Nucleophilic Substitution at Tetrahedral Boron. Methylamine–Diarylborane Substrates

Fergus J. Lalor, Timm Paxson, and M. Frederick Hawthorne*[1]

Contribution from the Department of Chemistry, The University of California, Riverside, California 92502. *Received September 28, 1970*

Abstract: Six methylamine–di(para-substituted phenyl)boranes have been synthesized and subjected to nucleophilic displacement reactions with 2,2-diphenylethylamine in diglyme solution. All reactions were strictly first order in amine–borane and suggestive of an SN1-B mechanism involving the rate-determining dissociation of amine–borane. The effect of nucleophile identity, the effect of leaving group bulk, thermodynamic activation parameters, α-deuterium secondary kinetic isotope effect, and a Hammett treatment ($\log k/k_0 = \rho\Sigma\sigma$; $\rho = -3.25$) satisfactorily support the proposed SN1-B mechanism.

In two previous papers of this series[2,3] it was demonstrated that SN1-B and SN2-B mechanisms exist for nucleophilic displacement reactions at tetrahedral boron reaction centers in amine–borane substrates with tri-*n*-butylphosphine nucleophile. The previous results proved that the SN2-B mechanism was commonly observed in the cases of the simplest amine–boranes[2] such as $Me_3N^+-BH_3^-$ and $Et_3N^+-BH_3^-$ and in similar mono-B-substituted borane derivatives[3] which contained substituents having relatively low steric requirements, such as alkyl and aryl. However, in the case of trimethylamine-*tert*-butylborane,[3] a dominant first-order dissociation process prevailed which we have identified as the SN1-B mechanism. In this case the neopentyl-like steric requirements at the reaction center appeared to constrain an SN2-B transition state, while internal steric repulsion of the leaving amine group and the *tert*-butyl substituent enhanced the dissociation process. All three of the remaining isomeric trimethylamine–butylboranes displayed similar, although slower, first-order processes. In only one case was an SN1-B process observed which apparently arose through electronic stabilization of the transition state by electron release from the substituent. This particular substrate was trimethylamine-*p*-anisylborane. A second substrate, trimethylamine–mesitylborane, might also show this effect, although a large and superimposed internal steric compression effect may also enhance the dissociation process observed in this case. In view of these results it appeared to be imperative to investigate substrates which would clearly demonstrate SN1-B processes which were brought about largely by electronic stabilization of the electron-deficient SN1-B transition state. The present paper is therefore concerned with nucleophilic displacement reactions which occur in the amine–diarylborane system.

Results and Discussion

Methylamine–Diarylborane Substrates. At the outset, attempts were made to prepare trimethylamine–diarylboranes in order that the leaving group in the proposed displacement reactions would remain the same as that employed in our previous work. However, preliminary investigation[4] proved that trimethylamine–diarylboranes were unstable materials and could not be obtained in high purity. This instability is undoubtedly related to internal steric compression in the amine–borane, since methylamine–diarylboranes were subsequently shown to be stable materials.[4] This being the case, the latter class of materials were chosen as substrates for the present study. In order to simplify synthetic procedures and to enhance electronic substituent effects, the methylamine–di(para-substituted phenyl)-boranes were selected. In one case, a dimethylamine–diarylborane, the di(*p*-chlorophenyl) derivative, was successfully prepared and employed in rate studies.

Synthesis of the required methylamine–diarylboranes was accomplished through a variation of a previously published method[5] and involved the lithium aluminum hydride reduction of the diarylborinic acid followed by the addition of the amine. Table I records the characterization data obtained for these new compounds. Also included in Table I are data pertaining to one B-deuterated substrate, methylamine–di(*p*-chlorophenyl)-borane-*d*, obtained by the usual synthesis route with lithium aluminum deuteride as the reducing agent.

