release electrons to the boron atom. On the other hand, the lower stability of Py·*B*-*t*-9-BBN or Py·*B*-CH(CH_3)-$SiMe_3$-9-BBN, as compared to the ethyl derivative, must be attributed to the larger steric requirement of the *t*-Bu or the 1-trimethylsilylethyl group. It is clear, therefore, that it is necessary to consider both electronic and steric effects in accounting for the stabilities of these addition compounds.

Thus, by using ^{11}B or ^{13}C NMR, the extent of complexation can be assessed. However, the additional feature of the lability of such complexes can be observed by using ^{13}C NMR, providing a valuable tool for understanding better the nature of such compounds.

Experimental Section

General Procedures. Spectroscopic samples were prepared by literature methods[2-4,7,12] under a nitrogen atmosphere using oven-dried glassware. Compounds were transferred under nitrogen to a septum-sealed NMR tube containing NMR-grade $CDCl_3$. Reagent grade pyridine was predried over potassium hydroxide and distilled from calcium hydride. Spectra were recorded on a Varian FT-80A NMR spectrometer using Me_4Si (δ = 0.00 ppm) as an external standard for the ^{13}C spectra and $BF_3 \cdot OEt_2$ (δ = 0.00 ppm) as an external standard for the ^{11}B spectra. Sweep widths of 4000 and 8000 Hz were used, respectively, for these two nuclei. By use of either 8000 or 16 000 data points for the carbon data and 2000 data points for the boron data, the chemical shifts were reproducible from run to run to ±0.1 ppm for the carbon spectra and ±0.5 ppm for the boron spectra.

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Selective Reductions. 27. Reaction of Alkyl Halides with Representative Complex Metal Hydrides and Metal Hydrides. Comparison of Various Hydride Reducing Agents[1]

S. Krishnamurthy and Herbert C. Brown*

Richard B. Wetherill Laboratory, Purdue University, West Lafayette, Indiana 47907

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The approximate rates and products of the reaction of alkyl halides with representative metal hydrides and complex metal hydrides were examined in order to identify the most promising hydride reducing agents for the hydrogenolysis of alkyl halides. Among the various reagents tested, both lithium triethylborohydride and lithium aluminum hydride exhibit exceptional utility for the hydrodehalogenation reaction. Of the two most promising reagents, lithium triethylborohydride exhibits far greater hydride-transfer ability than does lithium aluminum hydride. Lithium trimethoxyaluminohydride, lithium tri-*tert*-butoxyaluminohydride, sodium borohydride, and lithium borohydride all react with primary alkyl iodides and bromides at a moderate rate; they are essentially inert toward alkyl chlorides. The reaction of alkyl halides with alane is quite slow; borane and dialkylboranes are essentially inert toward alkyl halides. Thus the study has defined those reagents which are most effective for hydrodehalogenation, as well as those reagents which can be utilized for reduction of functional groups with minimum attack on halogen substituents.

The chemistry of complex metal hydrides and metal hydrides has received considerable attention in recent years, especially for the selective reduction of various functional groups in organic molecules.[2] The discovery of sodium borohydride[3] in 1942 and of lithium aluminum hydride[4] in 1945 has revolutionized the procedures utilized for the reduction of organic functional groups. Since their discovery, a number of modified hydride reagents—both nucleophilic and electrophilic—have evolved from time to time. The reducing properties of each of these hydride reducing agents, namely, lithium aluminum hydride, lithium trimethoxyaluminohydride, lithium tri-*tert*-butoxyaluminohydride, sodium borohydride, lithium borohydride, lithium triethylborohydride, alane, borane, thexylborane, disiamylborane, 9-borabicyclo[3.3.1]nonane, are now well characterized.[2a] The reactivity of each of the above-mentioned reagents under standard reaction conditions toward representative organic compounds containing the most common functional groups, for example, aldehydes, ketones, epoxides, carboxylic acids and derivatives, aromatic nitro compounds, organosulfur compounds, etc., has been examined. Unfortunately, the reactivity of these reagents was not tested against alkyl halides. Furthermore, very little attention has been devoted to the hydrogenolysis of carbon–halogen bonds utilizing complex metal hydride and metal hydride as the source of hydrogen. The majority of such reactions reported in the literature were carried out with a slurry of lithium aluminum hydride in ethyl

(1) Partially based upon a thesis submitted by S. Krishnamurthy in partial fulfillment of the requirements for the degree of Doctor of Philosophy, Purdue University. A preliminary communication reporting the exceptionally powerful nucleophilic properties of lithium triethylborohydride in its reaction with alkyl halides appeared earlier: H. C. Brown and S. Krishnamurthy, *J. Am. Chem. Soc.*, **95**, 1669 (1973).

(2) (a) H. C. Brown and S. Krishnamurthy, *Tetrahedron*, **35**, 567 (1979); (b) *Aldrichimica Acta*, **12**, 3 (1979); (c) S. Krishnamurthy, *ibid.*, **7**, 55 (1974).

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(4) A. E. Finholt, A. C. Bond, Jr., and H. I. Schlesinger, *J. Am. Chem. Soc.*, **69**, 1199 (1947).

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Table I. Reaction of Lithium Aluminum Hydride and Sodium Aluminum Hydride with Representative Alkyl Halides in Tetrahydrofuran at 25 °C[a]

compd	reagent	reduction,[b,c] %						
		0.25 h	0.5 h	1.0 h	3.0 h	6.0 h	12.0 h	24.0 h
n-octyl iodide	$LiAlH_4$	99	100	100				
	$NaAlH_4$	96	100	100				
n-octyl bromide	$LiAlH_4$	84	97	99				
	$NaAlH_4$	47	62	80		92		
n-octyl chloride	$LiAlH_4$			4	19	37	56	73
	$NaAlH_4$			3	9	20		38
cyclohexyl iodide	$LiAlH_4$			3	6	12	17	29
	$NaAlH_4$				13	27		36
cyclohexyl bromide	$LiAlH_4$						2	4
	$NaAlH_4$				0	0	1	2
cyclohexyl chloride	$LiAlH_4$				0	0	0	tr
	$NaAlH_4$				0	0	0	tr

[a] In all cases, solutions were 0.25 M in the complex metal hydride and the substrate. [b] Reactions were followed by GLC using a suitable internal standard and authentic synthetic mixtures on columns A, B, and C. [c] Except where indicated, no olefins were detected.

ether or tetrahydrofuran (THF). Consequently, prior to the undertaking of any detailed study of the reaction of alkyl halides with a particular complex metal hydride or a metal hydride, it was of interest to examine the reactivity of a wide range of hydride reducing agents toward representative alkyl halides in order to identify the most suitable reagents for this transformation. The results of this investigation are presented in this paper.

