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Organoboranes. 23. Reaction of Organolithium and Grignard Reagents with α -Bromoalkylboronate Esters. A Convenient, Essentially Quantitative Procedure for the Synthesis of Tertiary Alkyl-, Benzyl-, Propargyl-, and Stereospecific Allylboranes

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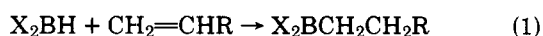
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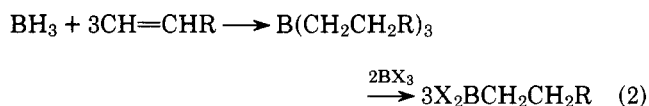
Treatment of trimethylene α -bromoalkylboronate esters in ether at -78°C with a wide variety of organolithium and Grignard reagents results in an essentially quantitative replacement of the α -bromine substituent by the corresponding organic group. Simple distillation provides, in high yield and purity, many novel, highly substituted organoboronate esters not available via hydroboration.

Organoboronate esters, $\text{RB}(\text{OR}')_2$, are becoming increasingly important as intermediates in organic synthesis. For example, their reaction with lithium aluminum hydride, LiAlH_4 , or aluminum hydride, AlH_3 , provides essentially quantitative yields of the corresponding monoalkylboranes, RBH_2 .² Their reaction with Grignard reagents provides a route to mixed trialkylboranes.³ In addition, organoboronate esters can make more efficient use of the boron-bound alkyl groups in certain synthetic transformations involving organoboranes where the utilization of only one alkyl group is inherent in the reaction. In these particular cases, only one-half of the alkyl groups, R, in dialkylboronates, $\text{R}_2\text{BOR}'$, and only one-third of the alkyl groups in trialkylboranes, R_3B , would be utilized.⁴⁻⁶ This would seriously limit the synthetic utility of the reaction if the alkyl group was derived from a valuable intermediate. The promising synthetic potential of organoboronate esters in such situations has recently been demonstrated by D. A. Evans.⁴ It was shown that in stereospecific olefin syntheses leading to prostaglandins the use of organoboronate esters can overcome the inefficient utilization of the alkyl group in trialkylboranes.

Perhaps the most convenient route to organoboronate esters is via hydroboration of olefins and acetylenes with catecholborane⁷ or dihaloboranes⁸ followed by esterification (eq 1).



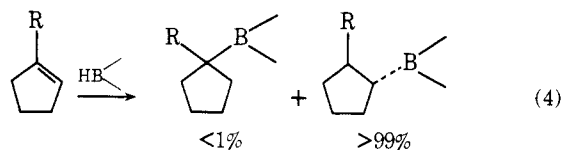
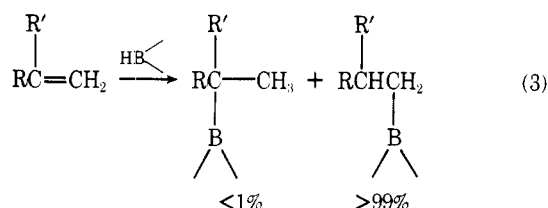
Hydroboration of olefins followed by subsequent redistribution of the trialkylboranes with boron halides⁹ or borate esters¹⁰ also provides a facile route to alkylboronate esters (eq 2).



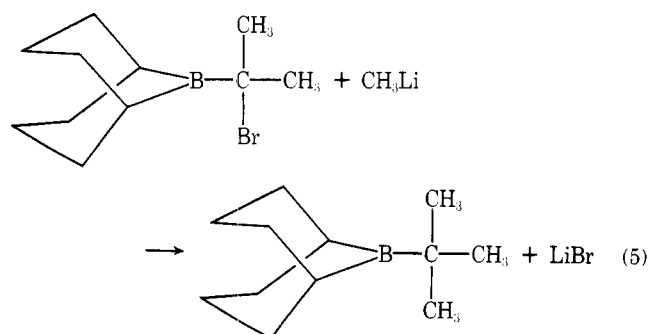
However, certain organoboronate esters cannot be obtained directly by hydroboration due to the remarkable regioselectivity inherent in the hydroboration reaction.⁶ Hydroboration of terminal olefins places the boron predominantly at the terminal carbon. Hydroboration of 1-substituted cycloalkenes places the boron nearly exclusively at the 2 position. While this exceptional regioselectivity has important implications in organoborane chemistry, it precludes, with few exceptions,^{6,11} the synthesis of tertiary organoboranes by direct hydroboration (eq 3 and 4).

