

n_D^{20} 1.4042, and 2.5 g., 8.5% yield, of capronitrile, b.p. 73° at 53–55 mm., n_D^{20} 1.4070.

C. Cyclohexanecarbonitrile.—Cyclohexanecarboxaldehyde, b.p. 63–66° at 23–24 mm., n_D^{20} 1.4507, was obtained in 71% yield.

D. Benzonitrile.—Benzaldehyde, b.p. 81–82° at 31 mm., n_D^{20} 1.5452, was obtained in 76% yield.

E. *p*-Chlorobenzonitrile.—Lithium triethoxyaluminumhydride (0.238 mole) was prepared in 238 ml. of ether. Into this stirred solution was added 32.7 g. (0.238 mole) of *p*-chlorobenzonitrile all at once at ice-bath temperature. The reaction mixture was hydrolyzed, after an hour, with 200 ml. of 5 *N* sulfuric acid. Ether was distilled and the resulting aqueous layer was steam distilled. *p*-Chlorobenzaldehyde, m.p. 47–47.5°, was obtained (27.9 g.) in 83.5% yield. Recrystallization from hot water did not change the m.p.

Reduction with Lithium Tri-*n*-butoxyaluminumhydride on a Preparative Scale.—The use of lithium tri-*n*-butoxyaluminumhydride is useful in cases where the removal of ethyl alcohol from the product offers difficulties.

Cyclopropanecarbonitrile.—In a 1-l., three-necked, round-bottom flask equipped with a condenser, dropping funnel, and stirrer, flushed with nitrogen, was placed 0.3 mole of lithium aluminum hydride in 300 ml. of ether (1 *M* solution). To this solution was added dropwise over a period of 75 min., 0.9 mole (66.6 g.) of 1-butanol, maintaining the temperature at –10 to –5°. The reaction was stirred for another 15 min. To this solution (–10°) was added 20.1 g. (0.3 mole) of cyclopropanecarbonitrile over 15 min., the temperature rising to 8°. The reaction was stirred for 1 hr. at 3° (ice bath) and then decomposed by 300 ml. of 5 *N* sulfuric acid. The ether layer was separated and the heterogen-

eous aqueous layer was extracted three times with 25-ml. portions of ether. The combined ether extracts were washed with sodium bicarbonate solution and water and then dried over sodium sulfate. The ether was concentrated through a small Vigreux column. The ether distillate was extracted with 130 ml. of sodium bisulfite solution (40%) to remove as adduct any aldehyde which would have passed over with the ether. Finally this solution was used to make the adduct of the aldehyde. This adduct was extracted four times with 35-ml. portions of ether to remove 1-butanol. It was decomposed by 42 g. of sodium bicarbonate suspended in 50 ml. of water at 0°. Cyclopropanecarboxaldehyde was steam distilled and the distillate was extracted with ether. The ether was dried over sodium sulfate and concentrated in a Todd fractionating column. Cyclopropanecarboxaldehyde, b.p. 97–98° at 726 mm., n_D^{20} 1.4302 (lit.³⁰ b.p. 97–100° at 740 mm., n_D^{20} 1.4302), was isolated in a yield of 13.8 g., 65.7%.

2,4-Dinitrophenylhydrazones.—Three of the 2,4-dinitrophenylhydrazones have not been previously described in the literature: (1) The bis-2,4-dinitrophenylhydrazone of adipaldehyde, crystallized from glacial acetic acid, m.p. 190°. *Anal.* Calcd.: C, 45.57; H, 3.82; N, 23.62. Found: C, 45.31; H, 3.99; N 21.11. (2) The 2,4-dinitrophenylhydrazone of γ -phenoxybutyraldehyde, crystallized from ethanol, m.p. 112–113°. *Anal.* Calcd.: C, 58.52; H, 4.912; N, 17.06. Found: C, 58.50; H, 5.02; N, 17.22. (3) The 2,4-dinitrophenylhydrazone of γ -phenoxybutyraldehyde, crystallized from ethanol, m.p. 96°. *Anal.* Calcd.: C, 55.8; H, 4.68; N, 16.27. Found: C, 55.67; H, 4.80; N, 16.42.

(30) H. C. Brown and A. Tsukamoto, *J. Am. Chem. Soc.*, **83**, 4549 (1961)

[CONTRIBUTION FROM THE RICHARD B. WETHERILL LABORATORY OF PURDUE UNIVERSITY, LAFAYETTE, IND.]

Selective Reductions. V. The Partial Reduction of Tertiary Amides by Lithium Di- and Triethoxyaluminumhydrides—A New Aldehyde Synthesis *via* the Dimethylamides^{1,2}

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The reduction of tertiary amides by lithium di- and triethoxyaluminumhydrides, conveniently synthesized *in situ* by the reaction of ethyl alcohol with lithium aluminum hydride, was explored as a useful synthetic route from the carboxylic acid to the corresponding aldehyde. With the exception of the highly hindered amide derivative *N,N*-diisopropyl-*n*-butyramide, a wide variety of *n*-butyryl tertiary amides were readily converted into *n*-butyraldehyde in satisfactory yields. The results realized for the simplest derivative, *N,N*-dimethyl-*n*-butyramide, were especially favorable. Moreover, the same procedure served to convert the dimethylamides of *n*-butyric acid, isobutyric acid, pivalic acid, and benzoic acid into the corresponding aldehydes in yields of 80 to 90%. Accordingly, the scope of this new aldehyde synthesis was explored by applying it to 24 representative acid derivatives. With the exception of conjugated unsaturated derivatives, such as crotonic and cinnamic, wide variation in structural type could be tolerated, with the corresponding aldehyde being produced in yields from 60 to 90%.

The ready availability of carboxylic acids makes it highly desirable to have available convenient synthetic routes from such acids to the corresponding aldehydes. The catalytic hydrogenation of acid chlorides⁴ and the Stephen reduction of nitriles⁵ have served for many years, but suffer from a number of disadvantages.

The preparation of aldehydes from various acid derivatives by reduction with lithium aluminum hydride has been widely studied.⁶ The most successful developments in this direction have involved the selective reduction of a number of tertiary amides. Thus, Wittig and Hornberger synthesized a series of unsaturated aldehydes, $C_6H_5(\dot{C}H=CH)_nCHO$ ($n = 1, 2, 4,$

and 5), by the partial reduction of the corresponding *N*-acylcarbazoles with lithium aluminum hydride.⁷ Similarly, Weygand and his co-workers demonstrated that the *N*-methylanilides could be utilized to produce a wide variety of aldehydes in good yields (60 to 90%).⁸ Moreover, it has been established that the partial reduction of the 1-acyl-3,5-dimethylpyrazoles^{9a} or the *N*-acylimidazoles^{9b} gives a general synthetic route to aldehydes from carboxylic acids. Finally, we recently reported that lithium aluminum hydride reacts with 1-acylaziridines to provide a synthetic route to the aldehyde.¹⁰

In these syntheses it is evident that the electronic and steric characteristics of the tertiary amide group are being utilized as a means of controlling the exceedingly powerful reducing action of the reagent, lithium aluminum hydride. The introduction of alkoxy substituents into lithium aluminum hydride provides a simple method of modifying the reducing power of the

(7) G. Wittig and P. Hornberger, *Ann.*, **677**, 11 (1952).

