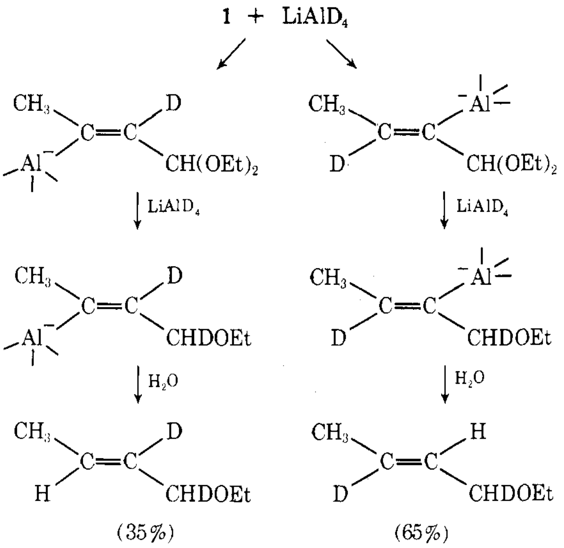
Scheme III



2-butynyl ethyl ether was found from the reaction of 1 with LAH after 24 hr. Therefore it appears that 2-butynyl ethyl ether **3** is too unreactive to be considered an intermediate in the reaction of 1 with LAH.

Based upon the results from the above experiments, the formation of the observed product *trans*-crotyl ethyl ether **4** from the reaction of 2-butynal diethyl acetal **1** with LAH can be explained by a pathway involving the nonregiospecific addition of LAH or LAD to the triple bond followed by hydrogenolysis of the acetal linkage (see Scheme III).

A number of the other experiments were also carried out. 2-Butynal diethyl acetal **1** was smoothly hydrogenolyzed by dichloroalane in ether to 2-butynyl ethyl ether **3**.

trans-Crotyl ethyl ether **4** can be obtained by the dichloroalane hydrogenolysis of *trans*-crotonaldehyde diethyl acetal **5** and is identical with the product of the LAH reduction of 2-butynal diethyl acetal **1**.

It was also determined that crotonaldehyde diethyl acetal **5** is 8 times more reactive than 2-butynal diethyl acetal **1**. Since the carbon–carbon double bond can stabilize a positive charge better than the carbon–carbon triple bond, the preceding result is consistent with the accepted mechanism of acetal hydrogenolysis which predicts the acetal producing the more stable carbonium ion to be more reactive, other factors, such as steric, being the same.[6]

Experimental Section

An F&M Model 700 gas chromatograph was used for glpc analyses. Nmr spectra were obtained with a Varian A-60 spectrometer on $CDCl_3$ solutions with TMS as an internal standard.

2-Butynal diethyl acetal 1 and 2-butynyl ethyl ether 3 were obtained from Farchan Laboratories, Willoughby, Ohio.

Trans-Crotonaldehyde diethyl acetal[9] 5 was prepared from *trans*-cortonaldehyde and triethyl orthoformate by a method previously described.[6]

trans-Crotyl ethyl ether[10] 4 was prepared by the dichloralane hydrogenolysis of *trans*-crotonaldehyde diethyl acetal by a method previously described.[5]

Competitive hydrogenolyses of 1 and 5 with alane were carried out according to the procedure of Davis and Brown.[5]

Reaction of 2-Butynal Diethyl Acetal 1 with $LiAlH_4$. This reaction was carried out by the procedure of Davis and Brown.[5] The reaction was repeated using $LiAlH_4$ but quenched with D_2O. The reaction was also carried out with $LiAlD_4$ and quenched with H_2O. In each there was obtained an 83% yield of *trans*-cortyl ethyl ether 4 and 12% of starting material. In each case the crotyl ethyl ether was subjected to nmr analysis in the following manner. In a glove bag with a nitrogen atmosphere, 63 mg of $Eu(fod)_3$ was weighed into an nmr tube and dissolved in 30 μl of $CDCl_3$. The glpc-purified crotyl ethyl ether was added to the nmr tube and the spectra were run. From the initial amount of 30 μl, the amount of crotyl ethyl ether was successively increased to 40, 50, 60, and finally 85 μl. The nmr spectra were run and analyzed as described.[8]

Registry No.—**1,** 2806-97-5; **4,** 1476-06-8; $LiAlH_4$, 16853,85-3.