Results and Discussion

Representative hydride reducing agents of different structural features and activities, such as lithium aluminum hydride ($LiAlH_4$), sodium aluminum hydride ($NaAlH_4$), lithium trimethoxyaluminohydride (LTMA), lithium tri-*tert*-butoxyaluminohydride (LTBA), sodium borohydride ($NaBH_4$), lithium borohydride ($LiBH_4$), lithium triethylborohydride ($LiEt_3BH$), alane (AlH_3), borane (BH_3), and 9-borabicyclo[3.3.1]nonane (9-BBN), were selected for this study. All of the reagents were tested toward primary alkyl iodide, bromide, and chloride at 25 °C. Several reagents which exhibit special promise for such hydrogenolysis were also tested against selected secondary alkyl halides.

Procedure for Rate and Product Studies. In all cases, clear solutions of the reducing agents in the appropriate ethereal solvent were utilized. The concentration of the alkyl halide was usually maintained at 0.25 M while the concentration of the reagent ranged from 0.25 to 0.5 M, depending upon the nature of the reagent. The solutions were maintained at 25 °C. In all reactions, except those involving aluminum hydride, the rate of the reaction was monitored by GLC at appropriate intervals of time for the production of alkane, utilizing a suitable internal standard. In the case of aluminum hydride reductions, the rate of reduction was monitored by analysis for residual "hydride", hydrolyzing aliquots at appropriate intervals of time.

Lithium Aluminum Hydride and Sodium Aluminum Hydride. Lithium aluminum hydride is an exceptionally powerful reducing agent, reacting rapidly with practically all organic functional groups.[5] A brief early study of the reaction of lithium aluminum hydride with alkyl halides led to the conclusion that the reaction is sluggish.[6] An exploratory study of the reaction of sodium aluminum hydride with representative organic functional groups revealed that it is as powerful a reducing agent as its lithium analogue.[7] Consequently, the reactivity of these two hydrides toward representative alkyl halides was examined. The reaction mixtures were formulated with concentrations of the substrate and the reagent of 0.25 M in THF at 25 °C. The reaction mixtures were examined by GLC at appropriate time intervals for the production of the alkane, utilizing a suitable internal standard. The results are summarized in Table I.

Table II. Reaction of Lithium Trimethoxyaluminohydride with *n*-Octyl Bromide in Tetrahydrofuran at 25 °C[a]

	time, h						
	0.25	0.5	1	3	6	18	24
n-octane formed,[b] %	18	25	33	45	50	52	55

[a] Reaction mixture was 0.25 M both in reagent and substrate. [b] Monitored by GLC analysis on column A using *n*-nonane as internal standard.

The results of these experiments clearly reveal that the reaction of lithium aluminum hydride with organic halides is far more facile than that realized by earlier workers.[6] Sodium aluminum hydride reduces alkyl halides at a rate that is considerably slower than that for lithium aluminum hydride.

Lithium Trimethoxyaluminohydride. Lithium trimethoxyaluminohydride is an active reducing agent, much closer in its reducing capabilities to lithium aluminum hydride than to other alkoxy derivatices, such as lithium tri-*tert*-butoxyaluminohydride.[8] Unlike lithium aluminum hydride, lithium trimethoxyaluminohydride has only one active hydride. Consequently, its reaction with halides and related substrates would be expected to follow a clean single-step pathway (eq 1).

$$RX + Li(CH_3O)_3AlH \rightarrow RH + (CH_3O)_3Al + LiX \quad (1)$$

Accordingly, reaction conditions identical with those utilized for lithium aluminum hydride (0.25 M in both reagent and substrate) were employed. Surprisingly, the reaction did not proceed as expected. Reduction proceeds rapidly to 50%, with further reduction being quite slow. Thus, with *n*-octyl bromide, 50% of the reduction was over in 6 h; at 24 h the reduction had proceeded only to 55%

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(8) H. C. Brown and P. M. Weissman, *J. Am. Chem. Soc.*, 87, 5614 (1965).

Table III. Reaction of *n*-Octyl Bromide with Lithium Aluminum Hydride and Lithium Trimethoxyaluminohydride in Tetrahydrofuran at 25 °C[a]

reagent	reduction,[b] % 5 min	0.25 h	0.5 h	1.0 h	3.0 h	6.0 h
$LiAlH_4$	84	100				
$Li(CH_3O)_3AlH$	10	28	44	65	94	100

[a] Solutions were maintained at 0.4 M in complex metal hydride and 0.1 M in *n*-octyl bromide. [b] Reactions were followed by GLC analysis on column A for the formation of *n*-octane.

Table IV. Reaction of Lithium Trimethoxyaluminohydride with Representative Alkyl Halides in Tetrahydrofuran at 25 °C[a,b]

compd	reduction,[c] % 5 min	0.25 h	0.5 h	1.0 h	3.0 h	6.0 h	12 h	24 h
n-octyl iodide	97	100						
n-octyl bromide	10	28	44	65	94	100		
n-octyl chloride					3	6		19
cyclohexyl iodide					14	20		46
cyclohexyl bromide					0	0		0
cyclohexyl chloride						0	0	0

[a] In all cases, solutions were 0.4 M in $Li(OCH_3)_3AlH$ and 0.1 M in substrate. [b] No olefins were detected on GLC. [c] Reactions were followed by GLC for the production of alkane, either on column A or B.

(Table II). Within 30 min of initiation of the reaction, the reaction mixture became gelatinous and turbid. It is probably that the reaction involves more than one step (eq 2–4).

$$Li(CH_3O)_3AlH + RX \xrightarrow{fast} RH + Al(CH_3O)_3 + LiX \quad (2)$$

$$Li(CH_3O)_3AlH + Al(OCH_3)_3 \rightleftharpoons Li[(CH_3O)_3Al\cdots H\cdots Al(OCH_3)_3] \quad (3)$$

$$Li[(CH_3O)_3Al\cdots H\cdots Al(OCH_3)_3] + RX \xrightarrow{slow} RH + LiX + 2Al(OCH_3)_3 \quad (4)$$

Consequently, to avoid these complications, we decided to utilize the reaction conditions that had been employed in our earlier exploratory studies of this reagent:[1] 0.4 M in reagent and 0.1 M in substrate. The rate of reduction of *n*-octyl bromide with lithium aluminum hydride was examined under the same conditions so that a meaningful comparison with the parent hydride could be made. All of these reactions were monitored by GLC analysis, utilizing a suitable internal standard. The results are summarized in Tables III and IV.