Kinetic Method. Preliminary investigation proved that methylamine–diarylboranes were, with one exception, not sufficiently soluble in the previously employed solvent,[2,3] *o*-dichlorobenzene, to allow kinetic studies to be made in this solvent. Consequently, the rate data were obtained in pure diethylene glycol dimethyl ether (diglyme) between 20 and 75° and only a limited solvent effect study was undertaken. Rate runs were made using the previously described[2,3] "flow method" and following each reaction to approximately 10% completion using the initial rate method and direct evaluation of $d[CH_3NH_2]/dt$ at known amine–borane and nucleophile concentrations. Since tri-*n*-butylphosphine did not form easily isolatable diarylborane complexes it was necessary to replace this previously employed[2,3] standard nucleophile by a primary amine, 2,2-diphenylethylamine, which was shown in control experiments to be a sufficiently nonvolatile and effective nucleophile which yielded the expected 2,2-diphenylethylamine–diarylboranes through the displacement reaction. Table II reports the kinetic results obtained in this study at a variety of temperatures and rate con-

---

(1) To whom correspondence should be addressed at the Department of Chemistry, the University of California, Los Angeles, Calif. 90024.

(2) W. L. Budde and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **93**, 3147 (71).

(193) D. E. Walmsley, W. L. Budde, and M. F. Hawthorne, *ibid.*, **93**, 3150 (1971).

(4) The authors are indebted to Dr. Brian Higginbottom for these results.

(5) M. F. Hawthorne, *J. Amer. Chem. Soc.*, **80**, 4293 (1958).

Table I. Analysis and Characterization Data for Para-Substituted Diarylamine–Boranes

Compound	Yield, %	Mp, °C	Analysis, % Calcd C	H	N	B	Halogen	Found C	H	N	B	Halogen
$(p\text{-}CH_3OC_6H_4)_2BHNH_3CH_3$	45	140–142	70.0	7.80	5.45	4.17		70.13	8.01	5.22	4.29	
$(p\text{-}CH_3C_6H_4)_2BHNH_2CH_3$	50	148–150	79.80	8.88	6.22	4.88		80.02	9.19	6.10	5.07	
$(p\text{-}CH_3C_6H_4)_2BDNH_2CH_3$	58	153	79.65	9.37	6.19	4.78		79.52	9.12	6.08	4.65	
$(C_6H_5)_2BHNH_2CH_3$	61	89–90.5	79.2	8.12	7.10	5.57		79.36	8.23	7.08	5.62	
$(p\text{-}FC_6H_4)_2BHNH_2CH_3$	65	90	66.98	6.07	6.01	4.64	16.30	67.04	6.49	5.98	5.02	16.04
$(p\text{-}ClC_6H_4)_2BHNH_2CH_3$	59	155–156	58.70	5.32	5.27	4.06	26.66	58.47	5.40	5.45	4.12	26.74
$(p\text{-}ClC_6H_4)_2BHNH(CH_3)_2$	61	127–128	60.04	5.77	5.00	3.86	25.32	60.23	5.83	5.31	4.02	25.40
$(p\text{-}BrC_6H_4)_2BHNH_2CH_3$	63	178	43.9	3.94	3.94	3.09	44.9	44.13	4.19	4.18	3.41	44.74

Table II. Rates of Reaction and Activation Parameters for Reactions of Para-Substituted Diarylmethylamine–Boranes with 2,2-Diphenylethylamine

