Journal of Organometallic Chemistry, 156 (1978) 149—157

CLEAVAGE OF α-(PHENYLTHIO)ALKYLBORANES WITH *N*-CHLOROSUCCINIMIDE. A CONVENIENT ROUTE TO MONOTHIOACETALS AND ACETALS *

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(Received March 14th, 1978)

Summary

α-(Phenylthio)alkylboranes, which are easily prepared by two different homologation processes, are deboronated by *N*-chlorosuccinimide in mildly basic methanol to form monothioacetals or, with excess reagent, dimethyl acetals. Both boronic esters and trialkylboranes react, the latter considerably faster. The reaction is specific for the sulfur-substituted alkylborane group, suggesting that initial chlorination occurs at sulfur. Under free radical conditions, α-(phenylthio)alkaneboronic esters are cleaved to α-(phenylthio)alkyl chlorides by either *N*-chlorosuccinimide or sulfuryl chloride. Pinacol phenylthio(triphenylstannyl)-methaneboronate with sulfuryl chloride yielded (phenylthio)dichloromethane, without any evidence of selectivity between carbon—tin and carbon—boron bond cleavage.

Introduction

Hydroboration and organoborane chemistry as developed by Professor H.C. Brown and his students owes much of its synthetic utility to the variety of ways in which the boron atom can be replaced by other functions in the final step [2]. We are pleased to report a new deboronation of α-(phenylthio)alkylboranes directly to monothioacetals or acetals, which serve as masked aldehydes in synthesis. The method was originally developed to solve a problem in our own boronic ester chemistry, but perhaps has more future utility with intermediates derived from hydroboration.

α-(Phenylthio)alkylboranes have been prepared by the homologation of trialkylboranes with lithium bis(phenylthio)methide and have been oxidized with

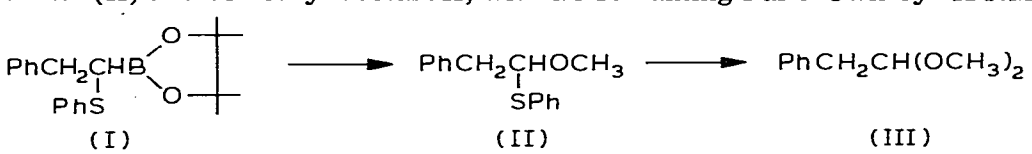
* Dedicated to Prof. Herbert C. Brown in recognition of his contributions to chemistry (Preliminary communication ref. 1)

hydrogen peroxide to form aldehydes [3] or rearranged and oxidized to carbinols [4]. Similar synthetic transformations of trialkylboranes have been accomplished with carbon monoxide [5,6], anions derived from methoxydichloromethane [7—9] or chlorodifluoromethane [10], and cyanide ion [11,12], and before now there has been no apparent advantage in using the sulfur compounds for these purposes.

Pinacol α-(phenylthio)alkaneboronates are easily prepared by alkylation of the lithio derivatives of pinacol (phenylthio)methaneboronate with alkyl halides [13]. The sterically hindered pinacol boronic ester group proved much more difficult to hydrolyze or to oxidize with hydrogen peroxide than we had hoped. However, observation of cleavage of the carbon—boron bond under free radical chlorination conditions led us ultimately to try *N*-chlorosuccinimide in mildly basic methanol, which had been reported to cleave α-methylthio (but not α-phenylthio) carboxylic salts to ketals [14].

Results

Monothioacetals and acetals. Pinacol 1-(phenylthio)-2-phenylethaneboronate (I) [13] treated with a small excess of *N*-chlorosuccinimide and sodium bicarbonate in anhydrous methanol (4 h at 25°C) yielded a mixture of the monothioacetal (II) and dimethyl acetal III, with no remaining I as shown by ^{1}H NMR.



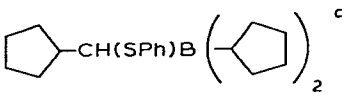
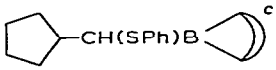
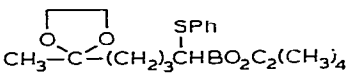
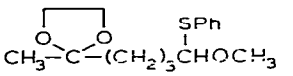
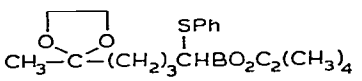
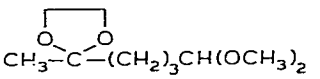
(I) (II) (III)

