Preparation of (2-Chlorovinyl)ethylchloroborane and Bis(2-chlorovinyl)ethylborane[1]

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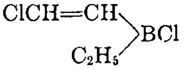
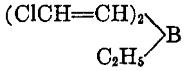
During the investigation to develop methods for the preparation of 2-chlorovinyl- and 2-chlorovinylethylboranes, (2-chlorovinyl)ethylchloroborane (I) and bis(2-chlorovinyl)ethylborane (II) were prepared for the first time. Both compounds are stable and have been fractionally distilled many times *in vacuo* without decomposition, rearrangement or disproportionation.



$$\begin{matrix} ClCH{=}CH \\ C_2H_5 \end{matrix}\!\!>\!BCl$$

I



$$\begin{matrix} (ClCH{=}CH)_2 \\ C_2H_5 \end{matrix}\!\!>\!B$$

II

Compound I was prepared in two ways: (a) in 25% yield by the interaction of ethyldichloroborane and tris(2-chlorovinyl)borane[2] and (b) in 90% yield by the reaction of ethyldichloroborane with acetylene (vinylation) with activated carbon as catalyst.

Compound II was prepared in 90% yield by the thermal disproportionation of I at atmospheric pressure. Preparation of II by vinylation of I was unsuccessful.

Attempts to prepare (2-chlorovinyl)diethylborane by the interaction of diethylchloroborane and (2-chlorovinyl)dichloroborane, by vinylation of diethylchloroborane and by disproportionation of II were also unsuccessful.

EXPERIMENTAL[3]

Preparation of (2-chlorovinyl)ethylchloroborane (I). (a) *Interaction of ethyldichloroborane and tris(2-chlorovinyl)borane.* A mixture consisting of 111.0 g. (1.00 mole) of ethyldichloroborane and 195.0 g. (1.00 mole) of tris(2-chlorovinyl)borane was refluxed under nitrogen for 4 hr. in a 500-ml. round-bottomed flask fitted with reflux condenser. The mixture was fractionally distilled under nitrogen to give 34.1 g. (0.25 mole) of I, b.p. 35° at 30 mm., and 42.1 g. (0.25 mole) of bis(2-chlorovinyl)chloroborane. The unconverted starting materials were recovered.

(b) *Vinylation of ethyldichloroborane.* All vinylation experiments were performed using the following apparatus and procedures. The entire system was assembled to permit manipulation under a nitrogen atmosphere. The reaction chamber consisted of a Pyrex tube 1 inch in diameter, 30 inches long, surrounded by a heating jacket. A coarse sintered glass disk sealed into the lower end of the tube supported the catalyst which was 150 cc. of activated carbon. The liquid was fed into the reactor either by a Corson-Cerveny microbellows pump or vaporized by passage of acetylene through the liquid. The products were condensed in an ice-cooled receiver which was attached to the bottom of the reactor and by a Dry Ice–acetone condenser. At the conclusion of each experiment the pyrophoric products were fractionally distilled under nitrogen. Some typical experimental results are given in Table I.

TABLE I

VINYLATION OF ETHYLDICHLOROBORANE

Expt. No.	Temp.	Time, Hr.	Mole Ratio $C_2H_5BCl_2/C_2H_2$	Yield, %
1	70	11	1/1.5	90
2	100	11	1/1.5	90
3	130	17.5	1/1.5	50[a]

[a] The low yield is due to disproportionation of (2-chlorovinyl)ethylchloroborane to give equimolar quantities of ethyldichloroborane and bis(2-chlorovinyl)ethylborane. This disproportionation begins at a temperature of about 115°.

Anal. Calcd. for $C_4H_7BCl_2$: C_2H_2, 19.03; B, 7.91; Total Cl, 51.82; Cl on B, 25.91. Found: C_2H_2, 19.00; B, 7.80; Total Cl, 51.73; Cl on B, 25.81.