Furthermore, certain groups, such as methyl, alkynyl, benzyl, propargyl, and many allyl, cannot be attached to boron through the hydroboration reaction.

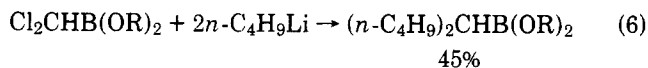
A great deal of progress has been made in the synthesis of "mixed" trialkylboranes possessing groups not available via simple hydroboration.¹²⁻¹⁵ However, the synthesis of organoboronate esters of this class is quite limited.¹⁶



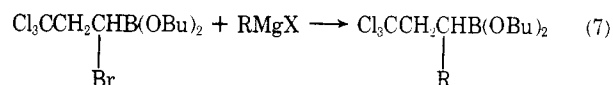
Possible routes to these organoboronate esters have been suggested in the literature. We reported that treatment of *B*- α -bromoisopropyl-9-borabicyclo[3.3.1]nonane with methyl-lithium provides an essentially quantitative yield of *B*-*tert*-butyl-9-borabicyclo[3.3.1]nonane, unavailable via hydroboration (eq 5).¹²



Rathke reported that diisopropyl dichloromethylboronate reacts with organolithium and organomagnesium reagents to provide secondary organoboronate esters (eq 6).¹⁷

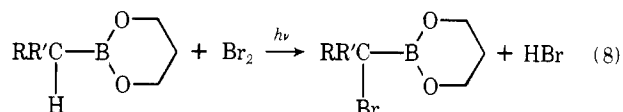


Matteson observed that the α -bromine in dibutyl 1-bromo-3,3,3-trichloropropylboronate could be substituted in variable yields by ethyl and certain aryl Grignard reagents (eq 7).¹⁸

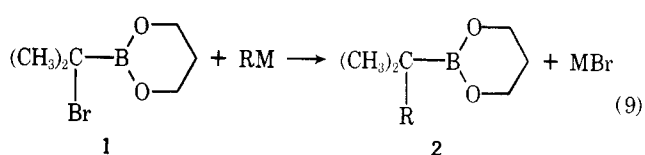


Unfortunately, the full synthetic scope and generality of these potentially valuable reactions have not yet been examined. This may have been due in part to the limited number of synthetic routes to the α -haloalkylboronate ester precursors.

We recently reported a convenient procedure for the synthesis of a wide variety of α -bromoalkylboronate esters in high yields (eq 8).¹⁹

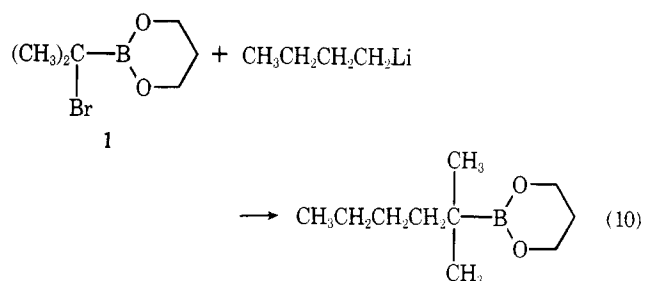


These easily obtainable α -bromoalkylboronate esters should permit a facile entry into previously unattainable organoboranes. However, most of these compounds possess a tertiary α -bromine, a feature not present in previous reactions of organometallics with α -haloalkylboronate esters. Thus, investigation appeared desirable to determine if such tertiary α -bromoalkylboronate esters 1 could be converted into new, highly substituted organoboronate esters 2 by reaction with representative organometallics (eq 9).