It is clearly evident from these results that lithium trimethoxyaluminohydride is significantly less reactive than lithium aluminum hydride toward alkyl halides.

Lithium Tri-*tert*-butoxyaluminohydride. Addition of 3 mol of *tert*-butyl alcohol to 1 mol of lithium aluminum hydride evolves 3 mol of hydrogen and gives a clear solution of lithium tri-*tert*-butoxyaluminohydride in THF.[9] It is an exceptionally mild reducing agent, closely resembling sodium borohydride in reducing characteristics.[10] The reactivity of this reagent toward *n*-octyl derivatives (iodide, bromide, and chloride) was examined. The reactions were carried out at concentrations that were 0.25 M in halide and in reagent.

Table V. Reaction of Lithium Tri-*tert*-butoxyaluminohydride with Representative Alkyl Halides in Tetrahydrofuran at 25 °C[a]

compd	reduction,[b,c] % 4 h	24 h
n-octyl iodide	45	70
n-octyl bromide	12	29
n-octyl chloride	0	0

[a] The reaction mixtures were 0.25 M in LTBA and alkyl halide. [b] The reactions were monitored and analyzed by GLC on columns A, B, and C. [c] No olefin was detected.

Table VI. Reaction of Sodium Borohydride with Representative Alkyl Halides in Anhydrous Diglyme at 25 °C[a]

compd	reduction,[b] % 0.25 h	0.5 h	1.0 h	3.0 h	6.0 h	12.0 h	24.0 h
benzyl bromide		37	50	60	71	74	86
n-octyl iodide	43	49	52	65	72		89
n-octyl bromide		14	22	32	32	51	58
n-octyl chloride		0	0	0	0	1.5	2.5
2-bromooctane	0	0	0	1	2	3	6

[a] In all cases, the solutions were 0.25 M in alkyl halide and $NaBH_4$. [b] Reactions were monitored by GLC for the alkane formed, on column A.

The results summarized in Table V clearly reveal that the reactivity of this reagent toward alkyl halides is far less than that of lithium trimethoxyaluminum hydride or of lithium aluminum hydride.

Sodium Borohydride. Sodium borohydride is a mild and highly selective reducing agent. It reduces aldehydes and ketones rapidly but is essentially inert toward all other functional groups.[11] Unlike lithium aluminum hydride, the unusual stability of sodium borohydride in aqueous solvents permits a greater variety of reaction conditions. It was observed that tertiary and secondary alkyl halides and tosylates undergo facile reduction with sodium borohydride in aqueous diglyme solvent.[12] These reactions are believed to proceed through the carbonium ion intermediate, which is effectively trapped by the hydride and converted to the corresponding hydrocarbon. In addition to being a convenient procedure for the reduction of tertiary and secondary derivatives, the reaction is highly useful for trapping and characterizing carbonium ions.

Several years ago it was observed in our laboratory that sodium borohydride in diglyme reacts with methyl chloride rapidly and quantitatively.[13] Accordingly, it was of interest to examine the reactivity of sodium borohydride toward alkyl halides under typical S_N2 conditions. Sodium borohydride is sparingly soluble in THF. Consequently, the reactions were carried out in anhydrous diglyme at 25 °C, utilizing a clear solution of sodium borohydride in that solvent. Reaction mixtures were maintained at 0.25 M,

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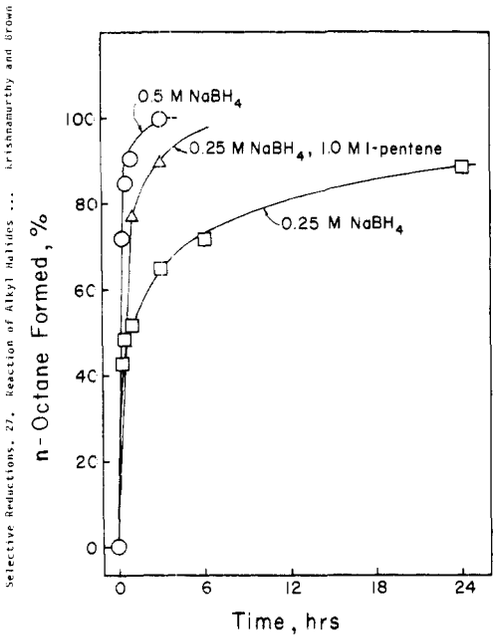

Figure 1. Rates of reduction of *n*-octyl iodide (0.25 M) with sodium borohydride in the presence and absence of 1-pentene (1.0 M) in diglyme at 25 °C.

in both reagent and alkyl halide. The results are summarized in Table VI.

From these results, it is evident that the reaction proceeds rapidly to 50%, with further reduction becoming very slow. Thus, *n*-octyl iodide is reduced to the extent of 50% in 0.5 h, and reduction of the remaining halide requires more than 24 h. The reaction must involve an initial rapid transfer of hydride, with concurrent formation of sodium diborohydride.[13] Subsequent hydride transfer by the diborohydride ion is relatively slow (eq 5–7).

$$NaBH_4 + RX \xrightarrow{fast} RH + BH_3 + NaX \quad (5)$$

$$NaBH_4 + BH_3 \xrightarrow{fast} NaB_2H_7 \quad (6)$$

$$NaB_2H_7 + RX \xrightarrow{slow} RH \quad (7)$$

If the mechanism of eq 5–7 is correct, it should be possible to avoid a break at 50% reduction either by increasing the concentration of sodium borohydride to 0.5 M or by conducting the reaction in the presence of a terminal olefin, such as 1-pentene. The olefin will scavenge the "borane" rapidly by hydroboration to the corresponding trialkylborane, thereby avoiding the formation of NaB_2H_7. Indeed, we were able to achieve rapid and smooth reduction of *n*-octyl iodide either by increasing the borohydride concentration to 0.5 M or by running the reaction in the presence of 1-pentene (Figure 1, Table VII). In the latter case, oxidation of the reaction mixture with alkaline hydrogen peroxide indicated 3 mol of pentanols for every mole of *n*-octane produced, clearly confirming that the borane produced had been scavenged by the olefin (eq 8 and 9).

$$NaBH_4 + n\text{-}C_8H_{17}I \rightarrow n\text{-}C_8H_{18} + BH_3 + NaI \quad (8)$$

$$BH_3 + 3CH_3CH_2CH_2CH{=}CH_2 \rightarrow R_3B \xrightarrow[H_2O_2]{NaOH} 3ROH \quad (9)$$

The results clearly indicate that the reaction of sodium borohydride with alkyl halides under S_N2 conditions is less facile than the corresponding reactions involving lithium aluminum hydride.