Preparation of bis(2-chlorovinyl)ethylborane (II). (a) *By disproportionation of (2-chlorovinyl)ethylchloroborane* (I). Compound I, 136.0 g. (1.00 mole), was subjected to fractional distillation at atmospheric pressure. During the disproportionation ethyldichloroborane began to distill (50.8°). When the temperature of the mixture reached 152°, a sharp rise in the temperature of the vapor occurred, indicating the completion of the disproportionation. The pressure was reduced and 85 g. (0.45 mole) of II, yield 90%, was recovered at 77–78° at 15 mm. The infrared spectrum indicated no B-Cl absorption.[3]

Anal. Calcd. for $C_6H_9BCl_2$: C_2H_2, 31.97; B, 6.64; Total Cl, 43.54. Found: C_2H_2, 31.90; B, 6.50; Total Cl, 43.56.

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[1] This research was performed under Contract AF 33(600)-33920 for the Wright Air Development Center.

[2] B. F. Clark, E. Gipstein, M. A. Higgins and P. R. Kippur, U. S. Patent 2,918,498 (Dec. 22, 1959); *Chem. Abstr.*, **54**, 7560f.

[3] A detailed report of the techniques, apparatus, and methods of analysis is to be published by H. G. Nadeau, D. M. Oaks, Jr., and R. D. Buxton in *Analytical Chemistry.*

A Spectral Study of the Reaction between Iodine and *N*,*N*-Dimethylaniline in Cyclohexane

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Although the iodination of arylamines in aqueous medium has been extensively investigated, there is little data in the literature concerning the iodination of arylamines in nonpolar solvents. The studies reported to date of the interaction of iodine with Lewis bases in nonpolar media have been concerned with the formation of charge transfer complexes. The observation and determination of the charge transfer complex of benzene

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[1] Taken in part from a thesis submitted in partial fulfillment of the requirements for the M.S. degree.

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and iodine by Benesi and Hildebrand[3] has stimulated research in molecular complexes for the past decade. Recently Tsubomura[4] has reported the formation of a charge transfer complex between *N*,*N*-dimethylaniline and iodine in heptane solutions of low concentration (of the order of 3×10^{-5}-*M*). The present study, which was initiated prior to this report, confirms this finding. Moreover, it appears that in more concentrated solutions the charge transfer complex is the precursor of an ionic amine-iodine complex which is an intermediate in the formation of *p*-iododimethylaniline.

When cyclohexane solutions containing iodine and dimethylaniline at concentrations of the order of magnitude of $10^{-4}M$ were allowed to interact at 25°, no precipitate was observed even after seventy-two hours. In these cases no *p*-iododimethylaniline could be detected spectrophotometrically in the reaction mixture. When solutions at concentrations of $4 \times 10^{-3}M$ in iodine and $2 \times 10^{-3}M$ in dimethylaniline or higher were maintained at 25°, a slight precipitate was observed after an induction period which decreased with increasing initial concentrations. At this point in the reaction the presence of *p*-iododimethylaniline was first observed.

In a typical experiment cyclohexane solutions of iodine and dimethylaniline were equilibrated at 25.00 ± .05° and then mixed to give 100 ml. of a solution initially $4.40 \times 10^{-3}M$ in dimethylaniline and $7.58 \times 10^{-3}M$ in iodine. One milliliter aliquots of this reaction mixture were removed at various intervals of time and diluted 1:100 to stop the reaction. The spectra of the resulting solutions were then measured.

The spectral changes observed in the iodination of dimethylaniline are shown in Figs. 1 and 2. These curves are corrected for the absorbance due to molecular iodine. Two distinct processes appear to be taking place. Fig. 1 indicates the initial formation of a substance that results in a 4–5 mμ shift in the position of the amine spectrum. This initial change in the spectrum corresponds to the formation of the charge transfer complex of iodine and dimethylaniline as reported by Tsubomura[4] on the basis of iodine-band shifts. Further support for this belief is indicated by measurement of the absorption at 300 mμ. As can be seen from Table I an increase is noted during the time interval corresponding to the initial shift in the spectrum. Both dimethylaniline and *p*-iododimethylaniline exhibit small and equal absorbance at 300 mμ, so that the increase in absorption at 300 mμ during the initial phase of the reaction can not be the result of ring iodination.

