The F^{19} n.m.r. spectrum in benzene exhibited three multiplets at 24.8, 50.7, and 57.0 p.p.m.

3,3′-Dibromohexafluorobiphenyl-4,4′-dicarboxylic Acid (XI).—*n*-Butyllithium (58 ml., 0.09 mole, 1.54 *N* in *n*-hexane) was slowly added to a stirred solution of 3,3′,4,4′-tetrabromohexafluorobiphenyl (11.5 g., 0.02 mole) in 100 ml. of dry THF under nitrogen, so that the reaction temperature did not exceed −60°. During the addition, the initially colorless solution became yellow-orange. When the addition was complete, the resulting white slurry was stirred for 1 hr. at −70°. Gaseous carbon dioxide was introduced into the reaction mixture at such a rate as to ensure that the reaction temperature never exceeded −55°. After carbonation at low temperature for 0.5 hr., the mixture was allowed to warm to room temperature as carbonation was continued. The mixture was then hydrolyzed with 200 ml. of 6 *N* HCl. The two-phase mixture was extracted three times with 200-ml. portions of ether. The combined ether extracts were dried ($MgSO_4$) and distilled *in vacuo*. The white solid was collected and washed with petroleum ether (b.p. 30–60°). The product was recrystallized from nitrobenzene, affording 7.4 g. (85%) of white powder, m.p. 310–313°.

Anal. Calcd. for $C_{14}H_2Br_2F_6O_4$: C, 33.10; H, 0.40; Br, 31.5; F, 22.4; neut. equiv., 254. Found: C, 32.42; H, 0.41; Br, 32.7; F, 22.5; neut. equiv., 242.

The F^{19} n.m.r. spectrum in ethanol exhibited absorption at 27.8, 53.5, and 62.1 p.p.m.

Hexafluorobiphenyl-3,3′,4,4′-tetracarboxylic Acid (XII).—3,3′-Dibromo-2,2′,5,5′,6,6′-hexafluorobiphenyl-4,4′-dicarboxylic acid (9 g., 0.018 mole) in 400 ml. of dry THF was treated with 50 ml. (0.079 mole) of 1.58 *N* *n*-butyllithium in *n*-hexane. A negative Color Test IIA was obtained 2 hr. after the addition was completed. The reaction mixture was then carbonated, hydrolyzed, and extracted with ether in the same manner as the preceding experiment. The combined ether extracts were evaporated *in vacuo*, affording a tacky tan solid. This product was triturated with petroleum ether (b.p. 30–60°) and then extracted with petroleum ether (b.p. 60–90°) for 4 hr. in a Soxhlet extractor. The product was dissolved in diethyl ether and passed through a silica gel column employing diethyl ether as the eluent. Evaporation of the ether afforded 7.3 g. (93%) of pale tan tetracarboxylic acid, m.p. 226–228° dec., which contained no bromine.

Anal. Calcd.: neut. equiv., 109.5. Found: neut. equiv., 119.

The F^{19} n.m.r. spectrum in acetone exhibits absorption at 35.9, 49.8, and 64.7 p.p.m.

Tetramethyl Hexafluorobiphenyl-3,3′,4,4′-tetracarboxylate (XIII).—Five grams (0.0114 mole) of the tetraacid XII in diethyl ether at 0° was treated with excess diazomethane solution. The solution was evaporated *in vacuo*, affording an oil. The oil was dissolved in petroleum ether (b.p. 90–120°) containing a small amount of diethyl ether. Slow evaporation of the solution yielded a white precipitate. This ester was collected and recrystallized from chloroform–petroleum ether (b.p. 60–90°), affording 4.0 g. (71%) of white needles, m.p. 106.5–108°.

Anal. Calcd. for $C_{20}H_{12}F_6O_8$: C, 48.59; H, 2.45; F, 23.1. Found: C, 48.43; H, 2.17; F, 23.4.

The F^{19} n.m.r. spectrum in acetone exhibits absorption at 35.6, 48.8, and 63.8 p.p.m.