Formation of acetal III was minimized and the monothioacetal II was produced in 72% yield when triethylamine was used in place of the bicarbonate and the amount of *N*-chlorosuccinimide was stoichiometric. Shortening the time to 3 h left a small amount of unconverted I. The use of two equivalents of *N*-chlorosuccinimide and somewhat longer reaction times gave exclusively phenylacetaldehyde dimethyl acetal (III). Standardized conditions were adopted, in which 10 mmol of the α-(phenylthio)alkylboron compound and 20 mmol of triethylamine in 40—50 ml of methanol at 25°C were treated with 12 mmol of *N*-chlorosuccinimide to form the monothioacetal, or 22 mmol to form the acetal. The results are summarized in Table 1. It was found in some cases that longer reaction times were necessary in order to achieve complete deboronation, and the reaction times tabulated are known to be sufficient but have not been proved necessary in all cases.

It was found that *B*-α-(phenylthio)alkyl-*B*,*B*-dialkylboranes from trialkylboranes and lithiobis(phenylthio)methane [3] are also deboronated readily. The reaction is faster than that of the boronic esters and the cleavage evidently occurs only at the α-(phenylthio)alkyl—boron bond, since only one equivalent of *N*-chlorosuccinimide is required in order to achieve high yields. Since only one alkyl group of the trialkylborane is utilized, a test was made of the possibility of using 9-borabicyclononane [2] as the hydroborating agent, and cyclopentene was successfully homologated to the monothioacetal of cyclopentenecarboxaldehyde.

TABLE 1

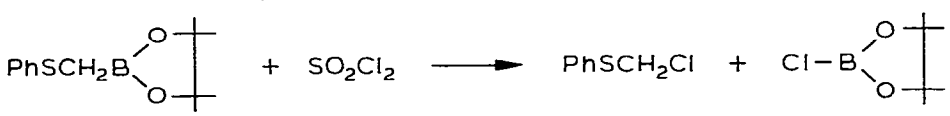
CONVERSION OF α-(PHENYLTHIO)ALKYLBORANES TO MONOTHIOAETALS AND ACETALS

Borane	Time (h) [a]	Product	Yield (%)	B.p. (°C/0.1 Torr)
CH_2=$CHCH_2CH(SPh)BO_2C_2(CH_3)_4$	10	CH_2=$CHCH_2CH(SPh)OCH_3$	65	80—82
$CH_3(CH_2)_3CH(SPh)BO_2C_2(CH_3)_4$	24	$CH_3(CH_2)_3CH(SPh)OCH_3$	69	82—84
$CH_3(CH_2)_3CH(SPh)B(n\text{-}C_4H_9)_2$ [b]	3	$CH_3(CH_2)_3CH(SPh)OCH_3$	71	82—84
 [c]	2		74	110-112
 [c]	15		60	110-112
	20		59	130-132
	12 [d,e]		73	62-64
$PhCH_2CH(SPh)BO_2C_2(CH_3)_4$	4	$PhCH_2CH(SPh)OCH_3$	72	124—125
$PhCH_2CH(SPh)BO_2C_2(CH_3)_4$	6 [e,f]	$PhCH_2CH(OCH_3)_2$ [g]	83	60—62
$PhCH_2CH_2(SPh)BO_2C_2(CH_3)_4$	10	$PhCH_2CH_2CH(SPh)OCH_3$	66	128—130
$PhCH_2CH_2(SPh)BO_2C_2(CH_3)_4$	13	$PhCH_2CH_2CH(OCH_3)_2$ [h]	79	60—62

[a] At 25°C except as noted. [b] Not isolated, yield based on tributylborane. [c] Not isolated, yield based on cyclopentene. [d] Refluxed. [e] With 2.2 equivalents of *N*-chlorosuccinimide. [f] With sodium methoxide in place of triethylamine as base. [g] ^{1}H NMR same as authentic sample (Aldrich Chemical Co.). [h] ^{1}H NMR same as published data [15].

The specificity of the reaction was demonstrated by subjecting 1,1-bis(ethylenedioxyboryl)-2-phenylethane, $PhCH_2CH(BO_2C_2H_4)_2$ [16], to similar conditions. After 18 h, 75% of this boronic ester was recovered unchanged. It may also be noted that such sensitive groups as a terminal vinyl or an ethylene ketal show no sign of being affected by the reaction conditions.

