from a small amount of insoluble matter, and chromatographed on 30 g. of acid-washed alumina. The first fraction was hexachloroethane, 0.63 g.

The second fraction, 3.0 g. of a colorless liquid, n_D^{27} 1.5842 was identified as *p*-chlorodiphenylmethane by identity of infrared spectrum with that of authentic material and by chromic acid oxidation in acetic acid to *p*-chlorobenzophenone, m.p. 73–74° after recrystallization from ethanol, mixture m.p. 73–74°. The *p*-chlorodiphenylmethane fraction gave a single peak on gas phase chromatography on a firebrick-silicone column with no peak at the position shown by an authentic sample of diphenylmethane. The third fraction, eluted from the alumina by ether, was a semisolid which resisted attempts at purification. The infrared spectrum was similar to but not identical with that of *p*-benzylphenyl *p*-benzylbenzoate.

Kinetic determinations were made in carbon tetrachloride at 80°, following the peroxide concentration by iodometric analysis.[27] Initial concentrations closely approximated the conditions of the product studies. The data are summarized in Table IV.

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CAMBRIDGE 39, MASS.

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(27) F. D. Greene, *J. Am. Chem. Soc.*, **78**, 2254 (1956).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MARYLAND]

Cleavage of Tetrahydrofuran during Reductions with Lithium Aluminum Hydride[1]

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A mixture of aluminum chloride and lithium aluminum hydride was shown to cleave tetrahydrofuran to *n*-butyl alcohol. There appears to be a direct relationship between the maximum amount of *n*-butyl alcohol produced under extended reflux and the theoretical amount of aluminum hydride produced. Although the reduction of most compounds with lithium aluminum hydride in tetrahydrofuran does not result in cleavage, the reduction of alkyl halides and benzylphosphonium halides under these conditions gave *n*-butyl alcohol and hydrocarbon in nearly equivalent amounts. Dioxane, diethoxyethane and di-*n*-butyl ether were cleaved with the mixed reagent, but at a much slower rate than was tetrahydrofuran.

Because of its unique solvent properties tetrahydrofuran has found extensive and successful use as a solvent for reductions with lithium aluminum hydride. However, during an investigation of the reductive cleavage of benzylphosphonium compounds[3] with lithium aluminum hydride in tetrahydrofuran, it was found that an excess of hydride was required for high yields and *n*-butyl alcohol was formed as a by-product by the reductive cleavage of the solvent. Therefore, a research program was undertaken in order to investigate this unusual reductive cleavage.

In general, the ether bond is resistant to attack by lithium aluminum hydride and other complex hydrides at temperatures to 80–100°.[4,5] When the oxygen is part of a ring possessing strain, such as ethylene oxide and thebain, or containing the N—C—O— grouping, cleavage takes place, but ordinary cyclic ethers, such as tetrahydrofuran, tetrahydropyran, and dioxane, are reported to be stable. Of course, activated ethers, such as allyl ethers and cyclohexyloxyacetic acid,[6] are known to be cleaved under vigorous conditions. It has been reported[7] that during the reduction of active carbon dioxide at 0° or active acetyl chloride at −78° in diethyl carbitol 4 to 7% of inactive ethanol was formed. In addition, Karrer *et al.*,[8] showed that lithium aluminum hydride in the presence of cobaltous chloride would cleave phenyl benzyl and phenyl allyl ethers in refluxing ethyl ether.

More recently, a mixture of lithium aluminum hydride and aluminum chloride has been suggested as a more specific reducing agent.[9] Eliel *et al.*[10] recently have applied this reagent to the reduction

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[1] This work was done in fulfillment of a contract with the Army Chemical Corps.

[2] Army Chemical Corps Postdoctoral Fellow, 1957–59.

(3) W. J. Bailey, S. A. Buckler, and F. Marktscheffel, *J. Org. Chem.*, in press.

(4) P. Karrer, *Angew. Chem.*, **62**, 334 (1950).

(5) N. G. Gaylord, *Reductions with Complex Metal Hydrides*, Interscience Publishers, Inc., New York, N.Y., 1956.

(6) M. Mousseron, M. R. Jacquier, M. Mousseron-Cavet, and R. Zagdoun, *Bull. soc. chim. France*, [5] **19**, 1042 (1952).

(7) J. D. Cox and R. J. Warne, *Nature*, **165**, 563 (1950); J. D. Cox and R. J. Warne, *J. Chem. Soc.*, 3167 (1950); and R. Ostwald, P. T. Adams, and B. M. Tolbert, *J. Am. Chem. Soc.*, **74**, 2425 (1952).