4,4′-Bis(N,N′-pentafluorophenyltrifluorophthalimide) (XV).—Five grams (0.0114 mole) of the tetracarboxylic acid XII in 50 ml. of xylene was heated to reflux temperature. After 2.5 hr., approximately 0.38 ml. (93%) of water had been collected in a Dean–Stark trap. Pentafluoroaniline (4.6 g., 0.025 mole) was added to the solution and it was heated to reflux temperature for 3 hr. An additional 0.34 ml. (83%) of water was collected. A small amount of insoluble material was filtered off and the filtrate was decanted into 300 ml. of petroleum ether (b.p. 30–60°). The precipitate was collected and recrystallized from benzene to afford 6.0 g. (72%) of white crystalline XV, m.p. 305.5–308°.

Anal. Calcd. for $C_{28}F_{16}N_2O_4$: C, 45.92; F, 41.5; N, 3.82. Found: C, 46.06; F, 41.6; N, 3.86.

F^{19} N.m.r. Data.—The F^{19} spectra were run on a Varian V-4300-2 D.P. spectrometer at 40.0 Mc./sec. Chemical shifts are reported in parts per million (p.p.m.) from trifluoroacetic acid.

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Selective Reductions. VI. The Reaction of Lithium Tri-*t*-butoxyaluminohydride with Phenolic Esters. A New Aldehyde Synthesis[1]

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In contrast to the comparative inertness of alkyl esters, phenyl esters of aliphatic carboxylic acids readily react with lithium tri-*t*-butoxyaluminohydride in tetrahydrofuran at 0°, forming the corresponding aldehydes in yields of approximately 70%. Except for the α,β-unsaturated and cyclopropyl derivatives, this preparative method appears to be generally applicable to the conversion of aliphatic and alicyclic carboxylic acids to the corresponding aldehydes. The mildness of the reagent may be particularly advantageous in cases where the molecule may contain other functional groups which might be reduced competitively by other, more vigorous reagents.

Numerous synthetic routes to aldehydes *via* carboxylic acid derivatives are now available, often with high yields, especially for aromatic derivatives. The disadvantages of Rosenmund's[3] hydrogenation of acid chlorides led to the application of more involved methods of preparing aldehydes,[4] such as Stephen's procedure,[5] which, although widely utilized in the past, is usually unsuccessful for aliphatic derivatives.

The suggestion that lithium aluminum hydride reduction of nitriles and tertiary amides could be controlled to yield aldehydes[6] led to some useful preparations of aldehydes by the lithium aluminum hydride reduction of N-methylanilides,[7] piperidides,[8] N-acyl-

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[1] Based upon a thesis submitted by P. M. Weissman in Aug. 1964, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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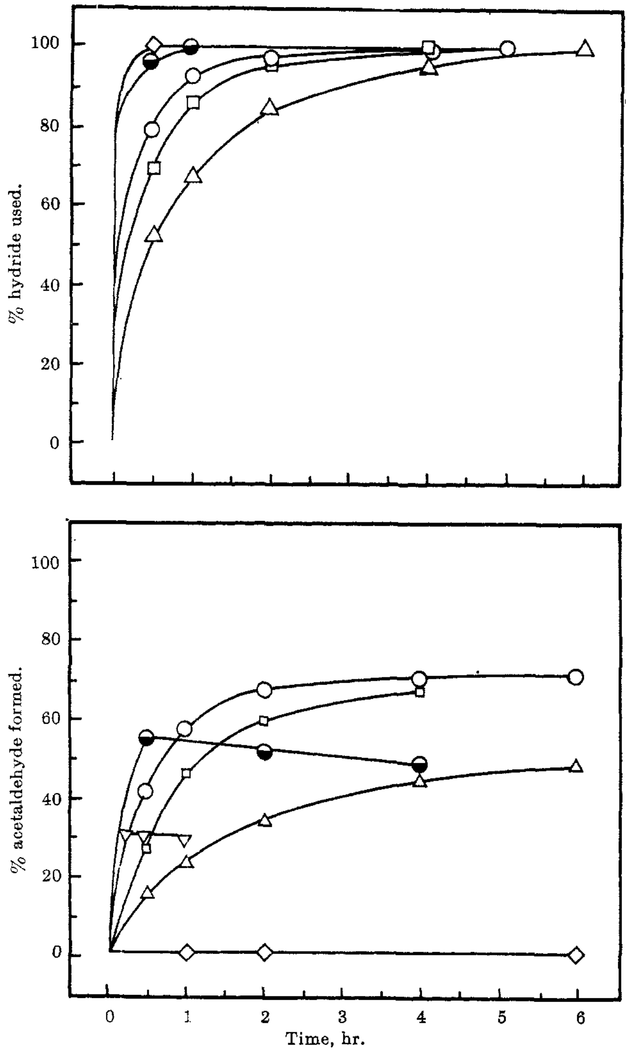

