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Selective Reductions. 28. The Fast Reaction of Lithium Aluminum Hydride with Alkyl Halides in Tetrahydrofuran. A Reappraisal of the Scope of the Reaction

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Clear solutions of lithium aluminum hydride in tetrahydrofuran reduce organic halides of different structural characteristics rapidly and quantitatively, commonly at 25 °C, to the corresponding hydrocarbons. The rates of reduction of organic halides observed in the present study are far faster than those realized by previous workers employing slurries of lithium aluminum hydride. The reaction exhibits the typical characteristics of a S_N2 substitution reaction, as revealed by the approximate rate studies with a representative series of alkyl halides: (I > Br > Cl; benzylic $\simeq$ allylic > primary > secondary > tertiary; *n*-butyl > isobutyl $\gg$ neopentyl; cyclopentyl > 2-octyl > cycloheptyl > cyclooctyl > cyclohexyl). Allyl and benzyl bromides are reduced instantaneously. *n*-Alkyl iodides and bromides are reduced rapidly and quantitatively in 15–30 min at 25 °C. *n*-Alkyl chlorides and secondary alkyl bromides, including the highly resistant cyclohexyl bromide, underwent facile reduction to completion in refluxing THF. Surprisingly, the organic halides that are resistant to normal nucleophilic substitution reactions—bromobenzene, β-bromostyrene, and *tert*-butyl bromide—all exhibit considerable reactivity toward lithium aluminum hydride. Thus, the present study has led to a better understanding of the scope and applicability of lithium aluminum hydride for hydrodehalogenation of alkyl halides.

In 1948 Johnson et al. reported the successful hydrogenolysis of alkyl halides by lithium aluminum hydride (two examples) and by heterogeneous suspensions of lithium hydride catalyzed by lithium aluminum hydride (10 examples).[2] Since that time, the hydrogenolysis of carbon–halogen bonds has become an important and frequently encountered transformation in organic synthesis. A number of hydride reducing agents or systems have evolved for this synthetic conversion.[3,4] Recently, we explored the reactivity of a number of complex metal hydrides and metal hydrides for the hydrodehalogenation of alkyl halides in order to evaluate and identify the more promising reagents for the hydrogenolysis of alkyl halogen bonds.[5] This study identified lithium triethylborohydride[4k] and lithium aluminum hydride to be the reagents of choice for rapid reduction of alkyl halides. It also revealed that the rates of reduction of alkyl halides with clear solutions of lithium aluminum hydride in tetrahydrofuran (THF) were far faster than those realized by earlier workers.[4a,b] Moreover, the reactions proceed with production of the corresponding alkane in essentially quantitative yield, free from significant side products (e.g., olefin produced via elimination).

This was surprising in view of the commonly accepted position that the reaction of alkyl halides with lithium aluminum hydride is somewhat sluggish. Such a misconception may be attributed to two possible reasons: (1) some of the earlier work in this direction were carried out on the assumption that all of the four Al–H bonds of lithium aluminum hydride have equal reducing capability, and (2) essentially all of the earlier work had employed slurries of lithium aluminum hydride in ethereal solvents rather than clear solutions. However, a few reports describing the facile reductive dehalogenation of vinyl, tertiary bridgehead, and cyclopropyl halides have appeared in the literature,[4c,d] emphasizing the need for a reappraisal of the scope of such reductions by lithium aluminum hydride.

In view of the dramatic differences between the rates of reduction of alkyl halides reported in the earlier studies and those realized in our exploratory study, we undertook to reexamine the scope and applicability of lithium aluminum hydride for the hydrodehalogenation of alkyl halides in detail. The results of this investigation are presented in this paper.

Results and Discussion

A representative series of organic halides with different structural features was selected to evaluate the effects of the leaving group and such structural features as branching at the α-carbon, branching at the β-carbon, vinylic, aryl, and benzylic moieties, ring size, bicyclic skeletons, etc.

In all experiments, crystal-clear solutions of lithium aluminum hydride in THF were employed. Such a solution was prepared by stirring commercial lithium aluminum hydride in freshly distilled THF under a nitrogen atmosphere followed by filtration to remove undissolved lithium aluminum hydride and insoluble impurities.