Compound[a]	Av $k_1 \times 10^5$, sec^{-1}	Calcd k_1 at 25°	Temp, °C	$\Delta H^{\ddagger}$, kcal/mol[b]	$\Delta S^{\ddagger}$, eu[b]
$(p\text{-}CH_3OC_6H_4)_2BHNH_2CH_3$	12.0	2.29×10^{-4}	20.2		
	22.8		24.9	26.0 ± 1.2	10.7 ± 2.0
	49.0		29.6		
$(p\text{-}CH_3C_6H_4)_2BHNH_2CH_3$	4.77	3.17×10^{-5}	29.4	30.7 ± 1.2	21.4 ± 2.0
	10.8		34.8		
	36.9		41.4		
	48.5		44.4		
$(C_6H_5)_2BHNH_2CH_3$	2.43	2.24×10^{-6}	34.8	34.4 ± 1.6	28.9 ± 1.5
	3.87		40.4		
	7.95		44.4		
	21.1		50.5		
$(p\text{-}FC_6H_4)_2BHNH_2CH_3$	1.89	1.07×10^{-6}	40.0	35.0 ± 2.0	29.4 ± 1.4
	4.56		45.0		
	10.7		49.8		
	24.2		55.0		
$(p\text{-}ClC_6H_4)_2BHNH_2CH_3$	3.14	1.06×10^{-7}	54.8	36.8 ± 1.6	37.8 ± 1.5
	6.44		59.5		
	14.3		64.0		
	38.7		70.3		
$(p\text{-}BrC_6H_4)_2BHNH_2CH_3$	2.25	8.71×10^{-8}	55.0	35.9 ± 1.2	27.3 ± 1.0
	4.90		60.0		
	11.1		64.8		
	40.8		73.4		
$(p\text{-}ClC_6H_4)_2BHNH(CH_3)_2$	9.61	2.70×10^{-6}	50.0	31.3 ± 2.6	17.0 ± 1.2
	26.3		54.9		
	45.6		59.9		
	92.4		65.0		
$(p\text{-}CH_3C_6H_4)_2BDNH_2CH_3$	3.22	2.51×10^{-5}	29.6	29.3 ± 0.5	15.6 ± 1.0
	8.13		34.9		
	19.3		41.3		
	33.1		44.4		
$(p\text{-}ClC_6H_4)_2BHNH_2CH_3$[c]	18.6	3.67×10^{-5}	39.6	27.8 ± 1.0	11.3 ± 1.2
	60.5		47.8		
	133.0		54.6		

[a] Solvent used was diglyme unless otherwise noted. [b] Error is average deviation. [c] Solvent used was *o*-dichlorobenzene.

stants calculated at 25° for each substrate. In every case the observed reaction was strictly first order in methylamine–diarylborane and reproducible to within ±3%. Nucleophile concentrations were varied from 0.025 to 0.40 *M*. In addition, control experiments proved that slow (by approximately 10^3) and erratic methylamine evolution occurred in the absence of added nucleophile. Figure 1 presents a typical plot of specific rate, $(d[CH_3NH_2]/dt)/[CH_3NH_2{}^+\text{–}BHAr_2{}^-]$ *vs.* instantaneous 2,2-diphenylethylamine concentration for the case of methylamine-di-(*p*-tolyl)borane. Substitution of 0.025 *M* $(n\text{-}Bu)_3P$ in one run and 0.75 *M* *n*-dodecylamine in another produced virtually identical first-order rate constants of 4.65×10^{-5} and 4.75×10^{-5} sec^{-1}, respectively. The data are plotted in Figure 1. The lack of dependency of the first-order rate constant upon nucleophile identity and the paucity of observed reactions in the absence of added nucleophile strongly support the exclusive operation of the SN1-B mechanism with the formation of a diarylborane intermediate as the product of the rate-determining step.

Thermodynamic Activation Parameters. Values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were calculated from the collected kinetic data and are presented in Table II. Inspection of the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values obtained suggested the existence of an isokinetic relationship. The isokinetic temperature which was evaluated by graphical means was approximately 470°K, well above the temperatures employed in this study. The range of $\Delta H^{\ddagger}$ obtained is reasonable if the ΔH_{diss} of the amine–boranes is in the range[2] of 20–30 kcal/mol. In addition the rather large and positive $\Delta S^{\ddagger}$ values suggest a transition state which is considerably less ordered than the reactant molecule in keeping with an SN1-B dissociation mechanism.

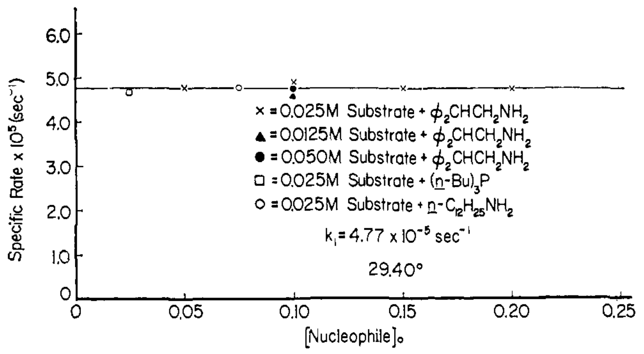


Figure 1. Plot of specific rate, (d[MeNH$_2$]dt)/[amine–borane]$_0$, *vs.* initial nucleophile concentration with methylamine–di(p-tolyl)borane substrate.