Table VII. Reaction of Sodium Borohydride with *n*-Octyl Iodide in the Presence and Absence of 1-Pentene in Diglyme at 25 °C

RX, mmol	$NaBH_4$, mmol	1-pentene, mmol	time, h	products, mmol: *n*-octane[c]	products, mmol: pentanols[d]
5[a]	5	0	0.5	2.45	
			1.0	2.57	
			3.0	3.25	
			6.0	3.6	
			24.0	4.45	
5[b]	10	0	0.25	3.6	
			0.5	4.25	
			1.0	4.55	
			3.0	5.00	
5[a,c]	5	20	1.0	3.87	12.0
			3.0	4.5	13.4

[a] Solutions were 0.25 M in $NaBH_4$ and RX. [b] 0.25 M in RX and 0.5 M in $NaBH_4$. [c] Analyzed on column B following oxidation by alkaline hydrogen peroxide. Ratio of 1- and 2-pentanols was found to be 96:4.

Table VIII. Reaction of Lithium Borohydride with Representative Alkyl Halides in Tetrahydrofuran at 25 °C[a]

compd	reduction, %: 0.5 h	1.0 h	4.0 h	6.0 h	12.0 h	24.0 h
n-octyl iodide	13	22	50	53	72	75
n-octyl bromide		3	11	14	22	39
n-octyl chloride					0	0

[a] The solutions were 0.25 M in $LiBH_4$ and the alkyl halide. [b] Reactions were followed by GLC on columns A, B, and C. No olefin was detected.

Lithium Borohydride. Preliminary exploratory studies indicate lithium borohydride to be a more powerful reducing agent than its sodium analogue toward organic functional groups.[14] Unlike sodium borohydride, it is soluble in tetrahydrofuran. Accordingly, we examined the reactivity of lithium borohydride in THF toward *n*-octyl derivatives (0.25 M in reagent and halide). The results, summarized in Table VIII, clearly reveal that the reactivity exhibited by lithium borohydride in tetrahydrofuran toward alkyl halides is considerably less than that of sodium borohydride in diglyme. The unusual reversal in the reactivity order ($NaBH_4 > LiBH_4$) in the present reaction may result from the greater polarity of diglyme, facilitating S_N2 displacements.

Lithium Triethylborohydride. The first synthesis of alkali metal trialkylborohydride was reported by Brown and Schlesinger in 1953.[15] Unfortunately, very little attention was paid to the reducing properties of these derivatives. The exceptional reducing characteristics of lithium trialkylborohydrides were first recognized in 1972.[16] Since then a number of alkali metal trialkylborohydrides have emerged as highly attractive reducing agents in organic synthesis.[2] The reactivity of lithium triethylborohydride toward representative alkyl halides has been examined in the present study. In all cases, the reaction mixtures were maintained at 0.25 M in the reagent and the substrate in tetrahydrofuran at 25 °C. The rate of the

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Table IX. Reaction of Lithium Triethylborohydride with Representative Alkyl Halides in Tetrahydrofuran at 25 °C[a]

compd	reduction,[b,c] %							
	5 min	0.25 h	0.5 h	1.0 h	3.0 h	6.0 h	12.0 h	24.0 h
n-octyl iodide	97	100						
n-octyl bromide	80	87	90	91	96			
n-octyl chloride		23	37	46	53	56	67	73
cyclohexyl iodide			18	25	42	50	58	63
cyclohexyl bromide					7	12	18	30
cyclohexyl chloride					0	0	0	tr

[a] In all cases, the solutions were 0.25 M in $LiEt_3BH$ and the substrate. [b] Reactions were followed by GLC on columns A, B, and C. [c] No olefin was detected.

reaction was monitored by GLC. The results are summarized in Table IX.

It is clearly evident from these experiments that the reaction of lithium triethylborohydride with alkyl halides is extraordinarily rapid. The reaction proceeds rapidly up to 50%, with further reduction being very sluggish. This suggests that 2 mol of lithium triethylborohydride are required for every mole of alkyl halide[17] (eq 10), as proposed earlier for lithium trimethoxyaluminum hydride (eq 2–4) and sodium borohydride (eq 5–7). A detailed discussion of the stoichiometric aspect of this reaction will be dealt with elsewhere.

$$RX + 2LiEt_3BH \rightarrow RH + LiEt_3B\cdots H\cdots BEt_3 + LiX \quad (10)$$

Aluminum Hydride. Lithium aluminum hydride is a "basic"-type (nucleophilic) reducing agent, whereas aluminum hydride is an "acidic"-type (electrophilic) reducing agent. A systematic comparative study of these reagents toward representative organic functional groups clearly revealed considerable differences in their reducing characteristics.[18] Consequently, we decided to examine the reactivity of aluminum hydride toward alkyl halides.

Reaction mixtures were maintained at 0.25 M in substrate and 0.33 M in aluminum hydride in tetrahydrofuran at 25 °C. The rate of reduction was followed by analysis for residual "hydride" at appropriate intervals of time. The results are summarized in Table X.

It is evident that the reaction of aluminum hydride with these alkyl and cycloalkyl halides is considerably slower than the corresponding reactions of lithium aluminum hydride.

Borane. Recently, borane–methyl sulfide (BMS) has emerged as an exceptionally stable and selective reducing agent for certain organic functional groups. Borane is a strong Lewis acid, its reactions involving preferential electrophilic attack at the centers of highest electron density. It exhibits markedly different characteristics from that of basic sodium borohydride. Reaction of *n*-octyl halides (0.25 M) with BMS (0.33 M) indicated that the reagent is essentially inert toward iodide, bromide, and chloride. The results are summarized in Table XI. It is evident that borane–methyl sulfide is essentially inert toward carbon–halogen bonds (iodine, bromine, and chlorine) under the reaction conditions.