Procedure for Rate and Product Studies. The general procedure used for the rate studies was to add 10 mmol of organic halide to 10 mmol of lithium aluminum hydride solution in sufficient THF to give 40 mL of solution. This makes the reaction mixture 0.25 M each in organic halide and $LiAlH_4$. The solutions were maintained at constant temperature (ca. 25 °C). The reaction was monitored by removing a known aliquot at appropriate intervals of time and analyzing for the residual "hydride" by hydrolysis. In some cases reactions were also monitored by GLC by analyzing for the appearance of alkane and the

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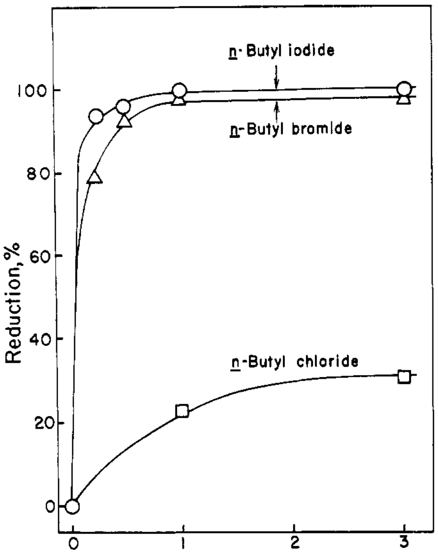

Figure 1. Rates of reduction of the *n*-butyl halides with lithium aluminum hydride in tetrahydrofuran at 25 °C (both reagents 0.25 M).

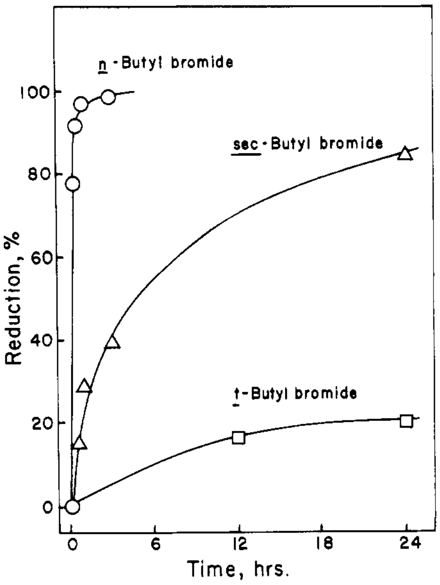

Figure 2. Rates of reduction of representative primary, secondary, and tertiary alkyl bromides with lithium aluminum hydride in tetrahydrofuran at 25 °C (both reagents 0.25 M).

disappearance of organic halide, using a suitable internal standard.

In order to establish the reaction products, we carried out individual reactions in the presence of a suitable internal standard. A number of alkyl halides underwent rapid reduction to completion, even under standard conditions (25 °C, 0.25 M in $LiAlH_4$ and in RX). Then the excess hydride was destroyed with water and the dry ethereal layer was subjected to GLC analysis for the formation of alkane and alkene and the presence of residual halide. In some cases, either the temperature alone or both the temperature and the concentration of $LiAlH_4$ were increased to decrease the reaction time.

Effect of Structure of the Alkyl Halide on Reactivity. Rates of reduction observed for *n*-butyl halides (Figure 1) and cyclohexyl halides clearly reveal that the rate of the reaction markedly decreases from the iodide to the bromide to the chloride (I > Br > Cl). Reactivity toward $LiAlH_4$ decreases from *n*-butyl bromide to *sec*-butyl bromide to *tert*-butyl bromide (Figure 2). Introduction of β-methyl substituents diminishes the reactivity of the halide toward $LiAlH_4$ (*n*-butyl bromide > isobutyl bromide ≫ neopentyl bromide; Figure 3). Interestingly, neopentyl bromide underwent reduction at a rate even slower than that of *tert*-butyl bromide.