α-**Deuterium Kinetic Isotope Effect.** The substrate methylamine-di(p-tolyl)borane bearing a deuterium atom on boron was examined, and the kinetic data are collected in Table II along with the corresponding $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values. The ratio k_H/k_D at 25.0° calculated from these data is 1.47. This value is higher than the α-deuterium effect usually found in systems which proceed by an SN1 carbonium ion mechanism. As an example, Streitwieser and coworkers have observed k_H/k_D values of 1.15 in the acetolysis of cyclopentyl tosylate at 50°.[6] These authors attributed the observed effect to zero-point energy differences in the C–H bending and stretching modes of tetrahedral reactant and essentially trigonal carbonium ion intermediate. Using reasonable values for these bending and stretching modes, they have calculated an approximate maximum effect of approximately 1.4. Since the necessary bending and stretching frequencies are not known for the amine–borane reactions, it is impossible to compute a reasonable value for k_H/k_D for the present case. However, the observed k_H/k_D value of 1.47 is not unreasonable for a limiting SN1-B reaction, since the changes in the vibrational frequencies of B–H and C–H bonds should be similar in going from a tetrahedral to trigonal state. Finally, it is interesting to note that the $\Delta F^{\ddagger}$ difference between the B–H and B–D systems apparently arises from a less favorable $\Delta S^{\ddagger}$ term seen in the B–D system.

Effect of Solvent and Leaving Group. Methylamine–di(p-chlorophenyl)borane was found to be sufficiently soluble in o-dichlorobenzene to allow the kinetics of the displacement reaction to be followed using 2,2-diphenylethylamine. Table II contains the collected rate data for this system and the associated $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values. The first-order rate constants obtained by extrapolation to 25.0° indicate that substitution of the less polar o-dichlorobenzene for diglyme enhances the rate by a factor of approximately 350. This effect lies in the $\Delta H^{\ddagger}$ term, since $\Delta S^{\ddagger}$ for the o-dichlorobenzene solvent reaction is less favorable by 26 eu. We attribute this effect[2,3] to the fact that the dipolar amine–borane substrate is more strongly solvated in the diglyme solvent and that the dispersal of this charge in the SN1-B transition state results in a higher $\Delta F^{\ddagger}$ in the more polar solvent owing to reactant stabilization.

Changing the leaving group from methylamine to dimethylamine (Table II) resulted in a rate enhancement of 25 at 25.0° in the di(p-chlorophenyl)borane system in diglyme solution. This effect must be attributed to an increase in bulk of the leaving group and the resulting increase of compression energy in the substrate, since dimethylamine is a stronger base than methylamine toward trimethylborane.[7] This enhancement of SN1-B reactivity in the dimethylamine case is seen to be due to a more favorable $\Delta H^{\ddagger}$ value, which compensates for a less favorable $\Delta S^{\ddagger}$ term as well.

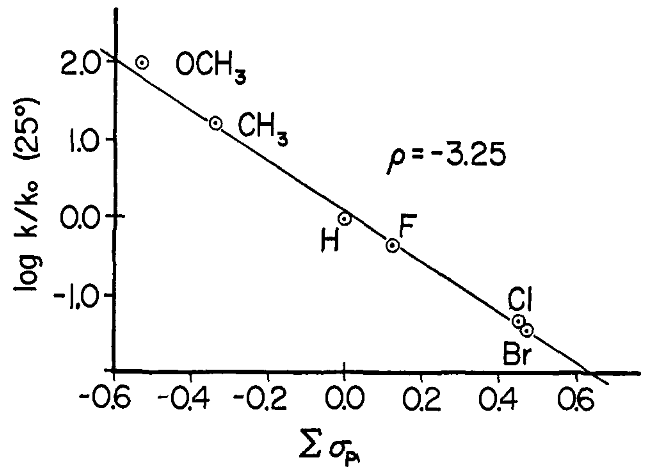


Figure 2. Plot of Hammett relationship using 2,2-diphenylethylamine nucleophile in diglyme at 25.0°.