(8) (a) F. Weygand and G. Eberhardt, *Angew. Chem.*, **64**, 458 (1952);

(b) F. Weygand, G. Eberhardt, H. Linden, F. Schäfer, and I. Eigen, *ibid.*, **65**, 525 (1953); (c) F. Weygand and H. Linden, *ibid.*, **66**, 174 (1954).

(9) (a) W. Ried and F. J. Königstein, *ibid.*, **70**, 165 (1958); (b) H. A. Staab and H. Braeunling, *Ann.*, **654**, 119 (1962).

(10) H. C. Brown and A. Tsukamoto, *J. Am. Chem. Soc.*, **83**, 4549 (1961)

(1) Based upon a thesis submitted by Akira Tsukamoto in June, 1959, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) A preliminary communication reporting some of the results in this paper was published earlier: H. C. Brown and A. Tsukamoto, *J. Am. Chem. Soc.*, **81**, 502 (1959).

(3) Research assistant on a grant provided by the Eli Lilly and Co., 1957–1959.

(4) K. W. Rosenmund, *Ber.*, **51**, 585 (1918).

(5) H. Stephen, *J. Chem. Soc.*, 1874 (1925).

(6) For a general review of these synthetic routes from carboxylic acid derivatives to the corresponding aldehydes, see E. Mosettig, "Organic Reactions," Vol. VII, John Wiley and Sons, Inc., New York, 1954, pp. 218–257.

reagent,¹¹⁻¹⁴ opening up a new means of achieving selective reductions.

For example, lithium tri-*t*-butoxyaluminumhydride is a highly selective reagent which has made possible the partial reduction of acid chlorides¹⁵ and phenyl esters¹⁶ to aldehydes, and the stereospecific reduction of steroids.¹⁷ Similarly, lithium trimethoxyaluminumhydride¹⁴ has proved very valuable for the stereospecific reduction of bicyclic ketones.¹⁸ Finally, lithium triethoxyaluminumhydride has proved applicable to the reduction of both aliphatic and aromatic nitriles to aldehydes in good yield.^{14,19}

Accordingly, we decided to explore the possible utility of these new alkoxy derivatives of lithium aluminum hydrides for the selective conversion of tertiary amides into the corresponding aldehydes.²⁰

Results and Discussion

The Reaction of Various Alkoxy Substituted Lithium Aluminum Hydrides with *N,N*-Dimethyl-*n*-butyramide.—Various alkoxy derivatives of lithium aluminum hydride can be prepared conveniently by adding the calculated amount of an alcohol to a standardized solution of lithium aluminum hydride in diethyl ether, tetrahydrofuran, or diglyme.^{13,14} The hydride reagents thus prepared²¹ were used *in situ* for the reduction of *N,N*-dimethyl-*n*-butyramide, adopted as a test amide.

All of the reactions were carried out under essentially identical conditions so as to make it possible to compare the results realized with the different reagents. As a consequence of this procedure, the yields observed may not necessarily be the maximum possible for the reaction in question. In all cases 1 equivalent of the hydride reagent was used per mole of the amide. In some cases the amide was added to the hydride reagent (normal addition); in others, the hydride was added to the amide (reverse addition).

The results revealed that 80 to 90% yields could be realized by the use of lithium di- and triethoxyaluminumhydride in ether solution at 0°. In the case of lithium triethoxyaluminumhydride there was no difference in the yield whether normal or reverse addition was utilized. In the case of lithium diethoxyaluminumhydride it was necessary to add the hydride to the amide to achieve a high yield, although normal addition was possible providing the reagents were mixed at -80° and then brought to the reaction temperature.

The experimental results are summarized in Table I.

The Reaction of Lithium Di- and Triethoxyaluminumhydride with Representative Tertiary Amides of *n*-Butyric Acid.—The partial reduction of tertiary amides by lithium aluminum hydride has proved to be very

(11) O. Schmitz-DuMont and V. Habernickel, *Ber.*, **90**, 1054 (1957).

(12) G. Hesse and R. Schrödel, *Ann.*, **607**, 24 (1957).

(13) H. C. Brown and R. F. McFarlin, *J. Am. Chem. Soc.*, **78**, 252 (1956) **80**, 5372 (1958).

(14) H. C. Brown and C. J. Shoaf, *ibid.*, **86**, 1079 (1964).

(15) H. C. Brown and B. C. Subba Rao, *ibid.*, **80**, 5377 (1958).

(16) H. C. Brown and P. M. Weissman, manuscript in preparation.

(17) O. H. Wheeler and J. L. Mateos, *Can. J. Chem.*, **36**, 14 (1958).

(18) H. C. Brown and H. R. Deck, manuscript in preparation.

(19) H. C. Brown and C. P. Garg, *J. Am. Chem. Soc.*, **86**, 1085 (1964).

(20) Attention should be called to the simple reduction of ethyl esters to aldehydes with diisobutylaluminum hydride: L. I. Zakharkin and I. M. Khorlina, *Tetrahedron Letters*, No. 14, 619 (1962).

(21) In some cases the reagents obtained in this manner are homogeneous. In other cases the evidence is that they are not. For example, the product formed by adding 2 moles of ethyl alcohol to lithium aluminum hydride appears to be nearly pure lithium diethoxyaluminumhydride, but that produced with 3 moles of ethyl alcohol appears to be largely lithium triethoxyaluminumhydride accompanied by significant quantities of the di- and tetraalkoxy derivatives (ref. 14). In spite of the uncertainty, in some cases, of the precise nature of the reagents thus obtained, the products will be referred to in terms of their gross composition, such as Li(EtO)₃AlH and Li(*i*-PrO)₃AlH.