Figure 1.—Relative rates of hydride utilization and aldehyde formation in the reaction of 1.0 *M* solutions of aryl acetates and LTBA in THF at 0°: O, phenyl; □, *p*-tolyl; △, *o*-tolyl; ●, *p*-chlorophenyl; ▽, *m*-chlorophenyl; ◇, *o*-chlorophenyl; ◇, *p*-nitrophenyl.

carbazoles,[9] 1-acyl-3,5-dimethylpyrazoles,[10] N-acylimidazoles,[11] and 1-acylaziridines.[12] The preparation of aliphatic aldehydes by the reduction of nitriles with lithium aluminum hydride was less successful.[13-15]

Addition of 2 or 3 equiv. of methyl, ethyl, or *t*-butyl alcohol to lithium aluminum hydride produces modified reagents which are often capable of more selective reductions than the parent compound.[16] Lithium di- and triethoxyaluminohydride were shown to produce aliphatic aldehydes in extremely high yield from the corresponding acyl dimethylamides,[17] and the reduction of nitriles with the triethoxy derivative is an excellent synthetic route to both aromatic and aliphatic aldehydes.[18]

Finally, two important communications recently reported the preparation of aldehydes from the reduction of esters with diisobutylaluminum hydride[19a] and sodium aluminum hydride.[19b]

Lithium tri-*t*-butoxyaluminohydride,[20] LiAlH(*t*-BuO)$_3$, has been used for the preparation of aldehydes from acid chlorides[20,21] and for the stereospecific reduction of steroidal ketones.[22-24] We recently explored the reactivity of this reagent in tetrahydrofuran[25] toward organic compounds containing representative functional groups and found it to be extremely selective—many groups readily reduced by lithium aluminum hydride exhibited no reaction, even after 24 hr. at 0°. Thus, for certain reductions of polyfunctional molecules, lithium tri-*t*-butoxyaluminohydride possesses an advantage over the reagents previously mentioned in avoiding undesirable side reactions.

In the course of studying the properties of this selective reagent, we noted that phenyl acetate, in contrast to alkyl esters, was readily reduced and acetaldehyde was present in the hydrolyzed product. Accordingly, we undertook to explore the scope of this reaction.

Results and Discussion

Reaction of Various Ring-Substituted Aryl Acetates with Lithium Tri-*t*-butoxyaluminohydride.—In order to explore the effect of the phenol component on the rate of reduction and yield of aldehyde, six representative esters were prepared by treating acetic anhydride with the sodium salts of *o*- and *p*-cresol, *o*-, *m*-, and *p*-chlorophenol, and *p*-nitrophenol. The acetates were then reduced by lithium tri-*t*-butoxyaluminohydride (LTBA),[26] both as 1.0 *M* solutions in tetrahydrofuran (THF), and the course of the reaction was followed by analyzing for residual hydride and for aldehyde at intervals.

The results (Figure 1, Table I) reveal that hydride is utilized at a faster rate than aldehyde is formed in the initial stages of the reaction and that the rate of reaction, as well as the yield, is sensitive to the electronic effects of the substituents. In the case of the chloro and nitro derivatives, the rates of reaction were increased, but the yields of aldehyde were negligible. A *p*-methyl group had no significant effect on either the rate or the yield, whereas the *o*-methyl derivative reacted considerably slower and produced a smaller yield.