Hammett Relationship. The substrates utilized in this study each carry two para-substituted phenyl rings and might be expected to obey a modified Hammett equation, log $k/k_0 = 2\rho\sigma$, where σ has the usual value. Alternatively, if the reactions studied passed through highly electron deficient transition states, the equation log $k/k_0 = 2\rho\sigma^+$, where σ^+ is derived from reactions termed *electrophilic side-chain reactions* by Stock and Brown,[8] is applicable. More recently, Nishida[9] has reported a study of polysubstituted benzhydryl chloride solvolyses and has found that the log $k/k_0 = \rho\Sigma\sigma^+$ relationship fails when strongly electron-releasing or electron-attracting substituents comprise one of the substituents. This was attributed to a perturbation of the ρ value by the addition of successive strongly interacting substituents. Consequently, it was of great interest to see which, if any, of the previously observed relationships were obeyed by the di(para-substituted phenyl)borane reactions. Figure 2 presents a typical Hammett plot for the reactions in question, and it is seen that the additive relationship log $k/k_0 = 2\rho\sigma$ holds very precisely over a wide range of σ values. The observed ρ value of -3.25 is in agreement with a moderately electron-demanding boron atom in the transition state. However, trial plots using σ^+ values failed to achieve any proper correlation of the data. We therefore conclude that the dissociation of trimethylamine–di(para-substituted phenyl)boranes are typical side chain reactions[8] and do not display the high electron-demanding properties of the related benzhydryl chloride solvolyses.[9]

Product Characterization. The expected 2,2-diphenylethylamine–di(para-substituted phenyl)boranes

---

[6] A. Streitwieser, R. H. Jagow, R. C. Fahey, and S. Suzuki, *J. Amer. Chem. Soc.*, 80, 2326 (1958).

[7] H. C. Brown, H. Bartholomay, and M. D. Taylor, *ibid.*, **66**, 435 (1944).

[8] L. M. Stock and H. C. Brown, *ibid.*, **81**, 3323 (1959).

[9] S. Nishida, *J. Org. Chem.*, **32**, 2695 (1967).

formed as reaction products were isolated and characterized in two cases, the di-*p*-bromo and di-*p*-methoxy systems. The characterized products were obtained from amine displacement reactions conducted in diglyme solution under conditions identical with those used in kinetic experiments. Yields of isolated products ranged from 70 to 80%. Since the di-*p*-bromo and di-*p*-methoxy substrates represent the most and least reactive systems investigated, we may conclude with confidence that the intervening systems examined also proceeded by the expected course to yield the corresponding 2,2-diphenylethylamine–di(para-substituted phenyl)boranes.

Conclusion. The reaction order, solvent polarity effect, α-deuterium secondary kinetic isotope effect, leaving group steric effect, and the Hammett relationship observed here all point to the operation of an SN1-B mechanism in the displacement reactions studied. Unlike the $Me_3N^+–BH_3^-$ and $Me_3N^+–BH_2^-$(alkyl) systems previously examined,[2,3] no second-order kinetic terms were observed; hence we conclude that the SN2-B mechanism does not function in amine–borane substrates in which reactant molecules are sterically constrained and are at the same time capable of yielding substituted borane intermediates stabilized by electron delocalization.

Experimental Section

Materials and Methods. Tri-*n*-butylphosphine, *o*-dichlorobenzene, and 2,2-diphenylethylamine were purified as previously described.[2,3] Diglyme solvent was purified as follows. Practical grade diglyme was obtained from the Ansul Chemical Co. Approximately 3.5 l. of diglyme was placed in a 5-l. three-necked flask fitted with a stirrer and reflux condenser bearing a nitrogen inlet. Sodium chips (20 g) were added and the mixture was heated to reflux under nitrogen overnight. The diglyme was then distilled into a 3-l. flask containing approximately 10 g of $LiAlH_4$. The diglyme was then distilled from that vessel under reduced pressure, bp 33–35° (1.0 mm), in the presence of nitrogen and collected in a 2-l. flask. The purified solvent was stored in a nitrogen-filled drybox at all times.