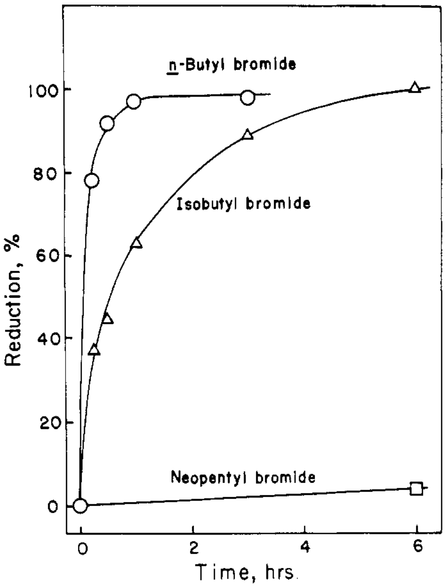

Figure 3. Rates of reduction of representative *n*-, iso-, and neoalkyl bromides with lithium aluminum hydride in tetrahydrofuran at 25 °C (both reagents 0.25 M).

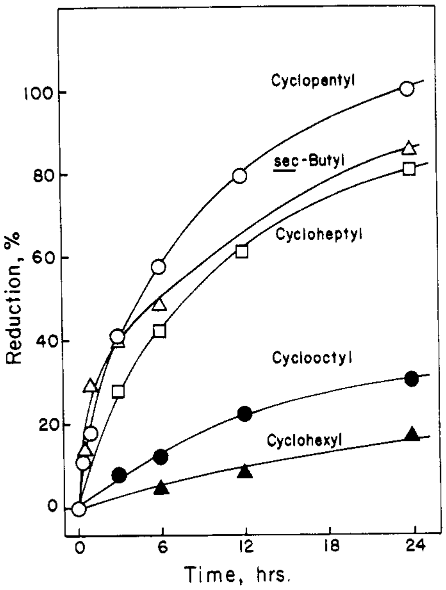

Figure 4. Rates of reduction of representative cycloalkyl bromides with lithium aluminum hydride in tetrahydrofuran at 25 °C (both reagents 0.25 M).

With cycloalkyl halide, the ring size has a pronounced influence on the rate of reduction. We examined a representative series of cycloalkyl bromides toward $LiAlH_4$. The reactivity follows the order: cyclopentyl > 2-octyl > cycloheptyl > cyclooctyl > cyclohexyl (Figure 4), exactly identical with the reactivity pattern observed in the S_N2 halide exchanges of cycloalkyl halides ($RBr + I^- \rightarrow RI + Br^-$).[6,7] Bicyclic halides, such as *exo*- and *endo*-2-bromonorbornane, are highly resistant to $LiAlH_4$ and react sluggishly.[8]

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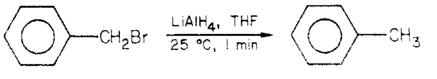
Allyl and benzyl bromides are reduced instantaneously by $LiAlH_4$. Surprisingly, vinyl bromide, β-bromostyrene and aryl halides (bromobenzene and 1-bromonaphthalene) exhibit considerable reactivity toward $LiAlH_4$. Indeed, this observation stimulated an extensive exploration of the reaction of aryl halides with $LiAlH_4$.[9]

Applicability and Scope. The rapid rate of reduction observed with most of the alkyl halides toward clear THF solutions of $LiAlH_4$ should provide a convenient synthetic procedure for hydrodehalogenation of alkyl halides under mild conditions. In order to establish the synthetic applicability, we carried out product studies for the reduction of representative alkyl halides. The results indicate that the reaction is much faster than previously realized and clean, resulting in essentially quantitative yields of the alkane as the single product. In all cases, no olefin or only traces of olefin formed as a side product from elimination.

In the present study, using clear solution of $LiAlH_4$ in THF, benzyl bromide was reduced to toluene in quantitative yield (1 min, 25 °C; eq 1). It was reported earlier[4b] that the reaction affords toluene in 78% yield in 2 h (35 °C, THF).



(1)

100%

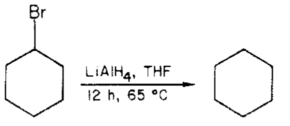
Likewise, *n*-octyl iodide and *n*-octyl bromide were reduced quantitatively to *n*-octane in 0.25 and 0.5 h, respectively, at 25 °C (eq 2). Trevoy and Brown[4b] utilized 10 h in refluxing THF (65 °C) to reduce primary bromides, such as 1-bromodecane (70% yield).

