to differ significantly in stability and acidity from the alkyl systems, but whose boron-11 and proton nmr spectra are sufficiently comparable to allow similar structural conclusions to be made. Because the formal loss of Cl^- from this compound would result in the possible formation of a *B*-chloro derivative of the hypothetical *nido*-$C_5BH_6^+$ ion, attempts were made to effect this conversion.

Experimental Section

Materials.—Sodium cyclopentadienide was obtained from the Eastman Chemical Co. as an 18% solution in tetrahydrofuran. The solvent was removed under reduced pressure. Boron trichloride, Matheson Co., was fractionated through −130° traps to remove HCl, and butyllithium in hexane was obtained from the Foote Mineral Co. Aluminum chloride was freshly sublimed. Most experimental procedures were carried out using conventional vacuum techniques.

Dichlorocyclopentadienylborane.—Since the reaction of boron trichloride and its vapor with cyclopentadienide was found to be highly exothermic, NaC_5H_5 was added as a powder to liquid BCl_3 previously cooled to −78°. This was accomplished by pulverizing the salt, freed from its solvent, tetrahydrofuran, under an inert atmosphere, and transferral of the powder to a rotatable side arm attached to the reactor vessel. Then sodium cyclopentadienide (75.9 mmol) was slowly added with stirring to 40 ml of boron trichloride maintained at −78°. The temperature was raised over a period of a few hours to 0° after which the reaction was allowed to continue for 3 hr more. The volatile components were removed at reduced temperature and pressure and fractionated through traps at −78° and −190°. When all the liquid BCl_3 had been removed from the reaction vessel, the insoluble brown solid residue remaining was gradually warmed to room temperature, and then, over a period of several hours, heated to ~300° while the volatiles were continued to be pumped through the cold traps. Approximately 0.3–0.4 ml of the product $C_5H_5BCl_2$ was retained in the −78° trap as a solid. Dichlorocyclopentadienylborane was a colorless liquid which darkened noticeably within an hour at room temperature. It had a vapor pressure of ~3 mm at 25°. The ^{11}B nmr spectrum was a singlet at about δ −47 ppm (neat) ($BF_3 \cdot OEt_2$, δ 0) which tended to broaden considerably at temperatures below −30°. In methylene chloride the chemical shift was −51 ppm. The proton spectrum exhibited four peaks with no observable fine structure in an apparent 1:1:1:2 ratio at τ 2.36, 3.14, 3.36, and 6.68, respectively, for the neat material. In chloroform the values were τ 2.16, 2.94, 3.17, and 6.66. The ^{11}B signals were observed to decrease in intensity after 5 min at room temperature with no new resonances appearing. The proton spectrum revealed a total decomposition of $C_5H_5BCl_2$ after 1 hr at 25° as evidenced by the loss of all olefinic signals and a growth in peaks at higher field attributed to hydrogen on saturated carbons.

The mass spectrum of the pure $C_5H_5BCl_2$ exhibited major peak envelopes at *m/e* 143–150 and 108–113 as well as a number of other peaks at lower masses. The parent region intensities were *m/e* 150 (rel intensity 9.4), 149 (3.3), 148 (62.0), 147 (20.7), 146 (100.0), 145 (31.5), 144 (17.7), and 143 (4.0). This corresponds to the monoisotopic species: at *m/e* 146, $^{12}C_5{}^1H_5{}^{10}B^{35}Cl_2$ (relative intensity 100.0); *m/e* 145, $^{12}C_5{}^1H_4{}^{10}B^{35}Cl_2$ (8.3); *m/e* 144, $^{12}C_5{}^1H_3{}^{10}B^{35}Cl_2$ (18.5).

Reaction of $C_5H_5BCl_2$ with Butyllithium.—About 0.11 mol of butyllithium in hexane was syringed into a dry 5-mm nmr tube, cooled to −196° and the system evacuated. Approximately 0.1 mmol of $C_5H_5BCl_2$ was then condensed into the tube. The ^{11}B nmr spectrum was obtained of the mixture at increasing temperature starting at −40°. Little change was observed in the chemical shift or appearance of the single peak even after standing at room temperature several days, the resonances appearing at about −49 ± 1.5 ppm depending on the temperature. The ^1H nmr spectrum at 25° showed only two doublets of approximately the same intensity appearing at τ 2.82 and 3.29 (J = 2.2 Hz and 1.9 Hz, respectively) which suggest the presence of olefinic hydrogens. The nmr sample was opened and the contents were fractionated to remove hexane. The only volatile product was butane.

Reaction of $C_5H_5BCl_2$ with Al_2Cl_6.—When dichlorocyclopentadienylborane was treated with aluminum chloride in either methylene chloride or chloroform, rapid and total decomposition of the borane to a dark brown sludge was the only reaction observed. This process, which was followed by ^1H nmr and ^{11}B nmr, was essentially complete in less than 1 hr at 25° as revealed by the loss of olefinic signals in the proton spectrum and the boron singlet in the boron spectrum. The decomposition of $C_5H_5BCl_2$ under these conditions appeared to be more rapid than in CH_2Cl_2 or neat in the absence of Al_2Cl_6.

Discussion

The reported preparative method of the reaction of a Lewis base adduct of a halodialkylborane with cyclopentadienide ion and subsequent treatment with a Lewis acid[1] was unsuccessful when boron trichloride was used in place of the halodialkylborane. However, low yields of dichlorocyclopentadienylborane are obtainable from the reaction of sodium cyclopentadienide directly with boron trichloride, the latter reactant also serving as solvent. This reaction is not without complications and these are commented upon.

The reaction between NaC_5H_5 and BCl_3 may be reasonably expected to produce $C_5H_5BCl_2$ and NaCl. However, when the reactants are carefully mixed, the only product isolated is a brown boron trichloride insoluble solid that shows no evidence of $C_5H_5BCl_2$.

$$NaC_5H_5 + BCl_3 \overset{0°}{\not\longrightarrow} C_5H_5BCl_2 + NaCl$$

The presence of this insoluble solid in the boron trichloride solution, coupled with the absence of a volatile product even near ambient temperature suggests that the initial substance may be $Na^+C_5H_5BCl_3^-$. This adduct appears quite stable at temperatures to 100°, but begins to decompose when heated at 150 to 250°.

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[1] H. Grundke and P. I. Paetzold, *Chem. Ber.*, **104**, 1136 (1971).