Effect of Reaction Temperature on the Reduction of Aryl Acetates with Lithium Tri-*t*-butoxyaluminohydride.—For the purpose of determining the optimum conditions for the synthesis of acetaldehyde from phenyl acetate, the reaction was studied at 0, 25, and −22°. Although increasing the temperature to 25°

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TABLE I

REDUCTION OF RING-SUBSTITUTED ARYL ACETATES WITH 1.0 *M* LITHIUM TRI-*t*-BUTOXYALUMINOHYDRIDE IN TETRAHYDROFURAN AT 0°[a]

Acetate	Reaction time, hr.	Yield of aldehyde, %[b]
Phenyl	4	71
p-Tolyl	4	67
o-Tolyl	6	48
p-Chlorophenyl	1[c]	56
m-Chlorophenyl	0.25	30
o-Chlorophenyl	0.5	0
p-Nitrophenyl[d]	1	0

[a] Procedure: to 40 mmoles of ester in 10 ml. of THF, 40 mmoles of reagent in 30 ml. of THF was added in 5 min. [b] Isolated as the 2,4-dinitrophenylhydrazone. [c] After 30 min. the yield was 55%. [d] Owing to the low solubility of the ester, the concentration of both reactants was only 0.5 *M*. The reaction temperature was −22°. At −78° no reduction occurred in 1 hr.

increased the rate of hydride consumption and lowering it to −22° decreased the rate markedly, both changes caused a large decrease in the yield of aldehyde from phenyl acetate (see Table II). It is noteworthy that the reduction of *p*-chlorophenyl acetate at −22° gave a 77% yield, the highest which has been attained. However, the increase of 6% over that obtainable with phenyl acetate at 0° did not justify alteration of the procedure to one which is more troublesome.

TABLE II

EFFECT OF REACTION TEMPERATURE ON THE REDUCTION OF ARYL ACETATES WITH LITHIUM TRI-*t*-BUTOXYALUMINOHYDRIDE IN TETRAHYDROFURAN[a]

Acetate	Temp., °C	Reaction time, hr.	Yield of aldehyde, %[b]
Phenyl	−22	12	48
	0	4	71
	25	0.25	48
m-Chlorophenyl	−78 to 0[c]	3	66
	0	0.25	30
p-Chlorophenyl	−22	8	77
	0	0.5	56

[a] For the experimental procedure, see footnote *a*, Table I. [b] Isolated as the 2,4-dinitrophenylhydrazone. [c] The reactants were mixed at −78° and allowed to warm to 0° over 2.5 hr.

Effect of Varying the Molar Ratio of the Reactants.—Several reactions were performed using the same techniques as outlined above, keeping the concentration of LTBA always 1.0 *M*, but varying the ester concentration. In this way, the molar ratio of reactants which affords the highest conversion of ester to aldehyde could be determined (Table III). Once again, it was found that the original conditions (hydride/ester = 1.0) gave the highest yield.

It is also obvious from all the preceding results that the reduction of phenyl esters at 0° when both reactants are present in 1.0 *M* concentration will be over within 4 hr. reaction time. Longer reaction times do not significantly decrease the aldehyde yields, provided there is not present a large excess of reagent.

Other experiments have also indicated that it is not important whether the hydride is added to the ester (reverse addition) or the ester is added to the hydride solution (normal addition). The rate of addition of the reactants is also not too significant, provided it is slow enough to prevent the reaction mixture from warming up. In the small-scale reductions, 40 mmoles of hydride was added in 5 min., longer addition times gave no improvement in yields.

TABLE III

REACTION OF 1.0 *M* LITHIUM TRI-*t*-BUTOXYALUMINOHYDRIDE WITH VARYING AMOUNTS OF PHENYL ACETATE AT 0°

LTBA, mmoles	Ester, mmoles	Mole ratio, hydride ester	Reaction time, hr.	Yield of aldehyde, %[a]
38.9	47.3	0.82	2–3	64
40	40	1.00	4	71
46	40	1.15	4–8	68
38.9	30	1.30	6[b]	66
30	20	1.50	6[b]	63
40	20	2.00	2[b]	47

[a] Isolated as the 2,4-dinitrophenylhydrazone. The yields are based on the amount of ester added in each case. [b] These reactions continued for longer times, but the amount of acetaldehyde gradually went down thereafter.