$$CH_3(CH_2)_6CH_2Br \xrightarrow[30\text{ min},\ 25\ ^\circ C]{LiAlH_4,\ THF} \underset{96\%}{CH_3(CH_2)_6CH_3} \qquad (2)$$

n-Octyl chloride and 2-bromooctane were rapidly reduced to *n*-octane in over 90% yield in refluxing THF (4 h); even at 25 °C, the hydrogenolysis proceeds to the extent of 70% in 24 h. Earlier workers claimed that *n*-butyl chloride does not react at 25 °C and 2-bromooctane is reported to be reduced in 30% yield in THF after 10-h reflux at 65 °C.[4a]

Cyclopentyl bromide and cycloheptyl bromide were converted to their corresponding cycloalkanes in over 90% yield in 24 h at 25 °C.

Cyclohexyl iodide was converted to cyclohexane in 93% yield in refluxing THF in 6 h. Even cyclohexyl bromide was converted to cyclohexane in 96% yield (1.0 M $LiAlH_4$, 12 h, 65 °C; eq 3).



(3)

96%

Surprisingly, unactivated aryl halides, such as bromobenzene, which are usually resistant to nucleophilic substitutions, underwent smooth reduction with $LiAlH_4$ in refluxing THF.[4k] Similarly, $LiAlH_4$ has been reported to reduce smoothly tertiary bridgehead, cyclopropyl, and vinyl halides, all structures which are normally resistant to nucleophilic substitution, to the corresponding hydrocarbons.[4c]

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

compound	% reduction 0.25 h	0.5 h	1.0 h	3.0 h	6.0 h	12.0 h	24.0 h
n-butyl iodide	94	96	100	100			
n-butyl bromide	78	92	97	98			
n-butyl chloride	16	23	23	21		62	82
sec-butyl bromide	10	14	29	39	47		84
tert-butyl bromide	2	6	10	14		16	20
isobutyl bromide	37	45	63	89	100	100	
1-bromo-2-methylpentane	24	38	57	87	100		
neopentyl bromide	0	0	0	0	4	4	8
β-bromostyrene	0	2	2	6	14		22
bromobenzene			6	10	14	20	28
1-bromonaphthalene		2	4	10	18	24	34
benzyl bromide	97	100	100				
allyl bromide	100	100	100				
cyclopentyl bromide	8	11	18	41	57	79	100
cyclohexyl bromide			0	4	4	8	16
cycloheptyl bromide		8	14	28	42	61	80
cyclooctyl bromide		4	8	8	12	22	30
cyclohexyl iodide		2	7	20	30	49	74
cyclohexyl chloride				2	2	4	6
exo-2-bromonorbornane				6	10	12	16
endo-2-bromonorbornane				4	4	8	12

[a] In all cases the solutions were 0.25 M in alkyl halide and $LiAlH_4$. [b] Reactions were followed by the decrease in active hydride concentration. In all cases only a negligible amount of hydrogen was evolved from the reaction mixture.

How could we account for the enormous difference observed in the rates of reduction of alkyl halides in the present study and those reported by earlier workers? The clear solution of $LiAlH_4$ in THF exists as solvent separated ion pairs, which enhance the nucleophilicity of the tetrahydroaluminate.[10] The earlier workers had used slurries of $LiAlH_4$ rather than clear solutions. Consequently, the insoluble impurities might have coated the undissolved $LiAlH_4$ and hindered both its solution and its reaction. Similar differences have been noted in the reduction of aryl halides with $LiAlH_4$. Further, a recent study has demonstrated the importance of solvents on the rate of reduction of alkyl halides with $LiAlH_4$.[11] Thus, changing the solvent from ether to THF dramatically enhanced the reactivity of $LiAlH_4$ toward halides.

Another factor that is responsible for the vast difference in the reaction rates between our studies and the previous workers is the stoichiometry. Earlier studies were con-

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(11) Krishnamurthy, S. *J. Org. Chem.* **1980**, *45*, 2550.