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Reduction of Quaternary Ammonium Salts with Lithium Triethylborohydride. A Convenient Method for the Demethylation of Substituted Trimethylammonium Salts

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Lithium triethylborohydride has recently been reported to be a source of remarkably nucleophilic hydride ion as demonstrated by its ability to rapidly reduce organic halides susceptable to S_N2 displacement.[1] In light of the apparent high nucleophilicity of this reagent it seemed that lithium triethylborohydride might serve as a source of hydride ion for the displacement of groups which are much poorer leaving groups than halide ions. We now wish to report that this reagent readily effects the displacement of tertiary amines from quaternary ammonium iodides in THF.[2] Results are shown in Table I.

As can be seen from the results in Table I, aromatic trialkylammonium iodides readily react with lithium triethylborohydride at room temperature to give the tertiary amine resulting from the displacement on an alkyl group by hydride ion. It is also evident that displacement occurs predominately on a methyl group in salts containing at least two methyl groups while an appreciable amount of deethylation is observed with phenyldiethylmethylammonium iodide which contains but one methyl group. The surprising increase in deethylation in this case may be due to an increased steric hindrance to the attack on the remaining methyl group.

It is worthy of note that while the above mentioned salts are readily demethylated at 25°, these displacements are considerably slower than those involving the displacement of halide ion. Under conditions in which *n*-octyl bromide is said to be completely reduced to *n*-octane (2 min, 25°),[1] *n*-

Table I
Reduction of Quaternary Ammonium Iodides with Lithium Triethylborohydride[a]

Quaternary Salts	Registry no.	Temp, °C	Time, hr	Product(s)[b] (% yield)[c]
$C_6H_5N(CH_3)_3I$	98-04-4	25	0.75	$C_6H_5N(CH_3)_2$ (100, 92[d])
		65	0.25	(100)
$C_6H_5N(C_2H_5)(CH_3)_2I$	1006-07-1	25	0.75	$C_6H_5N(C_2H_5)CH_3$ (96) + $C_6H_5N(CH_3)_2$ (4)
$C_6H_5N(C_2H_5)_2CH_3I$	1007-67-6	25	0.75	$C_6H_5N(C_2H_5)_2$ (66) + $C_6H_5N(C_2H_5)CH_3$ (33)
$C_6H_5CH_2N(CH_3)_3I$	4525-46-6	65	7.0	$C_6H_5CH_2N(CH_3)_2$ (100, 85[d])
		25	2.0	(< 5)
$CH_3(CH_2)_5N(CH_3)_3I$	15066-77-0	65	4.0	$CH_3(CH_2)_5N(CH_3)_2$ (100, 88[d])
		25	2.0	(< 5)
$CH_3C(CH_3)_2CH_2C(CH_3)_2N(CH_3)_3I$	53624-41-8	65	1.0	$CH_3C(CH_3)_2CH_2C(CH_3)_2N(CH_3)_2$ (100)

[a] Reductions were performed using 1.0 mmol of salt and 1.5 mmol of $LiEt_3BH$ in 5 ml of dry THF under nitrogen. [b] All products identified by comparison with authentic samples or through preparation of known derivatives of isolated products. [c] Yields were determined by glpc analysis with the aid of an internal standard unless otherwise noted. [d] Yield of isolated picrate salt.

pentyltrimethylammonium iodide suffers less than 5% reduction.

Quaternary ammonium salts of aliphatic amines are much less readily reduced, however, owing to the increased basicity of the tertiary amine and require longer reaction times at elevated temperatures for the quantitative liberation of the dealkylated tertiary amine. The addition of hexamethylphosphoric triamide, which often accelerates the rate of SN2 processes,[3] does not affect a noticeable increase in the rate of the reaction with these substrates.