The uniqueness of the reagent is illustrated by the fact that lithium aluminum hydride and lithium tri-*t*-methoxyaluminohydride gave no aldehyde under the same conditions.

Scope of the Reaction.—The phenyl esters of several representative carboxylic acids were prepared from the corresponding acid chlorides and reduced on a 40-mmole scale. In each case, the optimum conditions which had been previously established were employed.

Aliquots of the reaction mixture were removed and analyzed for hydride consumption and aldehyde yield. The results of all the test compounds are shown in Table IV.

TABLE IV

ALDEHYDE YIELDS FROM THE REDUCTION OF PHENOLIC ESTERS BY LITHIUM TRI-*t*-BUTOXYALUMINOHYDRIDE IN TETRAHYDROFURAN AT 0°[a]

Phenyl ester	Mole of addition[b]	Reaction time, hr.	Yield of aldehyde, %[c]
Acetate	R	4	71
Propionate	N	3	77
n-Butyrate	R	4	63
Isobutyrate	N	4	71
Pivalate	R	4	67
Caproate	R	4	71
Cyclopropylcarboxylate	R	10	0[d]
Cyclohexylcarboxylate	R	4	70
Chloroacetate	R	0.5	67
Phenylacetate	N	1	73
Phenoxyacetate	R	0.25	49
Crotonate	N	0.5	33
Cinnamate	R	2	60
Benzoate	R	4	0

[a] 40 mmoles of ester reacted with 40 mmoles of LTBA in a total volume of 40 ml. [b] R, hydride added to ester; N, ester added to hydride. [c] Isolated as the 2,4-dinitrophenylhydrazone. [d] After 10 hr. of a slow, continuous reduction, only 90% of the hydride was utilized.

The aldehyde yields shown in Table IV appear to be remarkably similar for all aliphatic compounds examined with the exception of the cyclopropyl and crotonyl derivatives. In contrast with most other metal hydride reductions of carbonyl compounds, methyl groups on the α-carbon affect neither the rate of reduction nor yield of aldehyde as illustrated by the series: phenyl *n*-butyrate, isobutyrate, and pivalate.

However, electron-withdrawing substituents on the carbon α to the carboxyl group, such as chloride, phenyl, and phenoxy, have a noticeable effect on reaction times. Only in the case of phenyl phenoxyacetate is the yield of aldehyde affected significantly. It is possible that this yield might be improved by a slight alteration of experimental conditions. In this case, since the reaction is completed so quickly, the exothermic reaction may have resulted in an initial spurt in temperature. If so, a slight decrease in reaction temperature would raise the yield considerably, as was observed for *p*-chlorophenyl acetate.

The inability to obtain aldehyde from the reduction of phenyl cyclopropylcarboxylate is puzzling. Moreover, the reduction is unusually slow—even after 10 hr. almost 10% of the hydride (3.9 mmoles) remained unreacted.

Investigation of the products resulting from the LTBA reduction of phenyl benzoate showed that half of the ester remains unreacted, whereas the other half is reduced to benzyl alcohol.

$$2MH + C_6H_5CO_2C_6H_5 \longrightarrow \xrightarrow{H^+} C_6H_5CH_2OH + C_6H_5OH$$

$$MH = LiAlH(t\text{-}BuO)_3$$

Finally, two representative esters were chosen for a large-scale preparation of the corresponding aldehydes. Phenyl cyclohexylcarboxylate was reduced to cyclohexylcarboxaldehyde in a 58.3% conversion, and caproaldehyde was isolated in 61.5% yield by the reduction of phenyl caproate with LTBA. The procedure recommended for preparations of this type is described in the experimental part.