TABLE I

YIELDS OF *n*-BUTYRALDEHYDE IN THE REDUCTION OF *N,N*-DIMETHYL-*n*-BUTYRAMIDE BY LITHIUM ALUMINUM HYDRIDE AND VARIOUS ALKOXY DERIVATIVES

Reagent ^a	Solvent ^b	Mode of addn. ^c	Hydride utilization, ^d %	Temp., °C.	Yield of aldehyde, ^e %
LiAlH ₄	EE	R	100	0	16 to 25
	EE	N	100	-80 to 25	43
	EE	R	100	-80 to 25	54
Li(MeO) ₃ AlH	EE	N ^f	40 to 80	0	20 to 50
	DG	R	100	0	55 to 65
	THF	R	100	0	50
Li(MeO) ₂ AlH ₂	EE	N ^f	100	0	41
Li(EtO) ₃ AlH	EE	N ^g	100	0	80 to 87
	EE	R ^g	100	0	83
	EE	N	100	0	85 to 89
	EE	R	100	0	86 to 92
	EE	N ^g	100	-80 to 0	73
Li(<i>i</i> -PrO) ₃ AlH	EE	N ^f	ca. 60	0	18
Li(<i>n</i> -PrO) ₃ AlH	EE	N	100	0	50 to 60
		R	100	0	66
	Li(<i>t</i> -BuO) ₃ AlH	DG or THF	0(60°)		
Li(<i>t</i> -BuO) ₂ AlH ₂	EE	N	ca. 70	0	38
Li(<i>n</i> -BuO) ₃ AlH	EE	R	100	0	63

^a Prepared by treating lithium aluminum hydride in the solvent with the appropriate quantity of alcohol. ^b EE, ethyl ether; THF, tetrahydrofuran; DG, diglyme. ^c R, hydride added to amide; N, amide added to hydride. ^d In all cases 1 mole of amide was used per mole of available "hydride." The reaction was carried out for 1 hr. at 0°, except where otherwise indicated. ^e As the 2,4-dinitrophenylhydrazones. ^f The reagent is insoluble in the solvent. ^g The slurry was used for the reduction.

sensitive to the structure of the amide group.⁷⁻¹⁰ Accordingly, it was important to examine whether the partial reduction of such amides by lithium di- and triethoxyaluminumhydride would likewise be sensitive to the structure of the amide.

Accordingly, a number of tertiary amides of *n*-butyric acid were synthesized and treated with lithium di- and triethoxyaluminum hydride under the standard reaction conditions (1 hr. at 0°).

The results are summarized in Table II.

TABLE II

YIELDS OF *n*-BUTYRALDEHYDE IN THE REDUCTION OF REPRESENTATIVE TERTIARY AMIDES OF *n*-BUTYRIC ACID BY LITHIUM ALUMINUM HYDRIDE AND SELECTED ALKOXY DERIVATIVES

<i>t</i> -Amide of <i>n</i> -butyric acid	Yield of aldehyde, ^b %			
	LiAlH ₄ ^a in ethyl ether	Li(MeO) ₃ AlH in diglyme	Li(EtO) ₃ AlH in ethyl ether	Li(EtO) ₂ AlH ₂ in ethyl ether
Dimethylamide	16-25	55-60	86-92	77-83
Diethylamide	22	5	59	47
Diisopropylamide	N.r. ^c	N.r. ^c	N.r. ^c	N.r. ^c
<i>N</i> -Methylanilide	58	47	69	82
Piperidide	33		68	67
Pyrrolidide	16	36	70	50
Aziriidide	88		87	83
Pyrrolidide	30 ^d		46 ^d	39 ^d

^a Ref. 10. ^b As 2,4-dinitrophenylhydrazones. The reactions were carried out by adding the hydride reagents to the amide solution (1 equivalent of the hydride to 1 mole of the amide) at 0°. The reaction time was 1 hr. Hydride consumption was essentially complete except for the diisopropylamide. ^c No reaction; the hydride was recovered under the reaction conditions. ^d Because of interference by the pyrrole reaction product, the analysis was by gas chromatography.

It is evident that except for the diisopropylamide derivative, where no reaction occurred under the mild conditions used, and the pyrrole derivative, where some attack on the heterocyclic ring was indicated, the yields

appeared to be quite good. Certainly, the yields realized with lithium di- and triethoxyaluminumhydride do not exhibit the wide fluctuations with structure of the amide group observed in the corresponding reductions with lithium aluminum hydride.

The Reaction of Lithium Di- and Triethoxyaluminumhydride with the Dimethylamides of Representative Acids.—From the synthetic point of view, it is desirable that the aldehyde yields should be relatively independent of the structure of the acyl groups. For example, although the reaction of lithium aluminum hydride with the *N*-methylanilides of carboxylic acids generally proceeds to give the aldehyde in reasonable yield,⁹ it was observed that this synthesis failed in the case of a relatively hindered acid.²² Treatment of the *N*-methylanilide of α -methyl- α -phenylbutyric acid with lithium aluminum hydride gave no aldehyde, only the corresponding alcohol.

Consequently, in order to test further the generality of this new aldehyde synthesis, we synthesized the dimethylamides of *n*-butyric acid, isobutyric acid, trimethylacetic acid, and benzoic acid, and subjected them to the action of lithium aluminum hydride, lithium trimethoxyaluminumhydride, and lithium di- and triethoxyaluminumhydride. It appeared that the increased branching at the α -position of the aliphatic acid derivatives and the substitution of phenyl in place of alkyl residues would provide a severe test of whether the reagents would prove sensitive to the steric and electronic characteristics of the acyl component.

The results are summarized in Table III.

TABLE III

ALDEHYDE YIELDS IN THE REDUCTION OF THE DIMETHYLAMIDES OF SEVERAL TEST ACIDS BY LITHIUM ALUMINUM HYDRIDE AND SELECTED ALKOXY DERIVATIVES

Dimethyl- amide RCON- (CH ₃) ₂	Aldehyde yields, ^a %			
	LiAlH ₄ in ethyl ether	Li(MeO) ₃ - AlH in diglyme	Li(EtO) ₃ - AlH in ethyl ether	Li(EtO) ₂ - AlH ₂ in ethyl ether
<i>n</i> -Butyryl	16–25	55–59	86–92	77–83
Isobutyryl	40–50	60–70	84–88	84
Pivalyl	55	51–61	86–88	76
Benzoyl	50–60	75–85	89–91	83

^a As 2,4-dinitrophenylhydrazones; conditions as described in footnote *a* of Table II.

The high yields realized with both lithium di- and triethoxyaluminumhydride for these four test derivatives are gratifying, with the yields achieved by the use of the triethoxy derivative tending to be several per cent higher than with the diethoxy derivative. The yields obtained by the use of lithium trimethoxyaluminumhydride are significantly less. Finally, the yields achieved with lithium aluminum hydride proved to be reasonable, except for the *n*-butyryl derivative, but considerably lower than those resulting from the use of the ethoxy derivatives.

Effect of Reaction Conditions on Aldehyde Yield.