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(9) B. R. Brown, *J. Chem. Soc.*, 2756 (1952); E. Wiberg and A. Jahn, *Z. Naturforsch.*, **7b**, 580 (1952); R. F. Nystrom, *J. Am. Chem. Soc.*, **77**, 2544 (1955).

(10) E. L. Eliel and M. Rerick, *J. Org. Chem.*, **23**, 1088 (1958); E. L. Eliel and V. G. Badding, *J. Am. Chem. Soc.*, **81**, 6087 (1959).

TABLE I

CLEAVAGE OF TETRAHYDROFURAN

Experiment No.	$LiAlH_4$,[a] Mole	$AlCl_3$,[b] Mole	Tetrahydrofuran, Ml.	Temp., °C.	Time of Heating, Hr.	Method of Addition of Reactants[c]	Isolation Procedure[d]	Yield of *n*-Butyl Alcohol, G.	Yield Based on AlH_3, %
1[e]	0.166	0.0395[f]	350	Reflux	11	M	A	12.1	103
2[g]	0.216	0.052[h]	700	Reflux	25.5	M	A	24.0	156
3[g]	0.19	0.048[h]	1150	Reflux	20	M	A	20.7	146
4	0.1	0.15	414	Reflux	13.8	N	B	11.7	119
5	0.1	0.1	364	Reflux	12	O	B	10.2	104
6	0.1	0.033	264	Reflux	13.8	N	B	11.5	117
7	0.05	0.005	132	Reflux	13.8	N	B	0.18	12
8A	0.075	0.0228	200	30	3	N	C	0.29	4
8B	0.075	0.0228	200	30	71	N	C	1.55	21
9A	0.04	0.0133	106	105–110	1	N	D	0.67	17
9B	0.04	0.0133	106	105–110	3	N	D	1.66	42
9C	0.04	0.0133	106	105–110	16	N	D	3.32	84
10A	0.04	0.0133	106	105–110	16	N	D	3.67	93
10B	0.04	0.0133	106	105–110	24	N	D	3.83	97
11	0.04	0.0133	106	105–110	26	N	D	3.95	100
12	0.04	0.0133[i]	100	81	17.5	N	D	1.93	49
13A	0.04	0.0133[i]	100	80	73	N	D	2.29	58
13B	0.04	0.0133[i]	100	80	145	N	D	2.61	66
14	0.04	0.0133[i]	100	100	24	N	D	3.39	86
15A	0.04	0.0133[i]	100	100	72	N	E	3.27	83
15B	0.04	0.0133[i]	100	100	144	N	E	3.32	84
16	0.107	0.033	170[j]	Reflux	9	P	F	3.78	96
17	0.04	0.0133[i]	100	100	24	N	D	2.52	64

[a] Added as a standard solution in tetrahydrofuran unless otherwise specified. [b] Commercial grade unless otherwise specified. [c] Method M involved the formation of aluminum chloride or aluminum hydride during the reaction by reduction of a halogen compound. Method N involved the addition of a solution of aluminum chloride in tetrahydrofuran to the solution of lithium aluminum hydride. Method O involved the addition of a solution of lithium aluminum hydride in tetrahydrofuran to a solution of aluminum chloride. Method P involved the addition of a lithium aluminum hydride solution to a benzene solution of aluminum chloride. [d] Method A involved the decomposition of the reaction mixture with a 20% sodium potassium tartrate solution, followed by extraction with ether and subsequent concentration of products. Method B involved removal of 70–85% of the tetrahydrofuran by distillation at atmospheric pressure, followed by decomposition of the residue with cold dilute sulfuric acid. Method C involved the removal of the tetrahydrofuran under reduced pressure over a 1-hr. period and treatment of the residue as in method B. Method D involved the removal of the tetrahydrofuran from the cold reaction mixture under 30–35 mm. pressure, followed by treatment of the residue as in method B. Method E involved the cooling of the reaction mixture with ice for 15 min. before treatment as in method D. Method F involved the direct decomposition of the reaction mixture with dilute sulfuric acid. [e] Reduction of benzyl chloride. [f] No aluminum chloride added; maximum amount theoretically produced from reduction of the benzyl chloride. [g] Reduction of methylethylpentylphosphonium iodide. [h] No aluminum chloride added; maximum amount theoretically produced from reduction of methylethylpentylphosphonium iodide. [i] Sublimed aluminum chloride. [j] Plus 60 ml. of benzene.

of acetals and ketals to the corresponding ethers and of cyclic acetals and cyclic hemithioacetals to the corresponding hydroxyethers and thioethers. A similar reagent, hydrogen chloride or bromide plus lithium aluminum hydride or sodium borohydride, has been used to cleave the acetal ring of spirostanols or spirostenols of sapogenins.[11] The use of *p*-toluenesulfonic acid or hydrogen sulfide in place of the hydrogen chloride was ineffective.