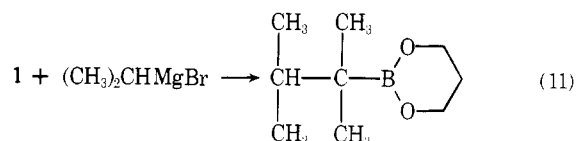


Results and Discussion

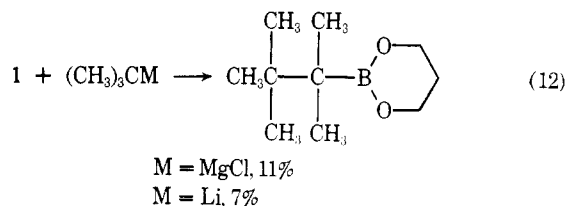
2-(1-Bromo-1-methylethyl)-1,3,2-dioxaborinane (1) (trimethylene α -bromoisopropylboronate) was selected as a representative substrate for study. Treatment of 1 in ether at -78°C with methyl lithium or primary alkyl lithium reagents such as *n*-butyllithium results in quantitative substitution of the α -bromine by the organometallic reagent. Simple distillation provides the highly substituted alkylboronates in high yield and purity (eq 10).



More reactive lithium reagents, such as isopropyl lithium, give substantially lower yields of alkylated product. However, the corresponding Grignard reagent provides an essentially quantitative yield of the *tert*-butylboronate ester (eq 11).

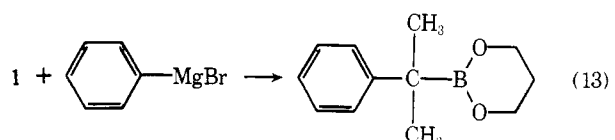


Only with the exceptionally hindered reagents, *tert*-butyllithium and *tert*-butylmagnesium chloride, does the reaction, at present, fail to provide high yields (eq 12).



Perhaps, even these low yields might be considered acceptable in view of the anticipated difficulties in making the exceptionally hindered triptylboronate ester by other methods.

Aryl organometallics, such as phenylmagnesium bromide, react cleanly with 1 to provide high yields of organoboronate esters with α -aryl substitution (eq 13).



Propargylboronate esters have been shown to undergo 1,2 additions to aldehydes and ketones,²⁰ but the synthesis of propargylboronate esters is generally difficult.²¹ Yet, alkynyllithium reagents, such as 1-hexynyllithium, readily react with 1 to provide high yields of the corresponding propargylboronate ester (eq 14).

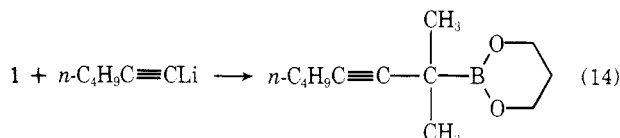
Alkenyllithium reagents react with 1 to provide tertiary allylboronate esters which cannot be obtained via hydrobo-

Table I. Preparation of 2-Alkyl-1,3,2-dioxaborinanes by Reaction of Organolithium and Grignard Reagents with 2-(1-Bromoalkyl)-1,3,2-dioxaborinanes