Stoichiometry of the Reduction.—To obtain a complete balance of reactants and products, the reduction of phenyl isobutyrate with LTBA was studied in detail. After adding 40 mmoles of ester to 45 mmoles of hydride solution and stirring at 0° for 4 hr., analysis of an aliquot showed that all the hydride was consumed and 28.3 mmoles of isobutyraldehyde was formed (by isolation of the 2,4-dinitrophenylhydrazone), a yield of 70.7%. Another aliquot was solvolyzed with ethylene glycol and subjected to gas chromatographic analysis. In addition to the aldehyde, 8.4 mmoles of isobutyl alcohol, 36.0 mmoles of phenol, and 4.0 mmoles of unreacted phenyl isobutyrate were found. Thus, a material balance of the reactants and products shows that (1) the ester is not quantitatively reduced, even though a 10% excess of hydride was present; and (2) quantitative yields under these conditions cannot be expected, since much alcohol is formed even while reactive ester remains present. The fact that hydride consumption is *initially* much faster than production of aldehyde, the two rates then becoming approximately equal toward the end of the reaction, can now be interpreted as being caused by a fast initial formation of alcohol. However, since the intermediate complex leading to aldehyde appears to be stable toward the reagent, as shown by the fact that a large excess of hydride does not significantly lower the amount of aldehyde formed (a 63% yield was obtained, even with a 50% excess of hydride), this fact seems peculiar.

One possible explanation is that the reagent itself is not a simple substance, but a mixture of two species, such as might exist in a dissociation of the reagent.

$$LiAlH(O\text{-}t\text{-}Bu)_3 \rightleftharpoons LiO\text{-}t\text{-}Bu + (t\text{-}BuO)_2AlH$$

One of these intermediates might form a stable complex, which is only slowly attacked by hydride, whereas the second species might either form an unstable intermediate (which can easily be further reduced to alcohol) or is a very potent reagent itself, capable of reducing even the complex mentioned above. However, since the objective of this study was the development of this new aldehyde synthesis and exploration of its scope of applicability, we did not further investigate this possibility.

Conclusion

When compared with many other hydride reagents, lithium tri-*t*-butoxyaluminohydride has the definite advantage of being inert toward many other functional groups. Consequently, one can prepare the aldehyde with this reagent either by reducing the acid chloride grouping or by reducing the phenyl ester, readily prepared from the acid chloride. Obviously, in most cases it would be preferable to proceed directly through the acid chloride. However, there are a number of groups which are not compatible with the acid chloride group, but which are not affected by the less reactive phenyl ester grouping. In such cases the ability to reduce the phenyl ester grouping selectively should greatly facilitate the desired synthesis.

Experimental Section

Materials.—Tetrahydrofuran was dried by distillation from lithium aluminum hydride. The LTBA reagent was obtained commercially as a white powder (Metal Hydrides, Inc., Beverly, Mass.) or prepared by adding *t*-butyl alcohol to a solution of lithium aluminum hydride in ether according to the method of Brown and McFarlin.[20] In either case, clear stock solutions with concentrations of about 1.5 *M* in tetrahydrofuran were used for the reductions.

Aryl Acetates.—The acetates were prepared by adding excess acetic anhydride to a cold aqueous solution of phenol or substituted phenol.[27]

Phenolic Esters.—In an attempt to find the best general method of preparing phenyl esters of aliphatic carboxylic acids (except acetic esters), a few methods were used. Some esters were made by adding the acid chlorides slowly to a solution of phenol in refluxing benzene containing magnesium powder.[28] Others were prepared by adding the acid chloride to a slurry of sodium phenolate in an inert solvent such as benzene or ether. The simplest method, apparently, was to add the acid chloride to phenol, without solvent, and to heat to remove hydrogen chloride.[29] Many phenolic esters were commercially available and were merely purified before use when necessary.