α-Chloroalkylphenyl sulfides. Treatment of pinacol (phenylthio)methaneboronate (IV) with sulfuryl chloride in carbon tetrachloride at 25°C resulted in rapid carbon—boron bond cleavage to form chloromethyl phenyl sulfide (94%) and 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (V) (63%).



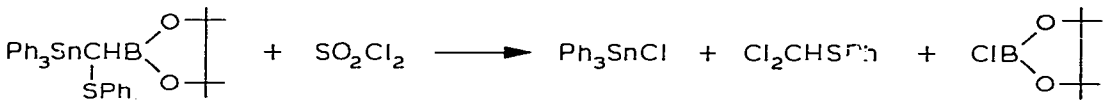
(IV) (V)

The formation of V as a stable, though not fully purified, product from this reaction is noteworthy, inasmuch as the reaction of pinacol with boron trichloride does not yield V but pinacolone and other decomposition products [17].

Sulfuryl chloride similarly cleaved propanediol (phenylthio)methaneboronate,

$PhSCH_2BO_2(CH_2)_3$, to $PhSCH_2Cl$ and $ClBO_2(CH_2)_3$ very rapidly at room temperature. Cleavage of pinacol 1-(phenylthio)-2-phenylethaneboronate (I) to the α-chlorosulfide, $PhCH_2CHClSPh$ [18], was also rapid and appeared quantitative on NMR examination of the crude product. However, on attempted distillation, hydrogen chloride was evolved and the isolated product was β-styryl phenyl sulfide, PhCH=CHSPh (83%) [19].

In the hope of making a chloro(phenylthio)methaneboronic ester, pinacol (phenylthio)(triphenylstannyl)methaneboronate (VI) was synthesized from the lithio derivative of IV [13] and triphenyltin chloride, but no evidence of preferential cleavage of the carbon—tin bond was observed. Treatment of VI with sulfuryl chloride in dichloromethane yielded dichloromethyl phenyl sulfide even when there was a deficiency of the chlorinating agent.



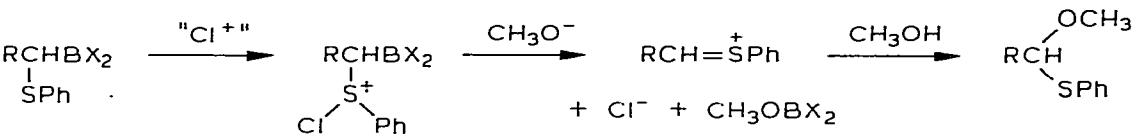
(VI) (V)

Only α-phenylthio substituted boron compounds appear to be affected by these free radical chlorination conditions. Refluxing bis(trimethylenedioxyboryl)methane, $CH_2[BO_2(CH_2)_3]_2$ [20], with sulfuryl chloride in dichloromethane (2 h) followed by distillation resulted in 95% recovery of the unchanged boronic ester.

N-Chlorosuccinimide was found to cleave the boronic esters I and IV in the same manner as sulfuryl chloride, except that refluxing in carbon tetrachloride (1 h) was required and the yields were slightly lower (75%). *N*-Bromosuccinimide appeared to cleave $PhSCH_2BO_2(CH_2)_3$ to $PhSCH_2Br$, based on NMR data from a single experiment.

Discussion

Mechanism. The selectivity of these reactions for the sulfur-substituted boron functions implies involvement of the sulfur in the transition state. It appears likely that the chlorination in methanol proceeds by a polar mechanism involving initial chlorination of the sulfur.



(X = alkyl or alkoxy)

Although a radical mechanism cannot be definitely excluded, it may be noted that the reaction with *N*-chlorosuccinimide proceeds in methanol at a significantly lower temperature than in carbon tetrachloride. The related cleavage of α-methylthio carboxylates also seems most consistent with a polar mechanism [14].

Cleavage under free radical conditions is postulated to involve a sulfur-stabilized radical in a chain mechanism.

$$\begin{array}{l} \text{RCHB(OR')}_2 + \text{Cl}^\cdot \rightarrow \text{RCHSPh} \xrightarrow{SO_2Cl_2} \text{RCH}\begin{array}{l}\text{Cl}\\ \text{SPh}\end{array} + SO_2 + \text{Cl}^\cdot \\ \text{SPh} \qquad\qquad + \text{ClB(OR')}_2 \end{array}$$

Free radical oxidation is known to cleave carbon—boron bonds even where an unstabilized (methyl) radical is formed [21]. The failure of $CH_2[BO_2(CH_2)_3]_2$ to undergo cleavage under mild conditions is consistent with the previous observation that dialkoxyborylmethyl radicals, $(RO)_2BCH_2^\cdot$, are difficult to generate [21], even though the boronic ester group does tend to stabilize an adjacent radical [22] and the generation of $(RO)_2B\dot{C}R'_2$ under radical bromination conditions has been found useful by Professor Brown and his coworkers [23].