Table X. Reaction of Aluminum Hydride with Representative Alkyl Halides in Tetrahydrofuran at 25 °C[a]

compd	reduction,[b] %							
	0.25 h	0.5 h	1.0 h	3.0 h	6.0 h	12.0 h	24.0 h	48.0 h
benzyl bromide		53	80	99				
3-bromo-propene	35	51	71	94	94			
n-butyl bromide		6	12	25		45	53	59
n-butyl chloride	0	0		19			24	
isobutyl bromide	0			23		27	32	
sec-butyl bromide	0				15		25	
cyclopentyl bromide	2	7		11		23	31	
cyclohexyl bromide	0	0		4		8		

[a] In all cases, solutions were 0.25 M in alkyl halide and 0.33 M in AlH_3. [b] Reactions were followed by the decrease in "hydride" concentration. In all cases, only negligible amounts of hydrogen were evolved from the reaction mixture.

Table XI. Reaction of Borane-Methyl Sulfide and 9-Borabicyclo[3.3.1]nonane with Representative Alkyl Halides in Tetrahydrofuran at 25 °C

compd	reagent	reduction,[a] % 24 h
n-octyl iodide	$H_3B{\cdot}SMe_2$[b]	0
	9-BBN[c]	0
n-octyl bromide	$H_3B{\cdot}SMe_2$	0
	9-BBN	0
n-octyl chloride	$H_3B{\cdot}SMe_2$	0
	9-BBN	0

[a] Monitored and analyzed by GLC. [b] Reaction mixtures were 0.33 M in BMS and 0.25 M in alkyl halide. [c] Reaction mixtures were 0.25 M in 9-BBN and 0.25 M in alkyl halide.

Dialkylboranes. A number of dialkylboranes have been synthesized by the hydroboration of certain hindered olefins (disiamylborane, dicyclohexylborane, diisopinocampheylborane) or appropriately structured dienes (9-borabicyclo[3.3.1]nonane, borepane, etc.).[19] Dialkylboranes are very mild selective reducing agents capable of introducing steric control in the reduction of cyclic ketones.[20] Consequently, it was of interest to test the reactivity of dialkylboranes toward alkyl halides. Of all of the dialkylboranes currently known, 9-borabicyclo[3.3.1]nonane exhibits certain unique advantages (stable solid, relatively insensitive to air, soluble in a number of solvents) over other dialkylboranes.[21] Accordingly, we examined the reaction of 9-BBN (0.25 M) with *n*-octyl halides (0.25 M). The results summarized in Table XI clearly indicate that 9-BBN also is essentially inert toward alkyl iodide, bromide, and chloride under the reaction conditions.

Other Hydride Reagents. In addition to the reagents discussed earlier, other hydride reducing systems have been

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proposed from time to time for the hydrogenolysis of the carbon–halogen bond.

Sodium bis(2-methoxyethoxy)aluminohydride reduces most of the alkyl and some aryl halides in refluxing benzene, toluene, or xylene[22] (eq 11 and 12).

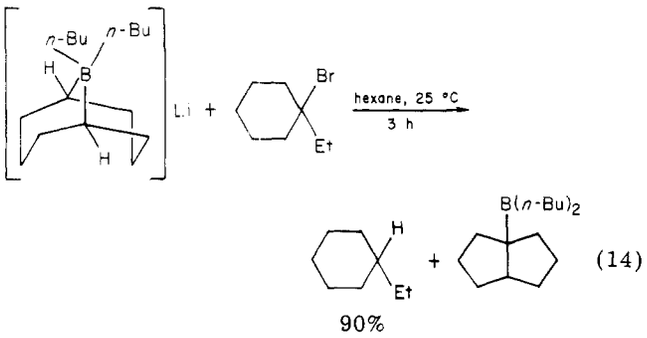
$$CH_3(CH_2)_5Br \xrightarrow[\text{PhH, 74 °C, 4 h}]{Na(CH_3OCH_2CH_2O)_2AlH_2} \underset{40\%}{CH_3(CH_2)_5CH_3} \quad (11)$$

$$C_6H_5I \xrightarrow[\text{PhCH}_3\text{, 110 °C, 1 h}]{Na(CH_3OCH_2CH_2O)_2AlH_2} \underset{45\%}{C_6H_6} \quad (12)$$

A complex copper(I) hydride has been demonstrated to be an efficient reagent for the dehalogenation of alkyl and aryl halides[23] (eq 13).

$$CH_3CHBr(CH_2)_5CH_3 \xrightarrow[\text{THF, 25 °C, 1 h}]{LiCuH_2} CH_3(CH_2)_6CH_3 \quad (13)$$

Recently, lithium di-*n*-butyl-9-borabicyclo[3.3.1]nonane "ate" complex derived from *B*-*n*-Bu-9-BBN and *n*-butyllithium has been found to reduce tertiary halides selectively while primary, secondary and aryl halides are essentially inert[24] (eq 14).



(14)

Unfortunately, time did not permit the inclusion of these reagents in the current study.

Comparison of Various Hydride Reagents. A systematic exploration of the reaction of alkyl halides with representative hydride reducing agents reveals that among the various reagents examined, lithium triethylborohydride and lithium aluminum hydride are the most favorable reagents for the hydrogenolysis of alkyl halides via S_N2 displacements. The dehalogenation reaction appears to be clean, yielding alkane as the only product in very high yields. Of the two, lithium triethylborohydride is significantly more powerful than lithium aluminum hydride and offers exceptional promise for the hydrogenolysis of alkyl iodide, bromide, and chloride under relatively mild conditions.

Lithium aluminum hydride reduces iodides and bromides rapidly at room temperature; the reduction of alkyl chlorides is relatively slow. Introduction of alkoxy substituents in lithium aluminum hydride significantly alters the reactivity toward the halides. Thus, lithium trimethoxyaluminohydride reacts with alkyl iodides with exceptional ease, far faster than with bromides and chlorides. This might be useful for selective deiodination in the presence of other halogens. Lithium tri-*tert*-butoxyaluminohydride is an exceptionally mild reducing agent capable of reducing only aldehydes, ketones, acid chlorides (to aldehydes), and phenolic esters (to aldehydes). The reagent is essentially inert toward alkyl bromides and chloride; alkyl iodides are reduced sluggishly. Accordingly, it should be possible to carry out such selective reductions in the presence of halogen substituents.