Small-Scale Reduction of Phenolic Esters with Lithium Tri-*t*-butoxyaluminohydride.—The reduction of phenyl acetate to acetaldehyde is typical of those reactions carried out on a 40-mmole scale. Phenyl acetate, 5.44 g. (40 mmoles), in 10 ml. of tetrahydrofuran was placed in a carefully dried 100-ml. flask equipped with a dry nitrogen inlet, magnetic stirring bar, and rubber septum for hypodermic syringe. To the stirred solution, maintained at 0°, 30 ml. of a tetrahydrofuran solution containing 40 mmoles of LTBA was added. After standard time intervals (0.5, 1.0, 2.0, 4.0, and 6.0 hr.), two aliquots were simultaneously removed for analysis. One portion was hydrolyzed to determine the hydride content of the reaction and the other was analyzed for aldehyde with 2,4-dinitrophenylhydrazine. After 4 hr. (the reaction mixture had become slightly viscous), no hydride re-

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mained and a 70% yield of the hydrazone, m.p. 145° (lit.[30] m.p. 147°), was isolated. After 6 hr. reaction time the yield apparently rose to 71%.

The same basic procedure was used to determine the rate of reduction and yield of aldehyde for other esters, the only differences being those attempts (mentioned in the Results and Discussion) to discover the optimum conditions for securing aldehyde, *e.g.*, reaction temperature, mode and rate of addition, and hydride:ester ratio (see Tables I–IV).

Reduction of Phenyl Cyclohexylcarboxylate to Cyclohexanecarboxaldehyde with LTBA on a Preparative Scale.—In a 500-ml. three-necked flask equipped with dry nitrogen inlet, pressure-equilibrated addition funnel, and magnetic stirrer bar, kept at 0°, 51.1 g. of phenyl cyclohexylcarboxylate (0.250 mole) and 30 ml. of THF were placed. LTBA, 194 ml. of a 1.29 *M* THF solution (0.250 mole), was placed in the addition funnel by means of a pipet and added dropwise over a period of 20 min. in two portions to the reaction flask.

The mixture was stirred for 5 hr. at 0°, after which a small aliquot was removed and added to 2,4-dinitrophenylhydrazine. A 67% yield of hydrazone, m.p. 166°, was isolated. Addition of 10 ml. of 5 *N* H_2SO_4 caused no evolution of hydrogen. The reaction mixture was then poured onto crushed ice in a separatory funnel and 200 ml. of pentane was added. The large amount of flocculent white precipitate which then appeared was dissolved by gradually adding almost 200 ml. of cold 5 *N* H_2SO_4 and continually shaking. The pentane layer was separated and the aqueous layer was extracted with 100 ml. of pentane. The combined organic extract was then washed with 100 ml. of water, shaken with solid sodium bicarbonate, and washed again with four 100-ml. portions of water. The organic layer was separated and dried overnight with magnesium sulfate. The solvent was then removed by distillation and the aldehyde was distilled under vacuum through a 6-in. column packed with glass helices. The first fraction [b.p. 25–50° (20 mm.)] was discarded, and 16.31 g. of cyclohexanecarboxaldehyde was collected, b.p. 56° (19.5 mm.), $n^{19.5}\mathrm{D}$ 1.4494 [lit.[17a] b.p. 76.5–77.5° (48 mm.), $n^{20}\mathrm{D}$ 1.4495], a yield of 58.3%.

Reduction of Phenyl Caproate to Caproaldehyde with LTBA on a Preparative Scale.—In a dry 500-ml. flask equipped with a dry nitrogen inlet, injection port covered with rubber septum, and magnetic stirrer bar, 57.68 g. of phenyl caproate (0.300 mole) and 10 ml. of THF were placed. To the stirred solution, kept at 0° in an ice bath, 233 ml. of 1.29 *M* LTBA solution in tetrahydrofuran (0.300 mole) was added over a period of 25 min. by means of a hypodermic syringe.