Synthetic utility. The alkylation of $PhSCHLiBO_2C_2(CH_3)_4$ [13] followed by the new oxidation method provides an efficient homologation of RBr to a protected aldehyde $RCH(SPh)OCH_3$ or $RCH(OCH_3)_2$. A similar transformation has been reported with $CH_3OCHLiSPh$ and an allylic halide [24], without elaboration of the yield or generality. Thus, the synthetic value of the route by way of the boronic ester intermediate is uncertain at the present time, although it would appear that there may be at least some utility in having a masked aldehyde, $-CH(SPh)B(OR)_2$, which differs significantly from an acetal in being more stable toward acid but which may be converted to an acetal at a later stage in a complex synthesis. (Work in progress by D.S.M. indicates that the carbon—boron bond of I largely survives treatment with hot 10% sulfuric acid, conditions sufficient to rearrange pinacol to pinacolone.)

The homologation of hydroboration products with $LiCH(SPh)_2$ followed by the new oxidation method accomplishes direct conversion of $RCH{=}CH_2$ to $RCH_2CH_2CH(SPh)OCH_3$ and analogous transformations of more highly substituted olefins. Since reasonable efficiency (60% overall) was achieved in the example where 9-BBN was used with cyclopentene, it appears that the utilization of only one alkyl group of R_3B will not be a limitation on synthetic applications.

In view of the carbon—tin bond cleavage during radical chlorination observed during this work, as well as the previously known oxidative decarboxylation of α-methylthio carboxylate salts [14], it appears likely that similar oxidative demetallations of other α-metallothioethers, RCH(M)SR', may prove feasible and useful, especially where M is a Group IV element.

Experimental

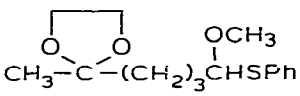
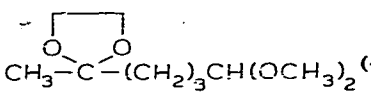
Tributylborane, borane dimethyl sulfide, and 9-borabicyclononane were obtained from Aldrich Boranes, Inc. Tetrahydrofuran (THF) was dried over sodium. Triethylamine was distilled from potassium hydroxide. Other chemicals were reagent grade. 60 MHz ^{1}H NMR spectra were obtained with a Varian EM-360 and calibrated against internal tetramethylsilane. Microanalyses were by Galbraith Laboratories, Knoxville, Tennessee.

General method for monothioacetals and acetals

To a solution of 10 mmol of the α-(phenylthio)alkylboron compound and 20 mmol (2.02 g) of triethylamine in 40—50 ml of anhydrous methanol was added portionwise 12 mmol (1.60 g) of *N*-chlorosuccinimide to form the monothio-

TABLE 2

^{1}H NMR AND ELEMENTAL ANALYSES OF MONOTHIOACETALS AND AN ACETAL

Compound	NMR ($CDCl_3$): δ (ppm)		Analysis (found (calcd.) (%)		
	O—CH—S	Other[a]	C	H	S
CH_2=$CHCH_2CH(SPh)OCH_3$	4.74	2.55 (t, 2, CH_2) 4.9—6.5 (m, 3, CH=CH_2)	68.13 (68.00)	7.30 (7.26)	16.53 (16.50)
$CH_3(CH_2)_3CH(SPh)OCH_3$	4.72	0.7—2.0 (m, 9, $(CH_2)_3CH_3$)	68.37 (68.52)	8.51 (8.63)	15.05 (15.24)
	4.50	1.20—2.0 (m, 9, C_5H_9)	70.48 (70.22)	8.14 (8.16)	14.65 (14.42)
	4.70	1.30 (s, 3, CH_3), 1.64 (m, 6, CH_2), 3.92 (63.80) (s, 4, OCH_2)	64.03 (63.80)	7.81 (7.85)	11.11 (11.35)
	(4.42)	1.32 (s, 3, (CH_3), 1.4—1.8 (m, 6, CH_2), 3.98 (s, 4, OCH_2)	57.86 (58.80)	9.05 (9.87)	— —
$PhCH_2(SPh)OCH_3$	3.88	3.12 (d, 2, CH_2	73.94 (73.73)	6.70 (6.60)	13.02 (13.12)
$PhCH_2CH_2CH(SPh)OCH_3$	4.60	2.08 (m, 2, CH_2), 2.80 (t, 2, CH_2)	74.55 (74.38)	6.96 (7.02)	12.53 (12.41)