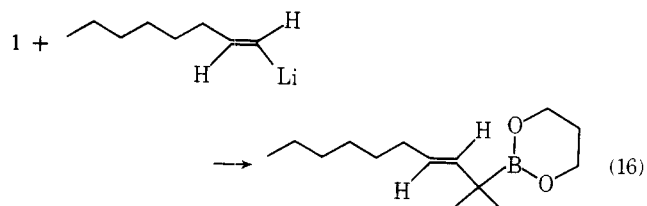
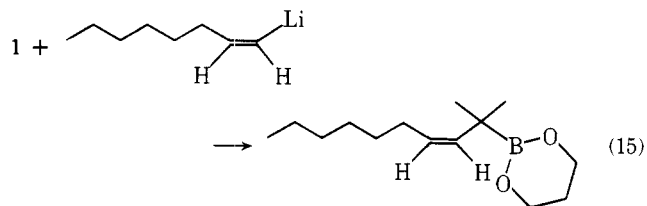
2-(1-Bromoalkyl)-1,3,2-dioxaborinane	Registry no.	Organolithium or Grignard reagent	Registry no.	2-Alkyl-1,3,2-dioxaborinane <i>B</i> -alkyl	Yield, ^a % (isolated)	Bp, °C (mm, Hg)
1	62930-29-4	RM		2		
1		CH ₃ Li	917-54-4	1,1-Dimethylethyl	100 (90)	78–80 (72)
1		<i>n</i> -C ₄ H ₉ Li	109-72-8	1,1-Dimethylpentyl	100	
1		<i>i</i> -C ₃ H ₇ MgBr	75-26-3	1,1,2-Trimethylpropyl	97 ^b (88)	74–75 (13)
1		<i>t</i> -C ₄ H ₉ MgCl	507-20-0	1,1,2,2-Tetramethylpropyl	11 ^c	
1		C ₆ H ₅ MgBr	108-86-1	1-Methyl-1-phenylethyl	96 ^d (92)	67–68 (0.05)
1		<i>n</i> -C ₄ H ₉ C=CLi	17689-03-1	1,1-Dimethyl-2-heptynyl	91	
1		<i>cis</i> -(<i>n</i> -C ₆ H ₁₃)-CH=CH(Li)	56318-79-7	(<i>Z</i>)-1,1-Dimethyl-2-nonenyl	85 ^e (77)	79–80 (0.04)
1		<i>trans</i> -(<i>n</i> -C ₆ H ₁₃)-CH=CH(Li)	37730-25-9	(<i>E</i>)-1,1-Dimethyl-2-nonenyl	85 ^f (73)	83–85 (0.05)
3	62930-31-8			4		
3		CH ₃ Li		1-Methylcyclopentyl	99 (89)	53–56 (3)
3		<i>n</i> -C ₄ H ₉ Li		1-Butylcyclopentyl	99 (90)	85–87 (3)
3		C ₆ H ₅ MgBr		1-Phenylcyclopentyl	94 (97)	64–67 ^g

^a GLC yields for 2-mmol reactions. Isolated yields for 20–30-mmol reactions. ^b Isopropyllithium gave 17%. ^c *tert*-Butyllithium gave 7%. ^d Phenyllithium gave 71%. ^e Product is ≥95% *Z* isomer. ^f Product is ≥95% *E* isomer. ^g Melting point from petroleum ether.

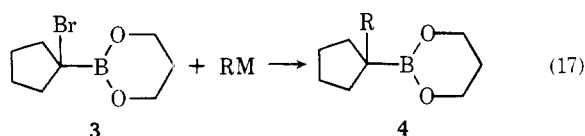
ration or the reaction of the corresponding allylic organometallic reagents with boronate esters or boron halides. Significantly, (*Z*)- or (*E*)-1-octenyllithium reacts with complete re-



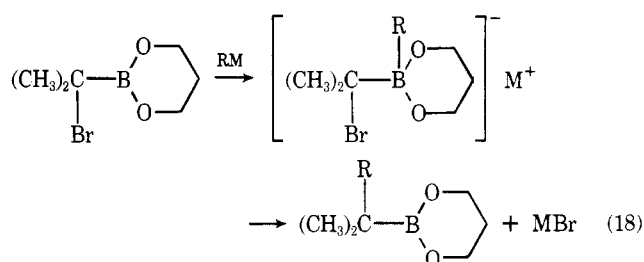
tention of configuration. Such a development holds great promise for natural products and pharmaceutical chemistry (eq 15 and 16).



The alkylation reaction of lithium and Grignard reagents with trimethylene α -bromocyclopentylboronate also gives excellent results (eq 17). It should be applicable to other α -



bromoalkylboronate esters, thus providing a facile procedure for the synthesis of a wide variety of novel, highly substituted organoboronate esters not readily available by other methods. We have thus far explored the reaction from the standpoint of its synthetic applications. It appears the mechanism would



be the same as previously proposed by Matteson (eq 18).¹⁸

The results of this study are summarized in Table I.