The solution remained clear during addition, but became slightly cloudy after 2 hr. reaction time. After 4 hr. a small aliquot was removed and added to 2,4-dinitrophenylhydrazine. A 71% yield of hydrazone, m.p. 104° (lit.[30] m.p. 104°), was isolated. Addition of 10 ml. of 5 *N* H_2SO_4 to the reaction mixture caused no hydrogen evolution. The whole reaction mixture was then poured onto ice–water and pentane was added. A large flocculent white precipitate appeared, which was dissolved by adding cold 5 *N* H_2SO_4 and shaking the total mixture. The organic layer was separated and the aqueous layer was extracted with 100 ml. of pentane. The combined organic extracts were washed with water, 5% sodium bicarbonate, and then with four more 100-ml. portions of water. The pentane solution was separated and dried overnight with magnesium sulfate. The low-boiling materials (pentane, THF, and *t*-butyl alcohol) were distilled off through a Vigreux column, and caproaldehyde was collected at 126–128° (752 mm.), $n^{19.5}\mathrm{D}$ 1.4048 [lit.[31] b.p. 126–128° (747 mm.)], yield 18.46 g. (61.5%).

Stoichiometry of the Reduction of Phenyl Isobutyrate with LTBA.—In the standard apparatus, 6.56 g. of phenyl isobutyrate (40 mmoles) in 10.0 ml. of THF was added all at once to 45 mmoles of LTBA in 30.2 ml. of THF solution. After 0.5, 1.0, 2.0, and 4.0 hr., samples were removed for analysis of hydride and aldehyde content. After 4 hr., when the hydride was all consumed, 28.3 mmoles of aldehyde was isolated as the 2,4-dinitrophenylhydrazone. An aliquot of the reaction mixture (2.0 ml.) was then removed and added to a 25-ml. volumetric flask and hydrolyzed with 0.8 ml. of ethylene glycol. The flask was then filled with THF and a sample of the mixture was analyzed by gas chromatography (200-ft. Golay columns, succinate polyester of butanediol and Ucon Polar, temperature programmed), using solutions of known concentration as standards. By this method, the total reaction mixture was found to contain 8.4 mmoles of isobutyl alcohol, 36.0 mmoles of phenol, and 4.0 mmoles of phenyl isobutyrate, in addition to the 28.3 mmoles of isobutyraldehyde previously determined.

Attempted Synthesis of Acetaldehyde from Phenyl Acetate with Lithium Aluminum Hydride.—In the usual apparatus, 10 mmoles of lithium aluminum hydride in 20 ml. of THF solution was added over a period of 15 min. to 47 mmoles of phenyl acetate in 20 ml. of THF solution. After 15 min. reaction time at 0°, hydrolysis of an aliquot showed that no hydride remained. However, no aldehyde could be detected upon addition of another aliquot to 2,4-dinitrophenylhydrazine.

Attempted Synthesis of Acetaldehyde from Phenyl Acetate with Lithium Trimethoxyaluminohydride at -15°.—In the usual apparatus, immersed in an ice–salt bath at approximately -15°, 19.6 mmoles of lithium trimethoxyaluminohydride in 57.5 ml. of THF solution was added in 15 min. to 2.72 g. of phenyl acetate (2.53 ml., 20.0 mmoles). Addition of aliquots of the reaction mixture to 2,4-dinitrophenylhydrazine solution after 30 and after 60 min. did not cause the precipitation of any hydrazone.

Attempted Synthesis of Benzaldehyde from Phenyl Benzoate.—In the standard apparatus 3.96 g. of phenyl benzoate (20 mmoles) was dissolved in 10.0 ml. of THF. To the stirred solution, kept at 0°, 20 mmoles of LTBA in 16 ml. of THF solution was added over a period of 5 min. After 4 hr. reaction time (tests showed the absence of hydride), an aliquot was added to 2,4-dinitrophenylhydrazone solution, but no aldehyde was detected. To determine the quantity of unreacted ester, a sample of the reaction mixture was injected into the gas chromatograph (200-ft. Golay column, succinate polyester of butanediol, 195°) without prior hydrolysis. Comparison with a standard solution of phenyl benzoate in tetrahydrofuran showed 8 mmoles of unreacted ester (40%) was present. Hydrolysis of another portion of the reaction mixture and identical analysis also indicated the presence of 9.2 mmoles of benzyl alcohol (46%).

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