Table II. Products of Reduction of Alkyl Halides with Lithium Aluminum Hydride in Tetrahydrofuran[c]

compound	time, h	temp, °C	reaction products	% yield[b,c]
benzyl bromide	0.017	25	toluene	100
1-iodooctane	0.25	25	*n*-octane	94
1-bromooctane	0.5	25	*n*-octane	96
			1-bromooctane	<2
1-chlorooctane	24	25	*n*-octane	73
1-chlorooctane	4	65	*n*-octane	94
			1-chlorooctane	7
2-bromooctane	24	25	*n*-octane	70
		65	*n*-octane	97
			2-bromooctane	<2
1-bromo-2-methylpentane	6	25	2-methylpentane	92
cyclopentyl bromide	24	25	cyclopentane	91
cyclohexyl bromide	24	25	cyclohexane	5
			cyclohexyl bromide	94
	12[d]	65	cyclohexane	96
cyclohexyl iodide	6	65	cyclohexane	93
			cyclohexene	<1
			cyclohexyl iodide	<1
cyclohexyl chloride	24	25	cyclohexane	trace
cycloheptyl bromide[e]	24	25	cycloheptane	94
			cycloheptyl bromide	4
neopentyl bromide	24	25	neopentyl bromide	93
exo-2-bromonorbornane	24	25	norbornane	3
β-bromostyrene	24	25	styrene	22
bromobenzene	24	25	benzene	20
			bromobenzene	79

[a] Unless otherwise stated, the concentrations of the alkyl halide and $LiAlH_4$ were 0.25 M. [b] All the yields reported were determined by GLC, using a suitable internal standard and authentic synthetic mixtures. [c] Except where indicated, no olefins were detected on gas chromatogram. [d] 1.0 M $LiAlH_4$. [e] 0.5 M in $LiAlH_4$.

ducted with the theoretical quantity of $LiAlH_4$, assuming the following stoichiometry (eq 4). In the present study,

$$LiAlH_4 + 4RX \rightarrow 4RH + LiAlX_4 \qquad (4)$$

1 equiv of $LiAlH_4$ was used for every RX (eq 5). Further,

$$LiAlH_4 + RX \rightarrow RH + AlH_3 + LiX \qquad (5)$$

our exploratory studies on aluminum hydride[12] reductions indicated the inertness of this reagent to alkyl halides, clearly pointing to the importance of employing *at least* 1 molar equiv of $LiAlH_4$ per RX for rapid hydrodehalogenation.

Conclusions

The rates of reduction of organic halides realized in this present study are far faster than those realized by earlier workers. The production of the corresponding hydrocarbon is clean and quantitative. For the hydrogenolysis of primary alkyl iodides, bromides, chlorides, and secondary alkyl bromides (both acyclic and cyclic), clear solutions of $LiAlH_4$ in THF offers promise where this transformation is required in synthetic operations.

Experimental Section

Materials. Reaction flasks were dried thoroughly in an oven overnight and cooled under a stream of nitrogen just prior to use. Tetrahydrofuran, bp 65 °C, was distilled from a slight excess of lithium aluminum hydride and stored under nitrogen. Lithium aluminum hydride was from the Ventron Corp. Most of the hydrocarbons and olefins were from the Phillips Petroleum Co., >99 mol % pure, and free of any isomers. Most of the halides were commercial products of the highest purity available. They were further purified by fractional distillation, when necessary. Alkyl iodides were generally freshly distilled before use. In all cases, the physical constants agreed satisfactorily with constants in the literature. In some cases, the compounds were synthesized by employing standard literature procedures. Commercial neopentyl bromide was found to be highly impure. The GLC analysis of the sample on a 5% SE-30 column, 6 ft × 0.125 in., and on a 5% Carbowax 20M column, 6 ft × 0.125 in., indicated the presence of at least five components (possibly all structural isomers). Pure neopentyl bromide was obtained from the mixture by preparative GLC on 10% Carbowax 20M column, 12 ft × 0.5 in.; $n^{20}\mathrm{D}$ 1.4375 [lit.[30] $n^{20}\mathrm{D}$ 1.4371]. *endo*-Bromonorbornane was provided by Dr. Clinton F. Lane (>99% pure by GLC, $n^{20}\mathrm{D}$ 1.5158). We are indebted to Dr. Lane for supplying us with this material.

GLC Analyses. Gas chromatographic analyses were carried out on a Varian 1200 series temperature-programmed gas chromatograph, equipped with a flame ionization detector, with controllable injection port and detector temperatures. The following columns were used: column A, 5% SE-30 on Aeropak 30, 12 ft × 0.125 in.; column B, 5% Carbowax 20M TPA on Aeropak 30, 12 ft × 0.125 in.; column C, 5% FFAP on Aeropak 30, 6 ft × 0.125 in.; column D, 30% adiponitrile on Firebrick, 3 ft × 0.125 in.