Equilibrium constants were calculated at times corresponding to the maximum in the 300 mμ absorption curve for the process:

TABLE I

Minutes	$[I_2] \times 10^3$	Abs. (300 mμ)
	Run 1	
	Initial DMA Concn. $4.40 \times 10^{-3}M$	
0.0	7.58	—
1.5	7.56	0.543
3.0	7.60	0.553
5.0	7.44	0.585
7.0	7.18	0.609
10.0	7.07	0.636
15.0	6.82	0.601
30.0	6.57	0.585
45.0	5.26	0.485
60.0	4.42	0.424
93.0	3.31	0.334
120.0	2.94	0.306
	Run 2	
	Initial DMA Concn. $4.40 \times 10^{-3}M$	
0.0	7.55	—
1.0	7.55	0.536
3.0	7.55	0.550
5.0	7.44	0.604
7.0	7.29	0.626
10.0	7.03	0.620
12.0	7.03	0.626
15.0	6.95	0.611
23.0	6.38	0.569
30.0	5.11	0.483
37.0	4.00	0.388
45.0	3.70	0.363
60.0	3.33	0.328
75.0	3.08	0.306
90.0	2.84	0.298
	Run 3	
	Initial DMA Concn. $4.30 \times 10^{-3}M$	
0.0	8.04	—
2.2	8.04	0.566
4.1	7.98	0.614
7.0	7.73	0.636
10.0	7.70	0.641
13.0	7.42	0.631
15.0	7.40	0.635
18.0	7.28	0.616
24.0	7.18	0.605
35.0	6.69	0.564
40.0	6.36	0.528
50.0	5.92	0.506
65.0	4.52	0.413
80.0	3.85	0.322
100.0	3.37	0.273
	Run 4	
	Initial DMA Concn. $2.15 \times 10^{-3}M$	
0.0	7.38	—
2.2	7.38	0.546
5.1	7.38	0.546
8.0	7.38	0.556
11.0	7.38	0.571
14.0	7.31	0.588
17.0	7.31	0.603
20.0	7.31	0.611
25.0	7.24	0.611
30.0	7.13	0.609
35.0	7.00	0.596
45.0	6.90	0.580
55.0	6.40	0.539
60.0	6.04	0.504
70.0	5.58	0.436
85.0	5.10	0.352
110.0	4.89	0.342

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(3) H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, **70**, 2382 (1948); **71**, 2703 (1949).

(4) H. Tsubomura, *J. Am. Chem. Soc.*, **82**, 40 (1960).

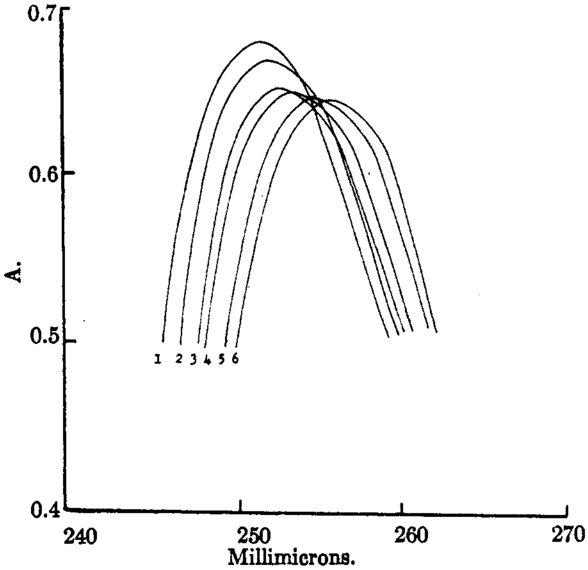


Fig. 1.—Reaction of 0.00758M iodine with 0.00440M dimethylaniline

Spectrum	Time (min.)
1	1.5
2	3.0
3	5.0
4	7.0
5	10.0
6	15.0

$$\text{Dimethylaniline} + I_2 \rightleftharpoons \text{Dimethylaniline}\cdot I_2$$

$$K = \frac{[\text{Dimethylaniline}\cdot I_2]}{[\text{Dimethylaniline}][I_2]}$$

The instantaneous concentrations are readily calculated from the known initial concentrations and the measured iodine concentrations. The calculated equilibrium constants are listed in Table II. These values are in reasonable agreement with the value of 18.8 ± 1.0 reported by Tsubomura[4] for complex formation at 27° in heptane solution.