In the previous experiments lithium triethoxyaluminumhydride was synthesized by adding 3 moles of ethyl alcohol to 1 mole of lithium aluminum hydride in ethyl ether. For larger scale experiments the evolution of large quantities of hydrogen appeared undesirable. Accordingly, it was established that the reagent prepared with 1.5 moles of ethyl acetate to 1 mole of lithium aluminum hydride gave identical results in this synthesis, and this procedure was adopted for further work. The reagent thus prepared contains a small quantity of a white solid, presumably lithium tetraethoxyaluminumhydride.¹⁴ No significant difference in results was noted, whether the reagent was utilized as a

slurry, as formed in the synthesis, or as a clear solution after removal of the precipitate by filtration. The effect of the mode of addition of the hydride reagent on the aldehyde yield was next examined. In general, addition of the hydride solution to the amide (reverse addition) gave the aldehyde in slightly better yields than addition of the amide to the hydride reagent (normal addition). However, we concluded that the greater simplicity of the normal addition procedure more than compensated for the minor decrease in yield. Consequently we adopted the practice of preparing lithium triethoxyaluminumhydride in the reaction flask and adding the dimethylamide directly to the reagent with no further treatment or manipulation.

The synthesis of lithium diethoxyaluminumhydride could likewise be achieved with 1 mole of ethyl acetate in place of 2 moles of ethanol and comparative experiments established that there was no measurable difference in the yields realized with the two materials. Unfortunately, the simple addition of the dimethylamide to the reagent at 0° proved unsatisfactory, resulting in very low yield. It proved necessary to add the dimethylamide to the reagent pre-cooled to -80°, followed by warming to the reaction temperature, 0 or 25°. Alternatively, good yields could be realized by adding the reagent to the dimethylamide at 0 or 25° (reverse addition). Both of these procedures gave comparable yields, but it was concluded that the latter procedure (reverse addition) was somewhat more convenient, and it was adopted for further application.

The data supporting these conclusions are presented in the Experimental section.

Scope of the Reaction.—With the above experience behind us, the following general procedures were adopted. A round-bottom flask, fitted with a stirrer, thermometer, pressure-equalized dropping funnel, and condenser, was flushed with nitrogen and a nitrogen atmosphere maintained until the hydrolysis step. In the flask was placed a standardized solution of lithium aluminum hydride in ether (approximately 1.0 *M*). The flask was immersed in an ice bath and an appropriate quantity of ethyl acetate (1.5 moles per mole of lithium aluminum hydride) was introduced to the stirred solution in approximately 15 to 30 min. to form the reagent. This was followed by dimethylamide in ether (1 mole of amide per mole of reagent), added over a period of 30 min. (with large-scale reactions, these reaction times must be increased to maintain temperature control). The reaction mixture was allowed to stir for 1 hr., and then hydrolyzed with cold 5 *N* sulfuric acid. The aldehyde was recovered from the ether solution. In cases where isolation of the aldehyde was not desired, methanol was added to give a homogeneous solution, and an aliquot removed for aldehyde analysis with 2,4-dinitrophenylhydrazine.

In the case of lithium diethoxyaluminumhydride, the equipment was the same. The reagent was generated by adding 1 mole of ethyl acetate to the solution of lithium aluminum hydride in ether. The reagent was then transferred, over 30 min., with the aid of a transfer tube fitted with a stopcock and slight nitrogen pressure, into a stirred solution of the dimethylamide (2 moles of amide per mole of reagent) in ether at 0°. The solution was allowed to stir for 1 hr. at 0°, and then treated with sulfuric acid or methanol, as described for the triethoxyaluminumhydride procedure.

These standard procedures were then applied to the dimethylamides of some 24 representative acids. In a number of cases, the preparations were carried out on a relatively large scale and the aldehydes were isolated in order to establish that there were no serious dif-

difficulties in utilizing this procedure for preparative scale syntheses.

The experimental results are summarized in Table IV.

TABLE IV
YIELDS OF ALDEHYDES IN REDUCTION OF REPRESENTATIVE ACYL DIMETHYLAMIDES BY LITHIUM DIETHOXYALUMINOHYDRIDE AND TRIETHOXYALUMINOHYDRIDE

Aldehyde produced in reduction of corresponding dimethylamide	Yield of aldehyde, %			
	—Li(EtO) ₃ AlH—		—Li(EtO) ₂ AlH ₂ —	
	By analysis with 2,4-dinitrophenylhydrazine	By isolation	By analysis with 2,4-dinitrophenylhydrazine	By isolation
<i>n</i> -Butyraldehyde	80-90		85-90	
<i>n</i> -Hexaldehyde	82	73	74-80	60-67
Lauraldehyde			90	62
Stearaldehyde			92	
Isobutyraldehyde	82-87		89	
α -Ethylbutyraldehyde			79	
Pivalaldehyde	82-87	74	75	60-63
Cyclohexanecarboxaldehyde	78-83	78	80-85	70-72
Cyclopropanecarboxaldehyde	67		78	
10-Undecenaldehyde	85	73	87	69
Crotonaldehyde	0		0	
Cinnamaldehyde	7		9	
α -Chloropropionaldehyde	87 ^a		84 ^a	
Ethylthioacetaldehyde	70		69	
Phenylacetaldehyde			79	
α -Naphthylacetaldehyde			72	
Benzaldehyde	91	63-70	83	
α -Naphthaldehyde			81	
β -Naphthaldehyde	81	81		
<i>p</i> -Chlorobenzaldehyde	90	84-89	86	78
<i>o</i> -Chlorobenzaldehyde	80		80	77
<i>o</i> -Methoxybenzaldehyde	74		84	
<i>p</i> -Nitrobenzaldehyde	75	60		
Nicotinaldehyde			89	

^a The reaction was run at -20 to -30° .

The yields realized with lithium triethoxyaluminumhydride and with lithium diethoxyaluminumhydride were essentially comparable, ranging generally from 70 to 90% by analysis and from 60 to 80% by isolation for the various structural types examined, with one exception. Apparently, conjugated unsaturated derivatives, such as *N,N*-dimethylcrotonamide and *N,N*-dimethylcinnamamide, undergo attack at the double bond preferentially. Thus the reaction products from *N,N*-dimethylcrotonamide showed both *N,N*-dimethyl-*n*-butyramide and starting material, together with higher boiling materials, but no crotonaldehyde. The same products, although in different amounts, are formed in the attempted reduction of *N,N*-dimethylcrotonamide by lithium aluminum hydride.²³

Otherwise, both reagents proved to be satisfactory for the preparation of representative aliphatic, aromatic, and heterocyclic derivatives. Certain substituents that are normally susceptible to catalytic reduction in the Rosenmund synthesis are not attacked in the present procedure. Thus aliphatic aldehydes containing chloro, thio, and nonconjugated double bonds were obtained in highly satisfactory yield. The low yields encountered in the reduction of certain *o*-substituted aromatic acids by the Weygand⁸ and McFarlin-Subba Rao^{13,15} procedures were not encountered in

(23) Polymerization products were obtained in the related reaction of *N,N*-diethylcrotonamide with lithium aluminum hydride: H. R. Snyder and R. E. Putman, *J. Am. Chem. Soc.*, **76**, 33 (1954).