Dodecylamine was obtained from the Aldrich Chemical Co. and distilled twice at reduced pressure in a nitrogen atmosphere, bp 108° (2 mm). The purified amine, mp 47–48°, was stored in a vacuum desiccator over $CaCl_2$.

Infrared spectra were obtained with a Perkin-Elmer Model 137 spectrophotometer. Mass spectral analyses were obtained using a Hitachi Perkin-Elmer Model RMU-6D mass spectrometer.

Rate runs were carried out with Sargent thermistor-controlled thermostats using calibrated thermometers. Temperatures were accurate to ±0.01°.

Computation of rate data and least-squares data analysis were accomplished with an IBM/360 computer.

Preparation of Methylamine–Di(para-substituted phenyl)boranes. All amine-borane substrates employed in this study were produced by a modification of a previously reported procedure[5] starting with the corresponding diphenylborinic acid. The latter materials were prepared by the procedure of Coates and Livingstone[10] and purified by formation of the 2-aminoethyl esters. The reduction procedure is illustrated by the preparation of methylamine–di(*p*-chlorophenyl)borane. All results are presented in Table I.

Pure 2-aminoethyl *p*-chlorodiphenylborinate (29.4 g, 0.1 mol) was dissolved in the minimum amount of a 1:1 solution of acetone and methanol. Concentrated HCl (50 ml) was added, followed by the addition of ice. The borinic acid, which precipitated from solution, was isolated by filtration and thoroughly washed with cold water. (The unsubstituted borinic acid, $(C_6H_5)_2BOH$, is a liquid and was therefore placed in a round-bottom flask and dried under high vacuum. Upon hydrolysis of the di(*p*-fluorophenyl)-borinate, the corresponding acid appeared to be a liquid. With continued drying *in vacuo*, however, a crystalline solid was obtained.) The borinic acid was then dried over P_2O_5 overnight under high vacuum (yield 24.1 g, 96% based on the amount of ester used). Lithium aluminum hydride (4.67 g, 0.123 mol) was placed in a 2-l., three-necked flask equipped with a 500-ml pressure-equalizing dropping funnel, a stirring mechanism, and a Dry Ice condenser. The entire system was maintained in a dry nitrogen atmosphere. *Ca.* 500 ml of dry diethyl ether was added and the solution cooled to −78° with a Dry Ice–isopropyl alcohol bath. The borinic acid (24.1 g, 0.096 mol), dissolved in 400 ml of dry ether, was slowly added to the hydride–ether mixture over a 1.5-hr period. The cooling bath was removed and the reaction mixture allowed to warm to room temperature. The solution was stirred for an additional 2 hr and then cooled again to −78°. Monomethylamine (18.6 g, 0.60 mol) was added to the reaction solution from a trap in which the dry amine had been collected. The amine had been previously passed through two towers containing KOH and BaO, through a tower containing Pyrex wool and BaO, and finally into the trap (cooled to −78°), which also contained a small amount of BaO. The amine was forced into the reaction mixture by a dry nitrogen stream which first passed through the drying train, with the amine entering the reaction solution through a bubbler which was connected to the trap. After the amine addition was complete, the reaction mixture was allowed to warm to 0° at which time 7 ml of distilled H_2O was added to the solution to hydrolyze the excess hydride. Anhydrous $MgSO_4$ was added immediately after hydrolysis was complete and the solution was filtered. The ether was removed by rotary evaporation and the crude amine–borane dried *in vacuo*. Recrystallization of the amine–borane was accomplished by dissolving it in the minimum amount of dry ethyl ether and adding a small amount of pentane. The minimum amount of moisture was allowed to come into contact with the solution. The amine–borane was recrystallized at least twice before it was used for rate determinations.