Preparative gas chromatography was carried out on an Aerograph Model A90C instrument.

Preparation of Lithium Aluminum Hydride Solution in Tetrahydrofuran and Standardization. Standard solutions of lithium aluminum hydride in tetrahydrofuran were prepared in the following manner. In a typical experiment, 46 g of lithium aluminum hydride was added to 800 mL of THF (freshly distilled over $LiAlH_4$) and the mixture was stirred vigorously for 3 h at ca. 25 °C under a dry nitrogen atmosphere. 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 1-L flask with a rubber septum syringe inlet. The solution (ca. 1.3 M in lithium aluminum hydride) was standardized by removing a known aliquot with a hypodermic syringe, injecting into a glycerine–water–THF mixture (1:1:1), and measuring the hydrogen evolved.

Prepared in this manner and vigorously protected from atmospheric moisture, these solutions of lithium aluminum hydride appeared to be stable indefinitely.

Procedure for Rate Studies with Lithium Aluminum Hydride. All reductions were carried out under identical conditions under a dry nitrogen atmosphere. Hypodermic syringes were used to transfer solutions.

The reduction of *n*-butyl bromide is representative. A clean, dry 100-mL flask with sidearm and oven-dried was fitted with a magnetic stirring bar and a reflux condenser and connected to

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(12) Yoon, N. M.; Brown, H. C. *J. Am. Chem. Soc.* **1968**, *90*, 2927.

an inverted gas buret via a dry ice vapor trap. The side arm of the flask was fitted with a silicon rubber stopple. The flask was cooled in a dry nitrogen atmosphere. The reaction flask was immersed in a water bath at room temperature (ca. 25 °C). THF (24.7 mL) was introduced into the reaction flask, followed by 5.3 mL (10 mmol) of 1.89 M lithium aluminum hydride solution. Finally, 10 mL (10 mmol) of 1.0 M solution of *n*-butyl bromide in THF was introduced. The reaction mixture was stirred vigorously and the hydrogen evolved was measured. Simultaneously, a blank was run in which, instead of the 10 mL of alkyl bromide solution, 10 mL of tetrahydrofuran was added, all other conditions being the same.

After 15 min, 0.02 mmol of hydrogen had evolved per millimole of the halide. Now a 4.0-mL aliquot of the reaction mixture (1.0 mmol of halide) was removed with a hypodermic syringe and injected into a hydrolyzing mixture of 1:1 glycerine–water in tetrahydrofuran. The hydrogen evolved was measured by a gas buret. Immediately, 4.0 mL of the blank was also taken out and hydrolyzed and the hydrogen evolved was measured. The difference between the blank value and the reaction mixture in millimoles gives the amount of hydride used by 1 mmol of the compound. This revealed that 0.78 mmol of hydride had been utilized by 1 mmol of the halide for reduction in 15 min. In other words, 78% reduction had occurred. The reduction was complete in 1 h.

In general, the hydrogen evolution measurement, and the hydrolysis of the reaction mixture were done at 0.25, 0.5, 1, 3, 6, 12, and 24 h. The results for other alkyl halides are summarized in Table I.

In most cases, the hydrogen evolution from the reaction mixture was negligible, indicating that no β elimination occurred. The hydrogen evolved from the reaction mixture is an approximate measure of β elimination.

Procedure for Product Analysis. For establishment of the reaction products, separate reductions on a 5-mmol scale were carried out. Most of the reductions were carried out under standard conditions. In a few cases, the temperature or both the temperature and the concentration of lithium aluminum hydride had to be increased in order to decrease the reaction time. Analyses were carried out by gas chromatography, using a suitable internal standard. The reaction mixture was analyzed for the alkane, alkene (if any present), and the remaining halide (Table II).

The reductions of *n*-octyl bromide and cyclohexyl iodide are representative.