TABLE II

EQUILIBRIUM CONSTANTS AT 25° FOR CHARGE TRANSFER COMPLEX FORMATION AT TIME OF MAXIMUM ABSORBANCE AT 300 mμ

Run No.	Time (min.)	K (l./mole)
1	10	18.5
2	10	19.1
3	13	22.7
4	30	18.5

As can be seen from Fig. 2, after the initial spectral shift attributed to charge transfer complex formation, the absorption peak shifts further to give a spectrum identical to that of *p*-iodo-*N*,*N*-dimethylaniline. It is interesting that no ring iodination occurs before the intermediate is formed in sufficient concentration. As seen in Table I, the absorbance at 300 mμ increases during the first part of the reaction while the concentration of the charge transfer complex is building up. During this interval there is no evidence of the formation of *p*-iododimethylaniline. In the latter stages of the reaction, the absorbance at 300 mμ declines as the *p*-iododimethylaniline is formed. It is significant that in repeated experiments no ring iodination occurred without the initial formation of the precipitate which had been previously mentioned.

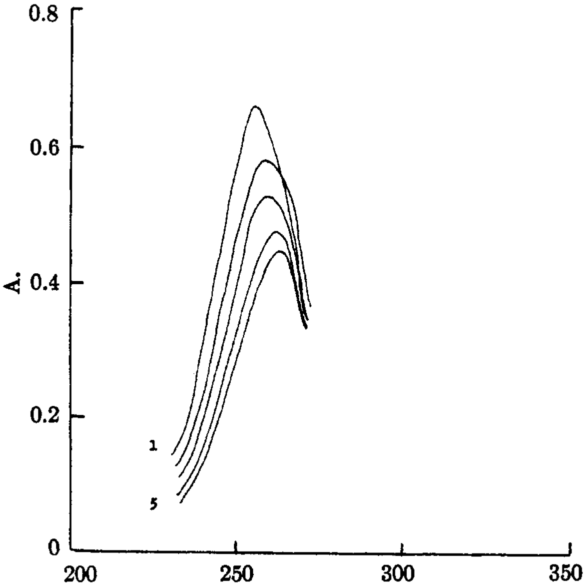


Fig. 2.—Reaction of 0.00758M iodine with 0.00440M dimethylaniline

Spectrum	Time (min.)
1	15.0
2	45.0
3	60.0
4	93.0
5	150.0

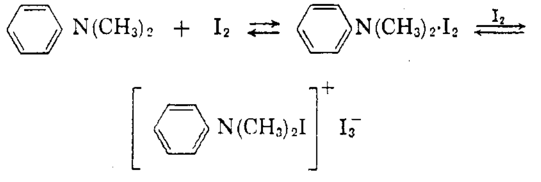
The precipitate formed during the initial stages of the interaction between iodine and dimethylaniline was removed and dissolved in isopropanol. The spectrum of the resultant solution was measured. Well defined peaks at 248, 290, and 358 mμ were observed. For comparison purposes the spectra of iodine in isopropyl alcohol and a solution containing equimolar amounts of potassium iodide and iodine in isopropanol were measured. The results are listed in Table III.

TABLE III

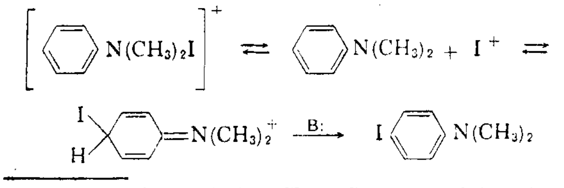
DEFINITION OF SPECTRA

Compound	Solvent	λ_{max} (mμ)	$\epsilon \times 10^{-3}$
N,*N*-Dimethylaniline	Cyclohexane	251–252	15.2
p-Iodo-*N*,*N*-dimethylaniline	Cyclohexane	264–265	26.4
Iodine	Cyclohexane	520–525	0.938
Iodine	Isopropanol	233	11.7
Iodine	Isopropanol	447	0.934
Iodine + KI (equimolar)	Isopropanol	220 (inflection)	8.62
Iodine + KI (equimolar)	Isopropanol	290	23.0
Iodine + KI (equimolar)	Isopropanol	360	13.3