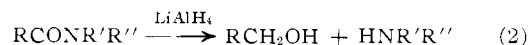
the test cases examined (*o*-chloro- and *o*-methoxybenzaldehyde). Partial reduction of the nitro group was observed in the reduction of *N,N*-dimethyl-*p*-nitrobenzamide with lithium triethoxyaluminumhydride. However, the desired aldehyde, *p*-nitrobenzaldehyde, was still produced in a yield of 75% by analysis and 60% by isolation of recrystallized material.

In view of these results it appears that the proposed procedure is relatively simple to apply and possesses wide applicability as a means of proceeding from the carboxylic acid to the corresponding aldehyde.

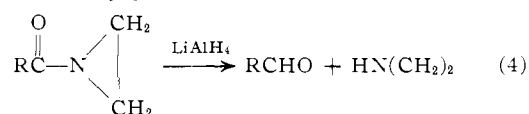
Theoretical Considerations.—The reduction of tertiary amides with excess lithium aluminum hydride generally yields the corresponding tertiary amine (1).²⁴



In some cases, reductive cleavage to alcohol and secondary amine has been observed^{22,25,26} (2).

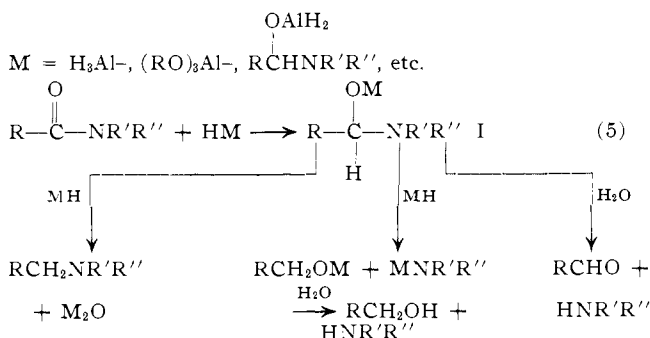


Finally, in the case of certain selected amides it has proved possible to control the reduction to the aldehyde in good yield⁷⁻¹⁰ (3, 4).



Although a number of different mechanisms have been proposed to account for these results,^{7,8,25,27} it appears to us that Weygand's proposal of a single common intermediate⁸ is capable of rationalizing all of the available data.

The first step of the reaction presumably involves a simple addition of the reagent to the carbonyl groups (5), forming the intermediate complex I.



This intermediate can react along three paths. Hydrolysis will convert it into the aldehyde and the amine. Nucleophilic attack by the hydride reagent on the carbon-oxygen bond will form the tertiary amine. Decomposition of the complex to aldehyde (immediately reduced by the reagent to the alcohol stage) and the amine, or a nucleophilic attack by the hydride reagent on the carbon-nitrogen bond, will give the same products following hydrolysis, namely alcohol and secondary amine.

The preparation of aldehydes from disubstituted amides in high yields by hydride reduction depends, therefore, upon an initial addition of 1 equivalent of

(24) R. F. Nystrom and W. G. Brown, *ibid.*, **70**, 3738 (1948).

(25) V. M. Micovic and M. L. Mihailovic, *J. Org. Chem.*, **18**, 1190 (1953).

(26) K. Banholzer, T. W. Campbell, and H. Schmid, *Helv. Chim. Acta*, **35**, 1577 (1952).

(27) N. G. Gaylord, *Experientia*, **10**, 166, 423 (1954).

hydride reagent to the carbonyl group that is considerably faster than any of the possible subsequent reactions.

In the reaction of 1 mole of lithium aluminum hydride with 4 moles of *N,N*-dimethyl-*n*-butyramide, the yield of *n*-butyraldehyde is only 16 to 25% (Table II). Therefore, the subsequent reaction of the initial complex I with a second equivalent of hydride must be faster than the first stage. By utilizing amide derivatives in which the lone pair of the nitrogen is not as available for resonance interaction with the carbonyl group, we increase the reactivity of the latter toward nucleophilic attack and favor the formation of the aldehyde. Thus, the *N*-methylanilide yields *n*-butyraldehyde in a yield of 58% and the aziridine provides the aldehyde in a yield of 88% (Table II).

An increase in the steric requirements of the alkyl group also appears to reduce the rate of the undesired second stage, so that the aldehyde is obtained in reasonable yield. Thus *N,N*-dimethylpivalamide is reduced by lithium aluminum hydride into trimethylacetaldehyde in a yield of 55% (Table III). However, it is obvious that this is usually a factor which is not under the control of the chemist seeking to proceed from a given carboxylic acid to the corresponding aldehyde.

Alternatively, one could increase the steric requirements of the amide group as a means of slowing down the second stage of the reduction. However, there is some evidence that this would require a careful balance between the steric requirements of the amide group and those of the acyl structure, since complexes (I) that are highly strained due to bulky groups in both moieties, exhibit an enhanced tendency to undergo decomposition.²⁸ The situation is further complicated by the fact that the aluminohydride anion itself undergoes a series of drastic changes in its steric requirements as it becomes substituted by one, two, or three amide residues as the reaction proceeds.²⁹

Consequently, it appears that a more practical solution to the problem is to modify the steric requirements of the reducing agent. The introduction of one, two, or three *t*-butoxy groups evidently introduces too large a steric factor, since lithium tri-*t*-butoxyaluminumhydride fails to reduce *N,N*-dimethyl-*n*-butyramide (Table I). Lithium trimethoxyaluminumhydride is not soluble in ether. In diglyme solution it provided reasonable yields, but not as high as those realized with the ethoxy derivatives in ether. It would appear either that the steric requirements of the ethoxy derivatives are more favorable, or that the lower solvating properties of the ether solvent favor association of the lithium cation with the intermediate complex I which is thereby stabilized against further attack.³⁰

Conclusion.—It appears from this study that the selective reduction of tertiary amides by lithium di- and triethoxyaluminumhydride provides a highly convenient synthetic route from the carboxylic acid to the corresponding aldehyde. In view of its simplicity and broad scope, it promises to develop into an important tool in the repertory of the synthetic chemist.

Experimental

Materials.—All commercially available chemicals were carefully purified by standard methods before use. Special care was given to the drying of the solvents, alcohols, and ethyl acetate, utilizing lithium aluminum hydride or calcium hydride as the final drying agents. Lithium aluminum hydride solutions in ethyl ether, tetrahydrofuran, and diethylene glycol dimethyl

ether (diglyme) were prepared and used as clear solutions. The composition of the solutions was established by analysis for hydride (by hydrolysis) and confirmed by analysis for aluminum (with 8-hydroxyquinoline). All apparatus was flamed in a dry nitrogen atmosphere and allowed to cool in that atmosphere prior to use.