Preparation of Methylamine–Di(*p*-tolyl)borane-*d*. The general procedure outlined above was employed except that $LiAlD_4$ (98%) was utilized in the reduction reaction and D_2O was employed to destroy the excess $LiAlD_4$.

A small sample of the amine–borane product was hydrolyzed with 1.0 *M* HCl in a 50:50 (v/v) solution of methanol–water in a calibrated vacuum system. The evolved gas was collected (99.5% of theory) and then analyzed by mass spectrometry. The H_2/HD ratio observed indicated at least 95% deuteration of the amine–borane.

Kinetic Method. The previously described[2] "flow apparatus" was utilized in all kinetic runs.

A typical kinetic run began with measurement of a known quantity of amine–borane and nucleophile. Each was weighed into a separate 25-ml volumetric flask. The saturator and the flasks were then filled with solvent in a nitrogen-filled drybox. The flasks were not filled completely to the mark, as they were to be temperature equilibrated. *Extreme* care was taken not to allow the solvent to come into contact with air or moisture. The necks of the volumetric flasks were first placed inside glass cylinders fitted with a side arm. In this way the tops of the flasks could be flushed with a stream of dry nitrogen when addition of solvent or removal of solution was necessary. The saturator was then coupled to the nitrogen flow which had previously been started, the reaction flask fitted to the saturator, and finally the titration vessel fitted to the reaction vessel. A layer of mercury was added to the titration vessel and the assembly placed in the bath. At this point the nitrogen flow was stopped until the reaction vessel was filled. After 0.5 hr equilibration time the volumetric flasks were leveled to the mark with solvent that had been previously placed in the bath. (The solvent was confined in a 100-ml flask which had a side arm attached to the top of the neck so that it also could be flushed with dry nitrogen when opened for use.) The flasks were momentarily taken from the bath, shaken 30 times, and returned to the bath.

At the end of an additional 0.5 hr equilibration time the nitrogen flow through the apparatus was commenced again. Water (100 ml) and the indicated amount of indicator were added to the titration vessel and the buret containing the standard HCl solution was placed in position. The stopple over the side arm of the reaction flask was removed and a 20.0-ml aliquot of nucleophile solution was pipeted from the volumetric flask into the reaction flask, followed by a 20.0-ml aliquot of amine-borane solution, using a second pipet. The stopple was quickly replaced and the timer started. The procedure now simply consisted of adding aliquots of standard acid and recording the time at which the acid aliquot was neutralized by the escaping amine.

---

(10) G. E. Coates and J. G. Livingstone, *J. Chem. Soc.*, 4909 (1961).

The raw data gathered from a rate determination consisted of a plot of milliliters of standard acid added as a function of time. Over approximately 10% of the reaction this plot was linear after a small induction period, the time necessary for the monomethylamine to reach a steady-state concentration in the reaction vessel. Therefore the rate of reaction was determined using the method of initial rates[2] and the direct determination of d[NH_2CH_3]/d*t* under initial reaction conditions of reactant concentrations. Initial nucleophile concentrations were varied from 0.025 to 0.40 *M*.

Product Characterization. The two 2,2-diphenylethylamine–di(para-substituted phenyl)boranes isolated as reaction products in this study were prepared by the following general procedure. Equimolar quantities (2.5 mmol) of the desired methylamine–borane and $(C_6H_5)_2CHCH_2NH_2$ (0.4932 g, 2.33 mmol) were weighed out and placed in the reaction flask of the kinetic apparatus. The saturator was filled with solvent in a nitrogen-filled drybox and fitted to the reaction flask into which the minimum amount of solvent necessary to dissolve the substrate and nucleophile was added. The *p*-bromo derivative was synthesized using both benzene and diglyme as solvents, while the *p*-methoxy derivative was synthesized using only diglyme. The kinetic apparatus was assembled as described above and placed in the constant temperature bath overnight. If diglyme was the solvent used, it was removed by vacuum-line techniques, the resulting oil taken up in the minimum amount of benzene, hexane added, and crystallization allowed to proceed at 0°. Otherwise, hexane was added directly to the benzene solution and crystallization allowed to proceed. The compounds were recrystallized twice again from a benzene–hexane solvent mixture. Yields were 70–80% of theory. The physical properties of the compounds follow. Di(*p*-bromophenyl) derivative, mp 148°. *Anal.* Calcd for $C_{26}H_{24}BNBr_2$: C, 59.91; H, 4.65; B, 2.07; N, 2.69; Br, 30.67. Found: C, 60.28; H, 4.68; B, 2.19; N, 2.56; Br, 30.62. Di-(*p*-anisyl) derivative, mp 118°. *Anal.* Calcd for $C_{28}H_{30}BNO$: C, 79.41; H, 7.17; B, 2.55; N, 3.31. Found: C, 79.64; H, 7.20; B, 2.41; N, 3.07.