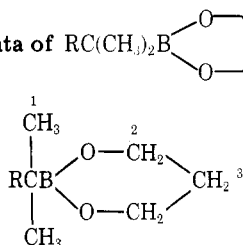
Summary

It is evident that the substitution of the α -bromine in α -bromoalkylboronate esters by reaction with organolithium and Grignard reagents provides a convenient procedure for the synthesis of many highly substituted organoboronate esters not readily available via hydroboration or other methods. Such novel organoboranes as tertiary alkyl-, benzyl-, and propargyl-, and stereospecific allylboronate esters are now available for the expanding scope of organoborane chemistry.

As a synthetic tool, alkyl halides are among the most versatile class of organic compounds. Likewise, organoboranes are exceedingly useful intermediates for further synthetic transformations. The α -bromoboranes are a class of easily obtained compounds possessing both of these desirable functionalities. Undoubtedly, they hold great promise for future synthetic developments.

Experimental Section

General Comments. General procedures for the manipulation of air-sensitive materials have been described elsewhere.⁶ Trimethylene α -bromoalkylboronate esters were synthesized as described previously.¹⁹ Methyl, *n*-butyl-, isopropyl-, and phenyllithium were commercially available (Alfa, Aldrich) and standardized by the Watson–Eastham method.²² The 1-hexynyllithium was prepared as a 0.5 M ether solution by a literature method.¹⁵ The (*Z*)- and (*E*)-1-octenyllithium reagents were prepared as 0.5 M ether solutions from the pure (*Z*)- and (*E*)-1-iodooctenes²³ by the method of Corey and Beames.²⁴ The Grignard reagents were prepared by the usual procedures²⁵ and standardized by the Watson–Eastham method. ¹H NMR spectra were recorded on a Varian T-60 (60 MHz) in CDCl₃ using (CH₃)₄Si (δ 0 ppm) as an internal standard. Infrared spectra were

Table II. Selected ^1H NMR Spectral Data of $\text{RC}(\text{CH}_3)_2\text{B}$ Obtained From Reaction of 1 with RM

R	Registry no	δ	δ C-1 (s, 6 H)	δ C-2 (t, 4 H)	δ C-3 (quin, 2 H)
CH ₃ - (CH ₃) ₂ CH-	63689-73-6	0.87 (s, 3 H)	0.87	3.97	1.88
	63689-74-7	0.77 (d, 6 H)	0.87	3.97	1.88
		1.51 (m, ~1 H)			
	63869-75-8	7.0-7.4 (m, 5 H)	1.30	3.85	1.73
	63689-76-9	0.88 (t, ~3 H)	0.93	3.97	1.95
		1.6-2.3 (m, ~2 H)			
		1.32 (br s, ~8 H)			
		5.54 (d, $J = 15$ Hz)			
		5.15 (pair of t, $J = 15$ and 5 Hz)			
	63689-77-0	0.97 (t, ~3 H)	1.00	4.00	1.90
		1.6-2.3 (m, ~2 H)			
		1.33 (br s, ~8 H)			
		5.32 (d, $J = 11$ Hz)			
		5.12 (pair of t, $J = 11$ and 5.5 Hz)			

recorded on a Perkin-Elmer 137 spectrophotometer and GLC analyses were performed on a Hewlett-Packard 5750-B dual thermal-conductivity gas chromatograph using a clean 6 ft \times 0.25 in. stainless steel column packed with 10% SE-30 on acid-washed, DMCS treated Chromosorb W for borane analyses and 10% DC 710 for alcohol analyses. Normal hydrocarbons (Phillips 99%) were used as internal standards. Correction factors were determined using isolated organoboranes or alcohols. Boiling points are uncorrected.