Acyl Disubstituted Amides.—Dimethylamides were in most cases prepared from the corresponding acid chlorides and 25% aqueous dimethylamine (procedure A). In a few cases, where the dimethylamides are highly soluble in water, the acid chlorides were treated with anhydrous dimethylamine in ethyl ether or benzene (procedure B). Physical constants and the procedure are summarized in Table V. All the *n*-butyramides, with the exception of the dimethylamide, were prepared from the acid chlorides and secondary amines following procedure B.³¹

Reduction of *N,N*-Dimethyl-*n*-butyramide with Lithium Alkoxyaluminumhydrides (Table I).—The reactions were run under identical conditions, unless indicated otherwise in Table I. The reduction of *N,N*-dimethyl-*n*-butyramide with lithium triethoxyaluminumhydride is typical of the procedure followed. Into a magnetically stirred solution of 10 mmoles of *N,N*-dimethyl-*n*-butyramide in 10 ml. of ethyl ether was added, over a period of 30 min., a solution of 10 mmoles of lithium triethoxyaluminumhydride in 40 ml. of ethyl ether (0.25 *M* solution) under cooling with an ice bath. The reaction mixture was stirred for an additional 1 hr. at the same temperature and decomposed with 20 ml. of methanol. The hydrogen evolved on decomposition was measured to determine the hydride consumption—92% of the theoretical. An aliquot of the reaction mixture was analyzed for the aldehyde with 2,4-dinitrophenylhydrazine.³² The precipitate filtered off was dried over phosphorus pentoxide *in vacuo* to a constant weight. The yield of 2,4-dinitrophenylhydrazone of *n*-butyraldehyde, m.p. 118–120° (lit.³³ 122°), was 89%.

Reduction of Representative Tertiary Amides of Butyric Acid (Table II).—The following is the general procedure. Fifty equivalents of each hydride reagent was added to a stirred solution of 50 mmoles of the *n*-butyramide derivative in 25 ml. of diethyl ether, over a period of 30 min., under cooling with an ice bath. The reaction mixture was stirred for 1 hr. at the same temperature and decomposed with methanol. The hydrogen evolved was measured in order to determine the hydride consumption. An aliquot of the reaction mixture was analyzed for the aldehyde with 2,4-dinitrophenylhydrazine. Ethylenimine and pyrrole are sensitive to mineral acids. Therefore, 1-*n*-butyrylaziridine and *N-n*-butyrylpyrrole were reduced in the same manner as above, but the reaction mixture was decomposed with a saturated aqueous solution of potassium sodium tartrate. An aliquot of the ethereal solution was analyzed for the aldehyde with 2,4-dinitrophenylhydrazine in the case of 1-*n*-butyrylaziridine. In the case of *N-n*-butyrylpyrrole, the ethereal solution was analyzed for *n*-butyraldehyde by gas chromatography (Aerograph, Model A-100-C with 10-ft. silicone column).

Reduction of Selected Dimethylamides (Table III).—The reduction of *N,N*-dimethylpivalamide with lithium diethoxyaluminumhydride is typical. To a stirred solution of 56.8 mmoles of pivalamide in 25 ml. of ethyl ether, was added over a period of 30 min. a slurry of 28.9 mmoles of lithium diethoxyaluminumhydride in 50 ml. of ethyl ether under cooling with an ice bath. The reaction mixture was stirred mechanically for 1 hr. and decomposed with methanol. The reaction product was worked up in the standard manner. The yield of 2,4-dinitrophenylhydrazone of pivalaldehyde, m.p. 208–210° (lit.³⁴ 208–209°), was 76%.

Effect of Reaction Conditions upon Aldehyde Yields. Lithium Triethoxyaluminumhydride.—The reduction was carried out by the standard method using lithium triethoxyaluminumhydride in ethyl ether, changing the conditions as specified in Table VI. The results are summarized in Table VI.

Effect of Reaction Conditions upon Aldehyde Yields. Lithium Diethoxyaluminumhydride.—The reduction was carried out in two ways. The amide was added to the slurry of lithium diethoxyaluminumhydride prepared from ethyl acetate and a solution of lithium aluminum hydride in ethyl ether cooled to –80° (Dry Ice bath). The reaction mixture was allowed to warm up to room temperature in a few hours with stirring. The reaction product was worked up by the standard method (procedure A). The hydride reagent, prepared in the same manner as above at 0°, was added to a stirred solution of amide in ethyl ether over a period of 30 min. under cooling with an ice bath. The reaction was permitted to proceed at 0° for another hour and worked up by the standard method (procedure B). The procedures were com-

(31) See Table III, ref. 10, for physical constants and literature references.

(32) H. A. Iddles and C. E. Jackson, *Ind. Eng. Chem., Anal. Ed.*, **6**, 454 (1934); H. A. Iddles, A. W. Low, B. D. Rosen, and R. T. Hart, *ibid.*, **11**, 103 (1939).

(33) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, pp. 229–230.

(34) C. F. H. Allen, *J. Am. Chem. Soc.*, **52**, 2957 (1930).

(28) A. W. Burgstahler, *J. Am. Chem. Soc.*, **73**, 3021 (1951).

(29) R. Fuchs and C. A. VanderWerk, *ibid.*, **74**, 5917 (1952).

(30) A similar explanation was invoked to account for the difference in results realized in the reduction of aliphatic nitriles with sodium and lithium triethoxyaluminumhydride, and in the use of the latter reagent in ether *vs.* tetrahydrofuran or diglyme (ref. 19).

TABLE V
 PHYSICAL CONSTANTS OF DIMETHYLAMIDES

Amide, N,N-dimethyl-	Procedure	M.p., °C.	-B.p.-----		n_D^{20}	Ref.
			°C.	mm.		
<i>n</i> -Butyramide	A	...	86.0	10	1.4418	a
Caproamide	A	...	88-89	7	1.4460	b
Lauramide	A	...	166.5-168	6	1.4571	c
Stearamide	A	38.5-40.5				d
Isobutyramide	A	...	81-82	28	1.4397	e
α -Ethylbutyramide	A	...	114-116	53.5	1.4449	f
Pivalamide	A	...	85.5	13	1.4451	g
Cyclohexylcarboxamide	A	...	100-100.5	5	1.4822	h
Cyclopropylcarboxamide	A	...	68	3	1.4704	i
Benzamide	A	42-43				j
α -Naphthamide	A	62-63				k
β -Naphthamide	A	87-88				l
<i>p</i> -Chlorobenzamide	A	56.5-57				m
<i>o</i> -Chlorobenzamide	A	...	121-122	4	1.5510	n
<i>o</i> -Methoxybenzamide	A	73.5-74.5				o
<i>p</i> -Nitrobenzamide	A	96.5-97.5				p
Nicotinamide	A	65-66				q
Phenylacetamide	A	43-43.5	120.5	3		r
α -Naphthylacetamide	A	65-66				s
10-Undecenamide	A	...	128-129	2	1.4655	t
α -Chloropropionamide	B	...	86.5-87.0	9	1.4700	u
Ethylthioacetamide	B	...	94.5-95.0	5	1.5014	v
Crotonamide	B	...	89-89.5	8	1.4842	w
Cinnamamide	A	99.5-100.5				x