Thus, lithium triethylborohydride is an excellent reagent for the selective demethylation of quaternary ammonium salts containing methyl groups. It seems likely that this remarkable reagent will find use in other reductions involving the displacement of poor leaving groups by hydride ion.

Experimental Section

Materials. The quaternary ammonium salts employed in this work were prepared by the treatment of the corresponding tertiary amines with excess methyl iodide in benzene. The *N,N*-dimethyl amines were obtained from commercial sources or by the methylation of the corresponding primary amines.[4] Physical properties of all materials were in agreement with published values. A 1 *M* stock solution of lithium triethylborohydride in THF was prepared as previously described.[1]

General Procedure for the Dealkylation of Quaternary Ammonium Salts. *N,N*-Dimethylaniline from Phenyltrimethylammonium Iodide. The following procedure illustrates the general procedure used for the reduction of all of the quaternary ammonium iodides reported in Table I. Variations in reaction time and temperature for specific salts are shown in Table I. To a suspension of 0.265 g (1.0 mmol) of phenyltrimethylammonium iodide in 5 ml of dry THF under a nitrogen atmosphere was added 1.5 ml of 1 *M* lithium triethylborohydride stock solution. The mixture was stirred at room temperature for 0.75 hr. The resulting homogeneous mixture was treated with 1.0 ml of 10% aqueous hydrochloric acid and the THF was removed under reduced pressure. The aqueous solution was made basic by the addition of sodium hydroxide and the tertiary amine was obtained by extraction of the aqueous phase with several small portions of ether. Addition of the ethereal solution of *N,N*-dimethylaniline to 5 ml of saturated picric acid in ethanol gave 0.322 g (92%) of *N,N*-dimethylaniline picrate, mp 161–162° (lit.[5] mp 163°).

Acknowledgment. We thank Washington State University for support of this research through a grant in aid.

Registry No.—Lithium triethylborohydride, 22560-16-3.

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Carboalkoxylation of Aryl and Benzyl Halides Catalyzed by Dichlorobis(triphenylphosphine)palladium(II)

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With the exception of allyl halides, the carbonylation of organic halides using palladium catalysts has received little attention because of the severe reaction conditions.[1–4] A recent study[5] of the carbonylation of dichlorobis(triphenylphosphine)palladium(II) (1) suggests it as a potential catalyst for the carbonylation of organic halides. Carbonylation of 1 in methanol in the presence of primary or secondary amines affords a mixture of carbonylpalladium(0) complexes 2 and 3, whereas in the presence of tertiary amines, chlorocarbomethoxybis(triphenylphosphine)palladium(II) (4) is formed. Treatment of 4 with methyl iodide or benzyl bromide yields the corresponding methyl ester.[5]

Since aryl, benzyl, and vinyl halides readily react with either finely divided palladium metal[6,7] or organophosphinepalladium(0) complexes[8,9] to form organopalladium(II) complexes, it appeared likely that the palladium(0) complexes 2 and 3 would react with organic halides *via* oxidative addition to afford organopalladium complexes which upon carbonylation would give acylpalladium(II) derivatives. Alcoholysis of the acylpalladium(II) compounds would afford esters and regenerate a palladium(0) complex in the presence of a base.[10] A catalytic cycle for the carbonylation of organic halides could also be achieved with the carbomethoxypalladium complex 4 if dihalobis(triphenyl-

$$\underset{1,\ L = PPh_3}{L_2PdCl_2} + CO + CH_3OH \xrightarrow[RNH_2]{RR'NH} \underset{2}{Pd(CO)L_3} + \underset{3}{Pd_3(CO)_3L_4}$$

$$1 + CO + CH_3OH \xrightarrow{RR'R''N} \underset{4}{L_2PdCl(CO_2CH_3)}$$