General Procedure. A dry flask equipped with magnetic stirrer, septum inlet, and pressure-equalized addition funnel was flushed with dry nitrogen and maintained under a positive pressure of nitrogen gas. The flask was charged with the appropriate trimethylene α -bromoalkylboronate ester and enough absolute ethyl ether to make the solution ca. 0.5 M in borane. The flask was cooled in a dry ice/acetone cold bath and 1 equiv of the organolithium or Grignard reagent was added to the addition funnel and diluted to ca. 0.5 M with ether (for methyl- and phenyllithium and Grignard reagents) or pentane (for *n*-butyl-, isopropyl-, and *tert*-butyllithium). The organometallic reagent was then added dropwise over 10-15 min while maintaining the reaction mixture at -78 to -60 $^{\circ}\text{C}$.²⁶ After the organometallic reagent had been added, the addition funnel was washed out with a small portion of the appropriate solvent and added over 3-5 min. In the case of 1-hexynyllithium and the (*Z*)- and (*E*)-1-octynyllithium reagents, the reagents were prepared as 0.5 M ether solutions in a separate flask at -78 $^{\circ}\text{C}$ and transferred directly to the reaction mixture over 3-5 min by a cold, double-ended needle. The reaction mixture was stirred at -78 $^{\circ}\text{C}$ for 10 min and warmed to room temperature where stirring was continued for 1.5-2 h. For reaction mixtures analyzed by GLC (2-mmol scale), an internal standard was added and the yield of borane determined directly. Alternatively, the success of the reaction was determined by oxidation of the reaction mixture with alkaline hydrogen peroxide⁶ and analyzing for the corresponding alcohols by GLC analysis. In preparative reactions (20-30-mmol scale), the reaction mixture was freed of partially dissolved magnesium or lithium salts by removing volatile components by aspirator vacuum and taking up the residue in 30-40 mL of pentane, allowing the salts to settle, and transferring the supernatant to a nitrogen-flushed, simple distillation apparatus. In order to ensure quantitative transfer of the product, the salts were washed one or two times with pentane (20 mL) and the washings transferred to the distillation assembly.²⁷ The pentane was removed by aspirator and the residual material vacuum distilled. Purities were $\geq 95\%$ by GLC or ^1H NMR analysis.

Product Identification. Organoborane products were characterized spectroscopically by their ^1H NMR (Table II) and infrared spectra. Further confirmation of the structures was obtained by alkaline hydrogen peroxide oxidation to give the corresponding alcohols in quantitative yields.⁶ The alcohols were compared to authentic samples either commercially available or obtained through the re-

action of the lithium or Grignard reagent with the appropriate ketone.²⁸ The trimethylene 1,1,2-trimethylpropylboronate, prepared by the reaction of isopropylmagnesium bromide and 1, was identical to a sample prepared by the reaction of 1,3-propanediol with thelyborane.^{6,11} Stereochemistry of the trimethylene (*E*)- and (*Z*)-1,1-dimethyl-2-nonylboronates was established by their ^1H NMR and infrared spectra.²⁹ The ^1H NMR of the *E* isomer showed resonances at δ 5.15 (1 H, doublet of triplets, $J = 15$ and 5 Hz) and 5.54 (1 H, doublet, $J = 15$ Hz), and the infrared spectra showed medium absorption at 10.2 μm . The ^1H NMR of the *Z* isomer showed resonances at δ 5.12 (1 H, doublet of triplets, $J = 11$ and 5.5 Hz) and 5.32 (1 H, doublet, $J = 11$ Hz), and the infrared spectrum showed medium absorption at 13.4 μm and none at 10.2 μm . The two isomers were stereochemically pure ($\geq 95\%$) by ^1H NMR.

Registry No.—Isopropyllithium, 1888-75-1; *tert*-butyllithium, 594-19-4; phenyllithium, 591-51-5.

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Synthesis and Reactions of 7,10-Methano-7,8,9,10,11,11-hexachloro-7,10-dihydrofluoranthene¹

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The synthesis of 7,10-methano-7,8,9,10,11,11-hexachloro-7,10-dihydrofluoranthene (**3**) is reported and its properties are studied. The absorption spectrum of this orange substance shows an enhanced K band that may reflect an intramolecular charge-transfer process. When **3** is irradiated with 360-nm light, no quadricyclene is detected nor does **3** show any other photochemical reaction at 360 nm. The reaction of **3** with methoxide, ethoxide, and isopropoxide nucleophiles occurs in a stereospecific manner to produce 7,10-methano-6b-alkoxy-7,8,9,10,11,11-hexachloro-6b,7,10,10a-tetrahydrofluoranthene.