Sodium borohydride in diglyme should provide a versatile method for the hydrodehalogenation of primary iodine and bromine and certain benzylic halogens in the presence of other functional groups, for example, carboxylic acid, ester, the nitro group, etc. Further, sodium borohydride reduction of primary and secondary halides can be carried out in dipolar aprotic solvents, such as dimethyl sulfoxide and sulfones.[25] Similarly, lithium borohydride in THF reduces primary iodides and bromides sluggishly; it is essentially inert toward alkyl chlorides under the reaction conditions.

Replacement of three of the four hydrogens in tetrahydroborate by alkyl groups dramatically enhances the hydride-transfer ability of the borohydride anion. Thus, lithium triethylborohydride reduces alkyl iodides, bromides, and chlorides with exceptional ease under mild conditions.

Aluminum hydride, an acidic reducing agent, exhibits far lower reactivity than lithium aluminum hydride (basic reagent) toward alkyl halides. Consequently, it is possible to reduce selectively more reactive functional groups without concurrent attack on reactive halogen substituents present in the same molecule, permitting the selective reduction of compounds such as halogen-substituted carboxylic acids, esters, amides, and nitriles. This possibility has been explored and indeed aluminum hydride is far superior to lithium aluminum hydride for such reductions.[26] Borane–methyl sulfide and other alkyl-substituted boranes, such as 9-BBN, are essentially inert toward alkyl iodides, bromides, and chlorides. Accordingly, these are excellent reagents for the selective reduction of carboxylic acids,[27] amides,[28] aldehydes and ketones,[29] and enones[30] and for the selective hydroboration of olefins[31] and acetylenes[32] in the presence of halogen substituents.

Conclusion

The reaction of alkyl halides with representative metal hydrides and complex metal hydrides was explored. Among the various reducing agents examined, lithium triethylborohydride and lithium aluminum hydride appear to be the reagents of choice for the hydrogenolysis of alkyl iodides, bromides, and chlorides. The results reveal that for such reductions, lithium triethylborohydride is far more effective and powerful than is lithium aluminum hydride. Lithium tri-*tert*-butoxyaluminohydride, lithium borohydride, and sodium borohydride should be useful for the reduction of alkyl iodides and bromides in the presence of other functional groups not affected by these reagents. Borane and dialkylboranes are essentially inert toward alkyl halides; consequently, this renders possible the se-

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lective reduction of many other reducible functional groups in the presence of halogen substituents. The present study has led not only to the identification of the best hydride reagents for the hydrodehalogenation of alkyl halides but also to an overall understanding of the reactivity of various reagents toward alkyl halides.

Experimental Section

Materials. Reaction flasks were thoroughly dried in a drying oven overnight and cooled down under a stream of dry nitrogen just prior to use. Tetrahydrofuran was dried and distilled over lithium aluminum hydride, bp 65 °C. Diglyme was dried over lithium aluminum hydride and vacuum distilled, bp 63 °C (14 mm). Solvents were stored under dry nitrogen. Reagent grade methanol (J. T. Baker Chemical Co.) was used without any additional purification. *tert*-Butyl alcohol was distilled over calcium hydride. Lithium aluminum hydride, lithium borohydride, sodium borohydride, and lithium hydride were from Ventron Corp. Borane–methyl sulfide and 9-BBN were from Aldrich Chemical Co. Sodium aluminum hydride was from Ethyl Corp. A standard solution of lithium tri-*tert*-butoxyaluminohydride solution in THF was synthesized from lithium aluminum hydride and 3 mol of *tert*-butyl alcohol.[9] Most of the hydrocarbons and olefins used as authentic samples were from Phillips 66 Petroleum Co. and were >99 mol % pure and free of any isomers. Alkyl halides utilized in this study were commercial products of the highest purity available. Triethylborane used was from Callery Chemical Co.

GLC Analyses. GLC analyses were carried out on a Varian 1200 series temperature-programmed gas chromatograph, equipped with a flame ionization detector with controllable injector and detector temperatures. All of the yields were determined by utilizing a suitable internal standard and authentic synthetic mixtures. All of the yields reported are actual rather than normalized. The following columns were used: column A, 5% SE-30 on Aeropak 30, 12 ft × 0.125 in.; column B, 5% FFAP on Aeropak 30, 6 ft × 0.125 in.; column C, 30% adiponitrile on firebrick, 3 ft × 0.125 in.

Preparation of Lithium Aluminum Hydride Solution in Tetrahydrofuran and Standardization. In a typical experiment, 22 g of lithium aluminum hydride was added to 600 mL of freshly distilled THF and stirred well at 25 °C for 3 h under dry nitrogen. The resulting solution was filtered under a slight positive nitrogen pressure through a 2-in. bed of tightly packed Celite, prepared on a sintered-glass disk, previously sealed into a large cylinder for enclosing the solution. The clear filtered solution was stored in a 500-mL flask with a rubber septum syringe inlet. The solution was standardized by removing a known aliquot with a hypodermic syringe, injecting into a glycerine–water–THF (1:1:1) mixture, and measuring the hydrogen evolved. The concentration was found to be 1.17 M in $LiAlH_4$.

Preparation of Sodium Aluminum Hydride Solution in Tetrahydrofuran. Sodium aluminum hydride (20 g) was added to 330 mL of THF, and the resulting mixture was stirred vigorously for 6 h under dry nitrogen. The resulting solution was filtered to give crystal clear solutions of sodium aluminum hydride in THF, whose concentration was found to be 1.05 M.

Preparation of Aluminum Hydride Solution in Tetrahydrofuran. Standard solutions of aluminum hydride were prepared by adding the theoretical quantity of 100% sulfuric acid to the standardized solution of lithium aluminum hydride. The following is representative of the procedure used.

A 250-mL flask with a side arm was fitted with a rubber syringe cap and a magnetic stirring bar, and the whole was connected to a gas meter via the reflux condenser and a dry ice trap. The flask was cooled under a stream of nitrogen and immersed in a water bath (ca. 25 °C). By means of hypodermic syringes, 63.5 mL of 1.5 M lithium aluminum hydride (80 mmol) and 53.5 mL of THF were introduced into the flask. A 3.94-g (2.14 mL) aliquot of 100% sulfuric acid (specific gravity 1.839) (40 mmol) was added, with vigorous stirring, drop by drop by means of a syringe to this solution. There was evolved 79 mmol of hydrogen. After 2 h of stirring, the solution was allowed to stand overnight to permit the lithium sulfate to settle. The clear supernatant solution was analyzed for hydride by hydrolysis. The concentration was found to be 0.71 M in AlH_3 (98% yield), whereas 0.73 M was expected on the basis of the stoichiometric equation.