^a n_D^{20} 1.4391; J. R. Ruhoff and E. E. Reid, *J. Am. Chem. Soc.*, **59**, 401 (1937). ^b n_D^{20} 1.4430; ref. a. ^c *Anal.* Calcd. for $C_{11}H_{23}NO$: C, 73.95; H, 12.85; N, 6.15. Found: C, 74.20; H, 13.00; N, 6.45. ^d M.p. 50.5-51.5°; H. Staudinger and K. Rössler, *Ber.*, **69**, 61 (1936). ^e n_D^{20} 1.4388; H. Rapoport and R. M. Bonner, *J. Am. Chem. Soc.*, **72**, 2783 (1950). ^f *Anal.* Calcd. for $C_8H_{17}NO$: C, 67.09; H, 11.96; N, 9.77. Found: C, 66.18; H, 11.71; N, 9.64. ^g B.p. 186.6° (745 mm.); N. I. Gavrilov, A. V. Koperina, and M. M. Klychareva, *Bull. soc. chim. France*, **21**, 775 (1945). ^h B.p. 135-140° (20 mm.); M. Mousseron, R. Jacquier, M. Mousseron-Conet, and R. Zagdoun, *ibid.*, **19**, 1042 (1952). ⁱ *Anal.* Calcd. for $C_8H_{11}NO$: C, 63.68; H, 9.80; N, 12.38. Found: C, 63.66; H, 9.98; N, 12.59. ^j M.p. 43°; H. Staudinger and N. Kon, *Ann.*, **384**, 114 (1911). ^k M.p. 62°; J. V. Braun, *Ber.*, **37**, 2685 (1904). ^l *Anal.* Calcd. for $C_{10}H_{19}NO$: C, 78.37; H, 6.57; N, 7.03. Found: C, 74.41; H, 6.90; N, 6.81. ^m M.p. 57-58°; A. V. Kirsanov and Yu. M. Zolofov, *Zh. Obshch. Khim.*, **21**, 1166 (1951); *Chem. Abstr.*, **46**, 1968 (1952). ⁿ *Anal.* Calcd. for $C_9H_{10}ClNO$: C, 58.86; H, 5.49; N, 7.63. Found: C, 58.86; H, 5.75; N, 7.79. ^o *Anal.* Calcd. for $C_{10}H_{13}NO_2$: C, 67.02; H, 7.31; N, 7.82. Found: C, 66.98; H, 7.41; N, 7.78. ^p M.p. 97°; H. Wenkner, *J. Am. Chem. Soc.*, **60**, 1081 (1938). ^q M.p. 50°; Y. Hukushima, *J. Chem. Soc. Japan*, **61**, 121 (1940). ^r M.p. 43-44°; ref. e. ^s *Anal.* Calcd. for $C_{14}H_{15}NO$: C, 78.84; H, 7.09; N, 6.57. Found: C, 79.01; H, 7.11; N, 6.76. ^t B.p. 186.5° (20 mm.); M. J. Th. Bornwater, *Rec. trav. chim.*, **26**, 411 (1907). ^u *Anal.* Calcd. for C_8H_9ClNO : N, 10.61. Found: N, 10.32. ^v *Anal.* Calcd. for $C_8H_{13}NOS$: C, 48.94; H, 8.90; N, 9.52. Found: C, 48.95; H, 8.99; N, 9.50. ^w B.p. 91.6-91.8° (14 mm.); K. W. F. Kohlrausch and A. Pongrantz, *Z. physik. Chem.*, **B27**, 193 (1934). ^x *Anal.* Calcd. for $C_{11}H_{13}NO$: C, 75.40; H, 7.47; N, 7.99. Found: C, 75.01; H, 7.76; N, 7.98.

TABLE VI

 EFFECT OF REACTION CONDITIONS ON YIELDS OF ALDEHYDES
 FROM DIMETHYLAMIDES WITH LITHIUM
 TRIETHOXYALUMINOHYDRIDE

Dimethylamide RCON(CH ₃) ₂	Yields of aldehyde, ^a %			
	Procedure A ^b At 0°	Procedure B ^c At 25°	Procedure C ^d At 0°	Proce- dure C ^d At 0°
<i>n</i> -Butyryl	86-92	77-85	80-90	87
<i>o</i> -Chlorobenzoyl	75-85	65	68	81
Pivalyl	87	80	82	87

^a Isolated as 2,4-dinitrophenylhydrazone. ^b A clear solution of lithium triethoxyaluminumhydride was added to the amide; hydride/amide = 1.00. ^c An ether solution of ethanol was added to lithium aluminum hydride followed by addition of amide; hydride/amide = 1.00. ^d Same as procedure B, except that hydride/amide = 1.20.

TABLE VII

 EFFECT OF REACTION CONDITIONS ON YIELDS OF ALDEHYDES
 FROM DIMETHYLAMIDES WITH LITHIUM
 DIETHOXYALUMINOHYDRIDE^a

Dimethylamide RCON(CH ₃) ₂	Yield of aldehyde, ^b %	
	Procedure A	Procedure B
<i>n</i> -Butyryl	80-83	85-90
Isobutyryl	78	80-85
Pivalyl	52	72-77
Caproyl	85	84-91

^a The mole ratio of lithium diethoxyaluminumhydride to amide was 0.5. ^b Isolated as 2,4-dinitrophenylhydrazone.

pared with respect to aldehyde yields and the results are summarized in Table VII.

TABLE VIII

 EFFECT OF HYDRIDE/AMIDE RATIO ON YIELDS OF ALDEHYDES
 FROM DIMETHYLAMIDES WITH LITHIUM
 DIETHOXYALUMINOHYDRIDE^a

Ratio hydride/amide	Temp., °C.	Aldehyde yield, ^b %		
		<i>n</i> -Butyryl	<i>n</i> -Caproyl	Cyclohexane carbonyl
1.00	0	80-90	79	74
1.00	c	...	77	72
1.10	0	89-91	90	80
1.10	c	...	79	81
1.20	0	88	91	83
1.20	c	89
1.30	0	...	90	90
1.30	c	83
1.40	0	...	85	83
1.40	c	79
1.50	0	80	82	82
1.50	c	80
2.00	0	66	...	50
2.00	c	52

^a The reaction was run for 1 hr. at the specified temperature by reverse addition; 50 mmoles of amide was used. ^b Isolated as 2,4-dinitrophenylhydrazone. ^c The reagent was added to a stirred solution of amide at room temperature. The reaction mixture was stirred for 30 min. at room temperature and refluxed for 30 min.

The effect of the mole ratio of the hydride to amide on the aldehyde yield was explored. The results are summarized in Table VIII.