[a] All the monothioacetals showed an OCH_3 singlet at δ 3.42—3.50 ppm (the acetal, δ 3.34 ppm) and a C_6H_5 absorption at δ 7.1—7.8 ppm.

acetal, or 22 mmol (2.93 g) of *N*-chlorosuccinimide to form the acetal, and the solution was stirred at 20—25°C for the time indicated in Table 1. (Some of the reactions were run on 1/3 this scale.) The solvent was removed under vacuum and the residue was treated with petroleum ether and filtered to remove insoluble salts. The solution was washed with water, then 7% sodium hydroxide solution, and dried over magnesium sulfate. The product was distilled. Boiling points are listed in Table 1, ^{1}H NMR and elemental analyses in Table 2.

Variations of general method for monothioacetals and acetals

In addition to variations footnoted in Table 1, the following are noted. (1) Phenylacetaldehyde dimethyl acetal. With sodium bicarbonate as base, 14 h at 25°C, 74% yield was obtained. (2) 3-Phenylpropionaldehyde dimethyl acetal. The same yield (77%) was obtained when sodium bicarbonate was used as base instead of triethylamine. (3) 1-Phenylthio-1-methoxypentane from tributylborane. To a solution of 20 mmol of bis(phenylthio)methyllithium [25] in 40 ml of THF stirred at —78°C was added 20 mmol of 1 *M* tributylborane in THF under argon. The solution was warmed to 25°C and stirred 1 h, 3.55 g (25 mmol) of methyl iodide was added, the solution was stirred 2 h, the solvent was removed under vacuum, and the residue was dissolved in 50 ml of methanol and treated with 4 g of triethylamine and 4.0 g (30 mmol) of *N*-chlorosuccinimide in the usual manner. (4) Methoxy(phenylthio)methylcyclopentane. Cyclopen-

tene was hydroborated with the theoretical amount of either 9-borabicyclononane or borane dimethyl sulfide (to make tricyclopentylborane) in THF, and the resulting borane solution was treated in the same manner as the tributylborane. For 10 mmol of 9-cyclopentyl-9-borabicyclononane or tricyclopentylborane, the amount of bis(phenylthio)methyllithium used was 15 mmol, methyl iodide 15 mmol, triethylamine 20 mmol, and *N*-chlorosuccinimide 12 mmol.

(Trimethylenedioxyboryl)(phenylthio)methane

Treatment of 10.4 g of (phenylthio)methaneboronic acid [13] with 4.56 g of 1,3-propanediol in 50 ml of THF 14 h at 25°C followed by distillation yielded 10.5 g (85%) of $PhSCH_2BO_2(CH_2)_3$, b.p. 114—116°C (0.1 Torr); NMR ($CDCl_3$) δ 1.84 (quintet, 2, CH_2), 2.35 (s, 2, S—CH_2—B), 3.98 (t, 4, O—CH_2), 7.2—7.5 (m, 5, C_6H_5) ppm. Found: C, 57.65; H, 6.22; B, 4.93; S, 15.33. $C_{10}H_{13}BO_2S$ calcd.: C, 57.72; H, 6.30; B, 5.19; S, 15.41%.

Pinacol (triphenylstannyl)(phenylthio)methaneboronate (VI)

Pinacol (phenylthio)methaneboronate (IV) was converted to the lithio derivative in the usual manner [13] with lithium diisopropylamide and tetramethylethylenediamine in THF, then treated with an equivalent amount of triphenyltin chloride and stirred 14 h at 25°C. The solution was concentrated under vacuum and the residue was treated with chloroform and insoluble material filtered out. Partial concentration followed by addition of methanol led to crystallization of the product, 73%, which was recrystallized from chloroform/methanol, m.p. 148—149°C; NMR ($CDCl_3$) δ 0.85 (s, 6, CH_3), 0.98 (s, 6, CH_3), 3.05 (s, 1, SCHSnB), 7.1—8.0 (m, 20, C_6H_5) ppm. Found: C, 62.24; H, 5.60; B, 1.90; S, 5.26; Sn, 19.73. $C_{31}H_{33}BO_2SSn$ calcd.: C, 62.14; H, 5.55; B, 1.80; S, 5.35; Sn, 19.81%.