We synthesized a quantity of 7,10-methano-7,8,9,10,11,11-hexachlorofluoranthene (**3**) as a compound for photochemical study. A molecule containing a norbornadiene moiety fused through the 1,2-bridge of acenaphthylene seemed a potentially rich source of photochemical intrigue.⁴ It was hoped that such a substance would exhibit photochemistry similar to that of norbornadiene-1,2-dicarboxylic acid anhydride⁵ and thus be convertible to a quadricyclene derivative.⁶ The bright orange crystals of **3** have currently resisted a variety of photolytic ring-closing conditions. However, we have found some interesting ground-state chemistry associated with **3**.

The study of the ground-state properties of **3** described herein has its genesis in our early attempts to synthesize **3**. During these initial studies, by-products were isolated that suggested that alkoxy groups were incorporated into the structure. Thus, the recent report by Davies and Adams⁸ concerning the reaction of nucleophiles with chlorine-substituted norbornadienes stimulated us to explore in detail the similar reaction upon **3**.

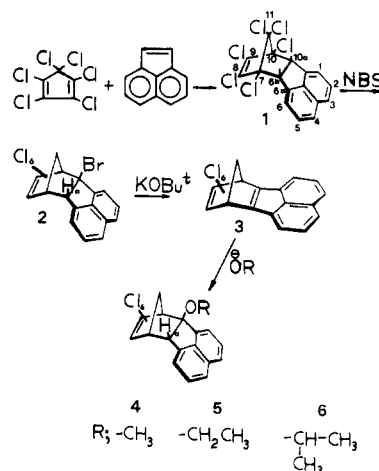
Results and Discussion

The synthesis of **3** involves the thermal [4 + 2] cycloaddition of hexachlorocyclopentadiene to acenaphthylene to form *endo*-7,10-methano-7,8,9,10,11,11-hexachloro-6b,7,10,10a-tetrahydrofluoranthene (**1**).^{9,10} This compound was treated with NBS in refluxing carbon tetrachloride to form the crude monobrominated derivative **2**. Subsequent treatment of crude **2** with warm potassium *tert*-butoxide in *tert*-butyl alcohol produced **3** in good yield. The mass spectrometric examination of **3** showed the expected isotopic cluster for a six chlorine atom containing molecule at M^+ of 420 through 426. The base peak at m/e 387 ($M - 35$) showed the isotopic clustering characteristic of five chlorine atoms.¹³ A minor $M - 105$ grouping occurred at m/e 315, 317, and 319, suggesting a fragment with three chlorine atoms lost. The NMR spectrum of **3** showed only the typical aromatic resonances at 7.2–7.8 ppm.

The UV-visible spectrum of a cyclohexane solution of **3** is shown in Figure 1 as compared to acenaphthylene dissolved in the same solvent. The feature of major interest is the

bathochromic shift and hyperchromic modification of the absorption band of acenaphthylene between 400 and 450 nm. This band has been classified as a K transition by Michl¹⁴ and theoretical CI-SCF-P-P-P calculations indicate that this transition involves substantial intramolecular charge transfer from the peri bridge to the naphthalene chromophore. The enhancement of the K band in **3** may represent additional charge transfer involving homoconjugation of the remote dichloroethene π system with the peri bridge of the acenaphthylene unit. The recent synthesis and characterization of 8*H*-cyclopent[*a*]acenaphthylene as orange needles¹⁵ casts some doubt on the existence of this proposed homoconjugative interaction because the remote double bond at position 8 and 9 is saturated in this molecule. We hope that studies now in progress will clarify the spectral interpretations.

The reaction of **3** with various alkoxides was pursued



analogous to the procedure in prior studies⁸ by refluxing an alcoholic mixture of **3** with the appropriate sodium alkoxide. We observed that there were qualitative rate differences and that the reaction of **3** with alkoxides occurred in the order $\text{CH}_3\text{O}^- > \text{CH}_3\text{CH}_2\text{O}^- > (\text{CH}_3)_2\text{CHO}^- \gg (\text{CH}_3)_3\text{CO}^-$. Methoxide and ethoxide addition proceeded smoothly. The addition of isopropoxide proceeded with difficulty, and some