TABLE IX
 YIELDS AND PHYSICAL CONSTANTS OF ALDEHYDES PREPARED BY LITHIUM TRIETHOXYALUMINOHYDRIDE

Amide, N,N-dimethyl-	Ratio hydride/ amide	Temp., °C.	Aldehyde					
			Yield, %	M.p., °C.	B.p., °C.	mm.	n_D^{20}	Ref.
Caproamide	1.0	0	73		122-126	750	1.4308	^a
Pivalamide	1.0	0	74		70-70.5	740	1.3788	^b
Cyclohexanecarboxamide	1.0	0	78		74-78	18	1.4499	^c
Benzamide	1.2	0	68		52-54	7	1.5450	^d
α -Naphthamide	1.2	0	81	62.4-63.0				^e
<i>p</i> -Chlorobenzamide	1.2	0	88	46.5-47.0				^f
<i>p</i> -Nitrobenzamide	1.2	0	73	100-105				^g
10-Undecenamide	1.0	0	53		99-102	10	1.4428	^h

^a B.p. 124-126° (747 mm.); G. B. Bachman, *J. Am. Chem. Soc.*, **55**, 4281 (1933). ^b B.p. 71-74° (730 mm.), n_D^{20} 1.3791; K. N. Campbell, *ibid.*, **59**, 1982 (1937). ^c B.p. 75-78° (20 mm.), n_D^{20} 1.4499; ref. 35. ^d B.p. 63-64° (13 mm.), n_D^{20} 1.5446; H. B. Hass and M. L. Bender, *J. Am. Chem. Soc.*, **71**, 1767 (1949). ^e M.p. 60-61°; P. P. T. Sah, *Rec. trav. chim.*, **59**, 1021 (1940). ^f M.p. 46-47°; "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 133. ^g M.p. 106°; ref. *f*, p. 441. ^h B.p. 101-103° (10 mm.); ref. 36.

 TABLE X
 YIELDS AND PHYSICAL CONSTANTS OF ALDEHYDES PREPARED BY LITHIUM DIETHOXYALUMINOHYDRIDE

Amide, N,N-dimethyl-	Ratio hydride/ amide	Temp., °C.	Aldehyde					
			Yield, %	M.p., °C.	B.p., °C.	mm.	n_D^{20}	Ref.
Caproamide	1.1	0	67	...	124-126	746	1.4038	^a
Lauramide	1.1	0	62	39-41	123-125	15	1.4345	^b
Pivalamide	1.1	25	63	...	70-72.5	747	1.3788	^c
Cyclohexanecarboxamide	1.1	25	72	...	76.5-77.5	18	1.4495	^d
<i>p</i> -Chlorobenzamide	1.1	25	78	46-47	^e
<i>o</i> -Chlorobenzamide	1.1	25	77	...	84.5-86.5	12	1.4657 ^h	^f
10-Undecenamide	1.1	0	69	...	100	10	1.4421	^g

^a B.p. 124-126° (747 mm.); G. B. Bachman, *J. Am. Chem. Soc.*, **55**, 4281 (1933). ^b B.p. 238°, m.p. 38-39.5°; R. R. Davis and H. H. Hodgson, *J. Chem. Soc.*, 84 (1943). ^c B.p. 71-74° (730 mm.), n_D^{20} 1.3791; K. N. Campbell, *J. Am. Chem. Soc.*, **59**, 1982 (1937). ^d B.p. 75-78° (20 mm.), n_D^{20} 1.4499; ref. 35. ^e M.p. 46-47°; "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 133. ^f n_D^{21} 1.56564; K. von Auwers, *Ann.*, **422**, 162 (1920). ^g B.p. 101-103° (10 mm.); ref. 36.

Preparation of Cyclohexanecarboxaldehyde with Lithium Triethoxyaluminumhydride.—The following procedure is representative of the preparative scale syntheses utilizing lithium triethoxyaluminumhydride.

In a 1-l., three-necked flask equipped with a condenser, a mechanical stirrer, and a dropping funnel was placed 0.375 mole of lithium aluminum hydride in ethyl ether (1.25 *M* solution) cooled by an ice bath. To the stirred solution of the hydride was added over a period of 2 hr. 0.563 mole of ethyl acetate. The reaction mixture was stirred for 30 min. at 0°. To the stirred slurry of the hydride reagent thus prepared, cooled with an ice bath, was added 58.2 g. (0.375 mole) of N,N-dimethylcyclohexanecarboxamide as rapidly as possible while avoiding too vigorous refluxing of the ethyl ether. The reaction mixture was stirred for 1 hr. at the same temperature and then decomposed with 5 *N* sulfuric acid. The ether layer was separated and the aqueous layer was extracted twice with 100-ml. portions of ether. The combined ether solution was washed with water, shaken with solid sodium bicarbonate, and washed again with water and dried over sodium sulfate. The ether was distilled off and the residue distilled at 74-78° (20 mm.), n_D^{20} 1.4499 [lit.³⁵ b.p. 77-78° (20 mm.), n_D^{19} 1.4505], yield 32.8 g., 78% of the theoretical.

In Table IX are reported the yields and properties of the aldehydes synthesized by application of this general procedure.

Preparation of 10-Undecenal by Lithium Diethoxyaluminumhydride in Ethyl Ether.—The following procedure is representative of the preparative scale syntheses utilizing lithium diethoxyaluminumhydrides. In a 500-ml., three-necked flask equipped with a condenser, a mechanical stirrer, and a dropping funnel was placed 220 ml. of 1.25 *M* solution of lithium aluminum hydride (2.75 moles) in ethyl ether. To the stirred solution of lithium aluminum hydride cooled by an ice bath was added over a period of 2 hr. 24.45 g. (0.275 mole) of ethyl acetate. The resulting hydride reagent (contained white precipitates) was transferred over a period of 30 min. by means of a bridge provided with a stopcock to a stirred solution of 105.2 g. of N,N-dimethyl-9-decenecarboxamide in 100 ml of anhydrous ether at 0°. The reaction mixture was stirred for 1 hr. at 0° and decomposed with 200 ml. of 3 *N* sulfuric acid under cooling. The ether layer was separated and the aqueous layer was washed with two 100-ml. portions of ether. The combined ether layer was washed with water, shaken with solid sodium bicarbonate, and again washed with water and dried over magnesium sulfate. The ether was distilled off and 10-undecenal distilled at 100° (10 mm.) [lit.³⁶ b.p. 101-103° at 10 mm.]; yield 58.4 g., 69.3% of the theoretical.

In Table X are reported the yields and properties of aldehydes synthesized by application of this general procedure.

(35) V. M. Rodinov and T. S. Kislera, *Chem. Abstr.*, **48**, 570 (1954)

(36) C. Grundmann, *Ann.*, **524**, 31 (1936).