Pinacol 1-phenylthio-3-butene-1-boronate

Pinacol (phenylthio)methaneboronate (IV) was converted to the lithio derivative and treated with allyl bromide in the usual manner [13], yield 65%, b.p. 132—134°C (0.1 Torr); NMR ($CDCl_3$) δ 1.16 (s, 12, CH_3), 2.2—3.0 (m, 3, CH_2CH), 4.9—5.4 (m, 2, $=CH_2$), 5.6—6.3 (m, 1, CH=), 7.2—7.7 (m, 5, C_6H_5) ppm. Found: C, 66.94; H, 7.92; B, 3.90; S, 11.25. $C_{16}H_{23}BO_2S$ calcd.: C, 66.21; H, 7.99; B, 3.72; S, 11.05%.

Ethylene ketal of pinacol 5-hexanone-1-boronate

The lithio derivative of pinacol (phenylthio)methaneboronate (IV) [13] was treated with the ethylene ketal of 5-chloro-2-pentanone in the usual manner and stirred 24 h at 25°C, yield 55%, b.p. 184—188°C (0.1 Torr); NMR ($CDCl_3$) δ 1.20 (s, 12, CH_3), 1.26 (s, 3, CH_3), 1.5—1.9 (m, 6, CH_2), 2.76 (t, 1, SCHB), 3.90 (s, 4, O—CH_2), 7.15—7.65 (m, 5, C_6H_5) ppm. Found: C, 63.52; H, 8.30; B, 2.70; S, 8.33. $C_{20}H_{31}BO_4S$ calcd.: C, 63.49; H, 8.26; B, 2.86; S, 8.47%.

Pinacol 1-(phenylthio)-3-phenylpropane-1-boronate

The lithio derivative of pinacol (phenylthio)methaneboronate (IV) was treated with 2-phenylethyl iodide in the usual manner [13], yield 72%, b.p. 176—180°C (0.1 Torr); NMR ($CDCl_3$) δ 1.18 (s, 12, CH_3), 1.9—2.3 (m, 2, CH_2),

2.6—3.0 (m, 3, CH_2 and SCHB), 7.15—7.65 (m, 10, C_6H_5) ppm. Found: C, 71.27; H, 7.73; B, 2.99; S, 9.02. $C_{21}H_{27}BO_2S$ calcd.: C, 71.19; H, 7.68; B, 3.05; S, 9.05%.

Radical deboronations of pinacol 1-(phenylthio)-2-phenylethaneboronate (I)

To a solution of 1.70 g (5 mmol) of I in 15 ml of carbon tetrachloride was added 0.68 g (5.1 mmol) of sulfuryl chloride. After 0.5 h at 25°C, the NMR spectrum showed an absence of I and the presence of $PhCH_2CHClSPh$ [18]. On distillation, gas was evolved and 0.88 g (83%) of 1-(phenylthio)-2-phenylethene [19] was isolated, b.p. 140—144°C (0.1 Torr), the NMR spectrum was consistent with that previously reported [26], *cis/trans* ratio 1/2. When 3 mmol of I was refluxed with 3 mmol of *N*-chlorosuccinimide in 15 ml of carbon tetrachloride (1 h), the NMR spectrum indicated that the product contained 5—10% 1-(phenylthio)-2-phenylethene but was mostly 1-chloro-1-(phenylthio)-2-phenylethane ($PhCH_2CHClSPh$). After distillation, washing with aqueous sodium hydroxide, and redistilling, 1-(phenylthio)-2-phenylethene was obtained (75%).

2-Chloro-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (V)

To a solution of 2.50 g (10 mmol) of pinacol (phenylthio)methaneboronate (IV) [13] in 25 ml of dichloromethane was added 1.49 g (11 mmol) of sulfuryl chloride. Distillation yielded 1.68 g of chloromethyl phenyl sulfide (94%) and 1.03 g (63%) of (V), b.p. 32—34°C (0.1 Torr), NMR ($CDCl_3$) δ 1.34 (singlet) ppm. Found: C, 47.10; H, 7.48; B, 6.57; Cl, 18.52. $C_6H_{12}BClO_2$ calcd.: C, 44.37; H, 7.45; B, 6.66; Cl, 21.33%. Other cleavages with sulfuryl chloride mentioned in the Results were run similarly.

Acknowledgment

We thank the National Science Foundation for support, grant number MPS 75-19557.

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