Acknowledgment. This research was generously supported by National Science Foundation Grants No. GP7735 and GP4922, for which the authors express their appreciation.

Dodecamethyldioxa[1.1]di-*p*-disilinocyclophane. A Novel Organosilicon Cyclophane

Fred Wudl,* Robert D. Allendoerfer, J. Demirgian, and J. M. Robbins

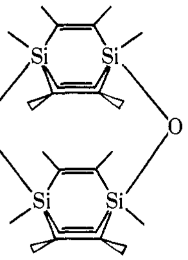
Contribution from the Department of Chemistry,
State University of New York at Buffalo, Buffalo, New York 14214.

Received October 7, 1970

Abstract: The title compound was prepared *via* high-dilution hydrolysis of 1,4-dichloropermethyl-*p*-disiline (**2**). This cyclophane exhibits high stability toward electron bombardment as evidenced by its very simple mass spectrum. Reduction of the cyclophane by potassium metal produces an unusual radical anion ($a^{H}{}_{Si-CH_3}$ = 1.25 G, $a^{H}{}_{C-CH_3}$ = 2.5 G, g = 2.00169) in which the unpaired electron is delocalized *via* transannular interactions which involve the Si–O–Si moiety only to a minor extent.

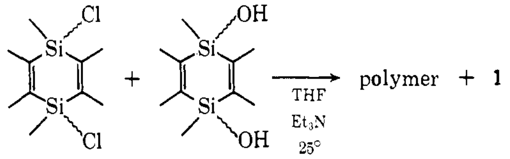
Although paracyclophanes containing silicon atoms at the bridge positions have been known for some time,[1] paracyclophane analogs with bridgehead silicon atoms have not been reported.

We present in this paper the isolation and evidence corroborating the structure determination of a [1.1]paracyclophane analog **1**.



1

In connection with other work we had the occasion to prepare a 1,4-dichloropermethyl-*p*-disiline[2] (**2**) *via* standard procedures.[3,4] Treatment of **2** with anhydrous hydrazine[5] afforded polymers plus a crystalline solid. The nmr ir, mass, and esr spectra (*vide infra*) of the crystalline compound, produced in 1–5% yield, agree well with structure **1**. Although this was an accidental synthesis, we succeeded in the preparation of **1** by an independent route which, of course, is an additional proof of structure.



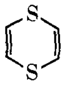
2

Compound **1** crystallizes from a dilute ether solution in perfect hexagonal prisms, is thermally stable, and sublimes near 268°. Its thermal stability allows purification *via* gas chromatography (60 × 0.6 cm column, SE-30 on silanized chromosorb W 30–60 mesh; injection, 300°; column, 200°; detection, 300°).

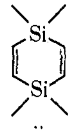
---

[1] H. Gilman, *Advan. Organometal. Chem.*, 7, 43 (1968).

[2] Heterocycles containing the nucleus i are described as *p*-dithiines. Because of the similarity between ii and i, we feel justified in calling compounds of type ii *p*-disilines. Application of this nomenclature shortens the name of substituted ii considerably.



i



ii

[3] W. H. Atwell and D. R. Wyenberg, *J. Amer. Chem. Soc.*, 90, 3438 (1968).

[4] Dow Corning Corp., British Patent 1,160,661 (1969); *Chem. Abstr.*, 71, 81512*j* (1969).

[5] L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Vol. I, Wiley, New York, N. Y., 1967, p 434.