This clear solution of aluminum hydride was used within 2 days after its preparation, since after 72 h, it slowly loses hydride activity at room temperature.

Preparation of Sodium Borohydride Solution in Diglyme. Sodium borohydride (6 g, 158 mmol) was added to 170 mL of diglyme, and the mixture was stirred under a static atmosphere of nitrogen. After 3 h, the stirring was stopped and the slight excess of sodium borohydride was allowed to settle. The clear solution was standardized by hydrolyzing 1-mL aliquots with glycerine, THF, and an aqueous hydrochloric acid mixture and measuring the hydrogen evolved. The concentration was found to be 0.83 M in $NaBH_4$.

Preparation of Lithium Triethylborohydride Solution in Tetrahydrofuran. A 500-mL, oven-dried flask, equipped with a side arm, fitted with a Teflon stopcock and a silicone rubber stopple, a magnetic stirring bar, and a reflux condenser connected to a mercury bubbler, was cooled down to room temperature under a dry stream of nitrogen. In the flask was placed 4 g (0.5 mol) of finely divided lithium hydride and 215 mL of THF. Then 35 mL (0.25 mol) of triethylborane was introduced, and the resulting mixture was vigorously stirred under nitrogen for 24 h at 25 °C. The resulting solution was filtered under a slight positive pressure of nitrogen to remove excess lithium hydride, resulting in a crystal clear solution of lithium triethylborohydride in THF. The solution was stored under dry nitrogen in a 500-mL flask with a side arm, closed with a rubber stopple for removing aliquots. The solution was standardized by removing a known aliquot with a hypodermic syringe, hydrolyzing with a THF–water–glycerine mixture (1:1:1), and measuring the hydrogen evolved. The concentration was found to be 1.0 M in $LiEt_3BH$ (100% yield) which is also the calculated concentration on the basis of the stoichiometric equation

$$\underset{0.5\ \text{mol}}{LiH} + \underset{0.25\ \text{mol}}{Et_3B} \rightarrow \underset{0.25\ \text{mol}}{LiEt_3BH}$$

The THF solution of lithium triethylborohydride is characterized by a strong broad absorption in the infrared at 4.83 μm (B–H). Maintained under nitrogen, these solutions are stable for long periods of time.

Preparation of 9-BBN Solution in THF. A standard solution of a 0.54 M solution of 9-BBN in tetrahydrofuran was prepared by dissolving the required quantity of the commercial solid in THF; standardization was accomplished by hydrolyzing with a MeOH–THF mixture and measuring the hydrogen evolved.

Reduction of *n*-Octyl Iodide with Lithium Aluminum Hydride. A clean 100-mL, oven-dried, flask equipped with a side arm, fitted with a silicone rubber stopple, a magnetic stirring bar, and a reflux condenser connected to a mercury bubbler, was cooled down under a stream of dry nitrogen. The reaction flask was immersed in a water bath (ca. 25 °C). Then 5 mL of tetrahydrofuran was injected into the reaction flask by a hypodermic syringe, followed by 5 mL (5 mmol) of a 1.0 M solution of lithium aluminum hydride and 5 mmol of *n*-nonane (in 5 mL of THF) to serve as the internal standard. Finally, 5 mmol (5 mL in THF) of *n*-octyl iodide was injected. The reaction mixture was now 0.25 M in both $LiAlH_4$ and *n*-octyl iodide. The mixture was stirred well. After 15 min, 1 mL of the reaction mixture was withdrawn by a hypodermic syringe, quenched with water, extracted with ether, and analyzed by GLC on column A. This revealed the presence of 99% *n*-octane and 1% *n*-octyl iodide. Analysis on column C revealed the complete absence of 1-octene.

Reduction of *n*-Butyl Bromide with Aluminum Hydride. A clean 100-mL flask with a side arm, dried in an oven, was fitted with a magnetic stirring bar and a reflux condenser, and the whole was connected to an inverted gas buret via a dry ice vapor trap. The side arm of the flask was fitted with a silicone rubber stopple. The flask was cooled down in a dry nitrogen atmosphere. The reaction flask was immersed in a water bath, maintained at room temperature (ca. 25 °C). Tetrahydrofuran (11.2 mL) was introduced into the reaction flask, followed by 18.8 mL (13.3 mmol) of a 0.71 M aluminum hydride solution. Finally, 10 mL (10 mmol) of a 1.0 M solution of *n*-butyl bromide in THF was introduced. The reaction mixture was now 0.33 M in AlH_3 and 0.25 M in alkyl

halide. The mixture was stirred vigorously and the hydrogen evolved was measured. Simultaneously, a blank was run in which, instead of 10 mL of alkyl bromide solution, there was added 10 mL of tetrahydrofuran, all other conditions being the same.

The rate of reduction was monitored by the analysis for residual "hydride" in the reaction mixture and the blank at appropriate intervals of time. The reaction proceeded only up to 59% in 48 h. There was no appreciable amount of hydrogen evolution, indicating the absence of any elimination.

Reaction of *n*-Octyl Bromide with Lithium Trimethoxyaluminohydride in THF. In all of these experiments, lithium trimethoxyaluminohydride was synthesized in situ just prior to use by adding 3 mol of anhydrous methanol to 1 mol of lithium aluminum hydride solution in THF.

A clean 100-mL oven-dried flask, equipped with a side arm, fitted with a silicone rubber stopple, a magnetic stirring bar, and a reflux condenser connected to a mercury bubbler, was cooled down under a stream of nitrogen. The reaction flask was immersed in a water bath at room temperature (ca. 25 °C). Then 8 mL (8 mmol) of a 1.0 M solution of lithium aluminum hydride was introduced into the reaction flask. This was followed by dropwise addition of 8 mL (24 mmol) of a 3.0 M solution of methanol over a period of 15 min. There was evolved 24 mmol of hydrogen. The resulting solution was stirred for an additional period of 15 min. Finally, 2 mL (2 mmol) of a 1.0 M solution of *n*-nonane (internal standard) followed by 2 mL (2 mmol) of a 1.0 M solution of *n*-octyl bromide was injected. The mixture was vigorously stirred. The mixture was now 0.4 M in $Li(OCH_3)_3AlH$ and 0.1 M in alkyl bromide.