***n*-Octyl Bromide.** A clean, dry 100-mL flask, oven-dried, equipped with a side arm fitted with a silicon rubber stopple, a magnetic stirring bar, and reflux condenser connected to a mercury bubbler, was cooled with 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 1.0 M solution of lithium aluminum hydride and 5 mmol of *n*-nonane (in 5 mL of THF) as internal standard. Finally, 5 mmol of *n*-octyl bromide (in 5 mL of THF) was injected. The reaction mixture was 0.25 M in both $LiAlH_4$ and bromide. The reaction mixture was stirred well. GLC analysis of the reaction mixture after 5 min indicated that 70% of the reduction had occurred. After 30 min, excess hydride was destroyed by slowly adding a 1:1 mixture of tetrahydrofuran–water dropwise through a hypodermic syringe. Then 3 mL of a saturated solution of sodium potassium tartrate was added to complex aluminum salts. After the mixture was dried, the ethereal layer was subjected to gas chromatographic examination on column A. The analysis revealed the presence of 96% *n*-octane and only 1–2% of *n*-octyl bromide. Analysis of the reaction mixture on column D indicated the absence of any olefin, 1-octene.

Cyclohexyl Iodide. The experimental setup was the same as in the previous experiment. Five milliliters of tetrahydrofuran was introduced into the reaction flask, followed by 5 mL (5 mmol) of 1.0 M lithium aluminum hydride solution and 5 mmol of toluene in 5 mL of THF in the order indicated. The reaction flask was heated carefully to reflux temperature. Then 5 mmol of cyclohexyl iodide (in 5 mL of THF) was introduced by a syringe. The reaction mixture was stirred well with a magnetic stirrer. After 6 h, heating was stopped and the reaction flask was cooled in an ice bath. Excess hydride was destroyed by adding a 1:1 mixture of tetrahydrofuran and water through a syringe. The condenser was washed with THF, and the washings were collected in the reaction flask so as to recover any volatile products from the condenser surface. Aluminum salts were complexed with a saturated solution of sodium potassium tartrate. The THF layer was dried with anhydrous Na_2SO_4. A standard authentic synthetic mixture was also prepared under identical conditions, as follows. Equimolar amounts of cyclohexane, cyclohexene, toluene, and lithium aluminum hydride were heated at reflux for 6 h and worked up exactly as the reaction mixture. Gas chromatographic examination on column C revealed the presence of 93% cyclohexane and less than 1% of cyclohexene and cyclohexyl iodide.

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Registry No. *n*-Butyl iodide, 542-69-8; *n*-butyl bromide, 109-65-9; *n*-butyl chloride, 109-69-3; *sec*-butyl bromide, 78-76-2; *tert*-butyl bromide, 507-19-7; isobutyl bromide, 78-77-3; 1-bromo-2-methylpentane, 25346-33-2; neopentyl bromide, 630-17-1; β-bromostyrene, 103-64-0; bromobenzene, 108-86-1; 1-bromonaphthalene, 90-11-9; benzyl bromide, 100-39-0; allyl bromide, 106-95-6; cyclopentyl bromide, 137-43-9; cyclohexyl bromide, 108-85-0; cycloheptyl bromide, 2404-35-5; cyclooctyl bromide, 1556-09-8; cyclohexyl iodide, 626-62-0; cyclohexyl chloride, 542-18-7; *exo*-2-bromonorbornane, 2534-77-2; *endo*-2-bromonorbornane, 13237-87-1; 1-iodooctane, 629-27-6; 1-bromooctane, 111-83-1; 1-chlorooctane, 111-85-3; 2-bromooctane, 557-35-7; lithium aluminum hydride, 16853-85-3.

Reactions of Spiro[fluorenetriazolines]

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Methylenefluorene **3a** adds regiospecifically to aryl azides **4** to give the corresponding spiro[fluorenetriazolines] **5**, which lead to the ring-enlargement products, 9-(arylamino)phenanthrenes (**9**), by pyrolysis and acid-induced reaction. Benzylidenefluorene **3b** reacts with **4** to give 9-(arylamino)-10-phenylphenanthrenes (**10**), instead of spirotriazolines.

We have previously investigated the reactions of quinone methides with aryl azides and the ring-enlargement reactions of the main products, spiro[anthronetriazolines] **1**, to dibenzo[*a*,*d*]cycloheptenedienes **2**.[1] This work has now

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