It is seen that the spectrum of the precipitate in isopropyl alcohol indicates the presence of triiodide as well as dimethylaniline. It is not likely, however, that the precipitate consists merely of dimethylaniline hydroiodide, the result of ring substitution. Nagakura[5] observed the formation of a similar ionic precipitate in the interaction of triethylamine and iodine in heptane where substitution seems improbable. Glusker and Miller[6] characterized the water-soluble precipitate formed when iodine is dissolved in γ-picoline by X-ray radial distribution methods. They concluded that no covalent bonds existed and that the structure was $Pc_2I^+I^-$. On the other hand, these authors also observed a precipitate which was water insoluble but soluble in organic solvents when water was added to a fresh solution of iodine in γ- picoline. This precipitate apparently had the structure of the charge transfer complex, $Pc{\cdot}I_2$. The precipitate observed by the present authors which was insoluble in cyclohexane but soluble in isopropyl alcohol may very well be an ionic species analogous to the structure assigned the water-soluble precipitate of Glusker and Miller. Moreover, when the precipitate observed in the present study was shaken with cyclohexane, molecular iodine was liberated. The spectrum of the extract when corrected for the absorbance of iodine had a maximum at 255–256 mμ and was apparently that of the dimethylaniline·iodine charge transfer complex. When the iodine was removed from the solution by means of sodium hydrosulfite, the spectrum was identical with that of pure dimethylaniline in cyclohexane. There was apparently no ring substitution at this point. This behavior does not seem likely if the precipitate observed during the course of the reaction were merely dimethylaniline hydroiodide. However, these observations might reasonably correspond to the following type of process for the formation of the precipitate:



Ring substitution might then involve the ionic intermediate in a direct reaction with uncombined dimethylaniline or in a process such as the following:



EXPERIMENTAL

Reagents. *N,N*-Dimethylaniline, reagent grade, was obtained from Fisher Scientific Co., dried over potassium hydroxide pellets for 1 week, then distilled at reduced pressure under Argon.

Cyclohexane, Shell Oil Co., was purified by passage through a column of Davison activated silica gel, then distilled through a meter-long fractionating column packed with glass helices. The resulting solvent showed an absorbance of less than 0.1 when compared to water in the reference beam at 235 mμ and measured in 10-mm. silica cells.

Iodine, analytical reagent, resublimed, was used directly as obtained from Mallinckrodt.

p-Iodo-*N,N*-dimethylaniline was prepared by a synthesis similar to the one reported by Brewster[7] for the preparation of *p*-iodoaniline. A mixture of 24.2 g. (0.2 mole) of dimethylaniline, of 25 g. (0.3 mole) of sodium bicarbonate and 167 ml. of water were cooled to 12–15°. With mechanical stirring, 42.4 g. (0.167 mole) of powdered iodine was added in 20 min. The mixture was stirred for an additional 20 min. allowing the mixture to warm to room temperature. One hundred milliliters of water was added to the mixture, the solid was filtered and washed with 500 ml. of water. The crude material was dried at 45°, at 300 mm. The dried crude product was crystallized from petroleum ether (b.p. 55–75°) then recrystallized two more times. The melting point of the crystals was 80.2°.

Anal. Calcd. for $C_8H_{10}IN$: C, 38.9; H, 4.08; I, 51.4%. Found: C, 39.4; H, 4.32; I, 51.9.

Identification of p-iodo-N,N-dimethylaniline from the iodination study. The reaction mixture was treated with charcoal to remove the iodine and the solution was then concentrated until crystallization began. The ultraviolet and infrared spectra were compared with the spectra of the compound obtained from the aqueous synthesis and found to be identical.

Measurements were made with a Beckman DU spectrophotometer using calibrated silica cells with optical path lengths of 10, 50 or 100 mm. The calibration of the instrument and cells was performed as described by Napoli, Senkowski, and Motchane.[8]

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[7] R. Q. Brewster, *Org. Syntheses*, Vol. II, 347 (1943).

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Reactive Methylene Compounds. I. Synthesis of Some Pyrazoles

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In the course of an investigation on reactive methylene compounds, the authors have had occasion to prepare pyrazole derivatives which have not previously been reported. These compounds are of