The reaction was monitored by GLC on column A for the formation of *n*-octane and the disappearance of *n*-octyl bromide with time. At 6 h, the reaction was essentially complete, as revealed by the presence of 99% *n*-octane and the absence of *n*-octyl bromide on the gas chromatograph.

Reaction of Sodium Borohydride with *n*-Octyl Iodide in Anhydrous Diglyme. The experimental setup was the same as in the previous experiment. Diglyme (6.5 mL) was introduced into the reaction flask followed by 6 mL (5 mmol) of a 0.83 M sodium borohydride solution in diglyme. Finally, 2.5 mL (5 mmol) of a 2.0 M *n*-nonane solution followed by 5 mL (5 mmol) of an *n*-octyl iodide solution in diglyme was added. The mixture was stirred vigorously. The solution was now 0.25 M in both $NaBH_4$ and alkyl iodide.

At appropriate intervals of time, 1 mL of the reaction mixture was withdrawn by a syringe, quenched with dilute HCl, extracted with ether, and analyzed by GLC on column A for *n*-octane and *n*-octyl iodide. At 0.5 h, 50% of the reaction was essentially complete. At 24 h, reduction had proceeded only to the extent of 89%.

Reaction of Sodium Borohydride with *n*-Octyl Iodide in the Presence of 1-Pentene in Anhydrous Diglyme. A typical reaction setup was assembled as in the case of the previous experiments. Into the reaction flask maintained at ca. 25 °C was injected 4.4 mL of diglyme followed by 6 mL (5 mmol) of a 0.83 M $NaBH_4$ solution, 2.5 mL (5 mmol) of a 2.0 M solution of *n*-nonane, 2.2 mL (20 mmol) of 1-pentene (freshly distilled over $LiAlH_4$), and finally 5 mL (5 mmol) of a 1.0 M solution of *n*-octyl iodide. The reaction mixture was now 0.25 M, in both $NaBH_4$ and *n*-octyl iodide and 1.0 M in 1-pentene. The mixture was vigorously stirred. After 1 h, the reaction flask was cooled in an ice bath at 0 °C, and 6 mL of a 3.0 M NaOH solution was added, followed by dropwise addition of 6 mL of 30% H_2O_2. The mixture was stirred at 50–55 °C for 1 h and then cooled to room temperature. Ether (20 mL) was added and the aqueous layer was saturated with anhydrous K_2CO_3. The dry ethereal layer upon gas chromatographic examination on column B indicated the presence of 3.87 mmol (77%) of *n*-octane and 12.03 mmol of pentanols (the ratio of 1-pentanol to 2-pentanol was 96:4).

Another run of this reaction was conducted under identical conditions except that it was allowed to run for 3 h. Then after the usual oxidation and workup, gas chromatographic examination revealed the presence of 4.5 mmol (90%) of *n*-octane and 13.4 mmol of pentanols.

In both of these experiments, no *n*-octanol was detected on GLC, indicating the absence of the elimination pathway.

Reduction of *n*-Octyl Iodide with Lithium Triethylborohydride. The apparatus was the same as in the previous experiments. Into the reaction flask maintained at 25 °C were injected 5 mL of THF and 5 mL of a 1.0 M solution in THF of lithium triethylborohydride (5 mmol), followed by 5 mL of a 1.0 M solution of *n*-nonane in THF to serve as an internal standard. Finally, 5 mL of a 1.0 M solution in THF of *n*-octyl iodide (5 mmol) was introduced. The reaction mixture was stirred vigorously. After 5 min, 1 mL of the reaction mixture was withdrawn by means of a syringe, quenched with water, extracted with ether, and analyzed by GLC on column A. This revealed the presence of 97% *n*-octane. After 15 min, a 100% yield of *n*-octane was realized. Analysis on column C revealed the complete absence of 1-octene.

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Registry No. Octyl iodide, 629-27-6; octyl bromide, 111-83-1; octyl chloride, 111-85-3; cyclohexyl iodide, 626-62-0; cyclohexyl bromide, 108-85-0; cyclohexyl chloride, 542-18-7; benzyl bromide, 100-39-0; 2-bromooctane, 557-35-7; 3-bromopropene, 106-95-6; butyl bromide, 109-65-9; butyl chloride, 109-69-3; isobutyl bromide, 78-77-3; *sec*-butyl bromide, 78-76-2; cyclopentyl bromide, 137-43-9; $LiAlH_4$, 16853-85-3; $NaAlH_4$, 13770-96-2; $Li(CH_3O)_3AlH$, 12076-93-6; $Li((CH_3)_3CO)_3AlH$, 17476-04-9; $NaBH_4$, 16940-66-2; $LiBH_4$, 16949-15-8; $LiEt_3BH$, 22560-16-3; AlH_3, 7784-21-6; $H_3B{\cdot}SMe_2$, 13292-87-0; 9-BBN, 280-64-8.

Annelations with Tetrachlorothiophene 1,1-Dioxide

Maynard S. Raasch

Central Research and Development Department,[1] Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898

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Tetrachlorothiophene 1,1-dioxide is a reactive, cheletropic Diels–Alder reagent. It has been used to annelate, with loss of sulfur dioxide, a large variety of olefinic compounds to form 1,2,3,4-tetrachloro-1,3-cyclohexadiene derivatives. Dehydrochlorination of these forms 1,2,4-trichloro aromatic compounds. Both double bonds in thiophene and *N*-methylpyrrole are annelated. Addition of tetrachlorothiophene dioxide to acyclic 1,5-dienes, which may contain a heteroatom, provides a facile synthesis of tetrachloroisotwistenes (**51**) and heteroisotwistenes (**56**) by a double Diels–Alder reaction. Acyclic 1,6-dienes lead to tetrachlorohomoisotwistene (**59**) and heterohomoisotwistenes (**61**). By use of 1,5-cyclooctadiene, *sym*-dibenzocyclooctatetraene, and 1,5-cyclononadiene, the more complex carbocycles **62**, **65**, and **66** are generated. Tetrabromothiophene dioxide reacts like the tetrachloro compound.

Although many thiophene 1,1-dioxides are known, the preparation of tetrachlorothiophene dioxide has not been reported, though there are unexemplified patent disclosures of it.[2] The compound appeared to offer high re-

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