Although the electrophilic cleavage of tetrahydrofuran, such as polymerization with boron trifluoride[12] and formation of δ-chlorobutyl acetate with acetyl chloride and zinc chloride,[13] is known, the reductive cleavage has not been reported. By use of vapor-phase chromatography we have verified that, in contrast to the reduction of the benzylphosphonium compounds which produced an equivalent amount of *n*-butyl alcohol,[3] the reduction of acetone in tetrahydrofuran or treatment of tetrahydrofuran alone with an excess of lithium aluminum hydride produced no detectable amount of *n*-butyl alcohol. Similarly, the addition of sodium chloride or lithium chloride had no effect. However, when benzyl chloride was reduced with an excess of lithium aluminum hydride, toluene plus nearly an equimolar amount of *n*-butyl alcohol were formed. Similarly, when aluminum chloride was added to tetrahydrofuran plus lithium aluminum hydride, *n*-butyl alcohol was produced. A reasonably comprehensive study was conducted on the reduction with the aluminum chloride-lithium aluminum hydride mixture, and the results are listed in Table I. Because of the difficulty in the determination of small quantities of *n*-butyl alcohol in a relatively large volume of tetrahydrofuran, the experiments were carried out on a large scale. Even so, the values are probably accurate only

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(11) H. M. Doukas and T. D. Fontaine, *J. Am. Chem. Soc.*, **73**, 5917 (1951); **75**, 5355 (1953).

(12) H. Meerwein, *Angew. Chem.*, **59**, 168 (1947).

(13) I. H. Helberger and H. Lautermann, *Ann.*, **586**, 158 (1954).

TABLE II

CLEAVAGE OF OTHER ETHERS

Solvent	Volume, Ml.	$LiAlH_4$,[a] Mole	$AlCl_3$,[b] Mole	Temp., °	Time of Heating, Hr.	Method of Addition of Reactants[c]	Isolation Procedure[d]	Product	Yield, G.
Di-*n*-butyl ether	340	0.1	0.033	Reflux	26.5	N	F	*n*-Butyl alcohol	0.45
Dioxane	720	0.1	0.033	Reflux	31	N	F	2-Ethoxyethanol	0.91
Dioxane	720	0.1	0.033	Reflux	24	N	F	2-Ethoxyethanol	0.87
1,2-Diethoxyethane	400	0.198	0.0606	95–105	24	N	F	2-Ethoxyethanol	4.16

[a–d] See footnotes for Table I.

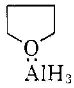
within ±10%. Nevertheless, the total number of experiments allows several definite conclusions: (1) The amount of *n*-butyl alcohol produced does not appear to depend on the order of addition of the three components. (2) The amount of *n*-butyl alcohol increases with increasing temperatures and time of reaction, reaching a maximum value after the mixture is heated under reflux from ten to twenty hours. (3) Although a variation in the ratio of aluminum chloride to lithium aluminum hydride from 1:0.68 to 1:3 did not appreciably affect the amount of *n*-butyl alcohol produced, there did appear to be a relationship between the amount of aluminum hydride that could be produced and the amount of alcohol obtained. If it is assumed that the equation[5]

$$AlCl_3 + 3LiAlH_4 \longrightarrow 4AlH_3 + 3LiCl$$

is applicable to these conditions, a fair agreement is obtained between the maximum amount of *n*-butyl alcohol produced and the maximum amount of aluminum hydride present, as indicated in the last column of Table I. Although this relationship holds quite well for the reduction of benzyl chloride with lithium aluminum hydride, more butyl alcohol is produced during the reduction of the benzylphosphonium salts than this relationship would predict. Since it has been shown that the reduction of alkyl halides takes place in two steps with the first step quite rapid,[14] one would expect that with an excess of hydride the reaction would proceed as follows:

$$C_6H_5CH_2Cl + LiAlH_4 \longrightarrow C_6H_5CH_3 + LiCl + AlH_3$$

The reduction of the benzylphosphonium salts may be more complex. Although Wiberg and Gösele[15] reported that no reductive cleavage of tetrahydrofuran occurred with aluminum hydride, an apparent duplication of their experimental conditions in our laboratory produced *n*-butyl alcohol[16] but in a lower yield than obtained in the other reductions with lithium aluminum hydride. Since it has been shown that aluminum hydride and tetrahydrofuran form a 1:1 complex and that the strength of the complex actually increases the reducing power of lithium aluminum hydride by aiding in the removal of a hydride ion,[17] it seems probable that this complex is involved in the reductive cleavage. The function of the aluminum complex apparently is to weaken the carbon-oxygen bond so that a rearrangement or an attack by a hydride reagent can proceed. Much more extensive data are required before an exact mechanism can be formulated with any certainty.



Since extensive cleavage took place with tetrahydrofuran, a study with other solvents that have been used for reductions with either lithium aluminum hydride alone or in mixtures with aluminum chloride was undertaken and the results are summarized in Table II. Thus at 105–110° 1,2-diethoxyethane and dioxane gave 19 and 8% yields, respectively, of 2-ethoxyethanol based on aluminum hydride, while di-*n*-butyl ether gave a 5% yield of *n*-butyl alcohol. The yield of the cleavage product appears to increase with the stability of the π-complex with aluminum hydride.

It can be concluded that tetrahydrofuran is not a good solvent for reductions with the lithium aluminum hydride–aluminum chloride reagent unless the reduction proceeds extremely rapidly. If a long period of reflux is required, a solvent with a much lower complexing power should be selected.

EXPERIMENTAL

All solvents were freshly distilled from lithium aluminum hydride before use. The amounts of each product of the reaction were determined by vapor-phase chromatography on a Perkin-Elmer Vapor Fractometer, Model 154-B. An internal standard of benzene or toluene was used with the "C" column (silicone grease on Celite). All heating under reflux was carried out with a heating mantle unless specified. When part of the solvent was removed by distillation at atmospheric pressure before further treatment of the residue, this time is included in the indicated reaction time. The reductions of acetone, benzyl chloride, and phosphonium

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[14] J. E. Johnson, R. H. Blizzard, and H. W. Carhart, *J. Am. Chem. Soc.*, **70**, 3664 (1948).

[15] E. Wiberg and W. Gösele, *Z. Naturforsch.*, **11b**, 485 (1956).

[16] In a private communication Dozent Dr. W. Zeil, Phys. Chem. Inst., Technische Hochschule, Karlsruhe, Germany, reported spectroscopic evidence for the cleavage of tetrahydrofuran by aluminum hydride.

[17] L. W. Trevoy and W. G. Brown, *J. Am. Chem. Soc.*, **71**, 1675 (1949); N. L. Paddock, *Nature*, **167**, 1070 (1951).

salts were carried out in a three-necked flask equipped with a mechanical stirrer. All other reductions were carried out by heating under reflux without stirring.

The standard solutions of lithium aluminum hydride in tetrahydrofuran were prepared as follows: A mixture of 62 g. of hydride in 2 l. of solvent was heated under reflux for 6 hr., cooled overnight and then filtered through glass wool under nitrogen. The concentration of lithium aluminum hydride was determined by the addition of an excess of 0.1*N* hydrochloric acid, followed by back-titration with standard 0.1*N* sodium hydroxide solution and by the addition of an excess of a standard solution of iodine in benzene, followed by back-titration with a standard sodium thiosulfate solution.[18]

Reduction of benzyl chloride in tetrahydrofuran. To a stirred solution of 6.3 g. (0.166 mole) of lithium aluminum hydride in 300 ml. of tetrahydrofuran, heated under reflux, was added a solution of 20.0 g. (0.158 mole) of benzyl chloride in 50 ml. of tetrahydrofuran over a 30-min. period. After the solution had been heated under reflux for an additional 5.6 hr., 270 ml. of tetrahydrofuran was removed by distillation through an 18-inch, helix-packed column over a 5-hr. period. The residue was diluted with 300 ml. of ether and cooled in an ice bath while 400 ml. of a 20% sodium potassium tartrate solution was added. After the aqueous layer was extracted with two 75-ml. portions of ether, the combined ether layers were dried over magnesium sulfate. The solvents were removed by distillation through a 10-inch, helix-packed column to yield 25.3 g. of a residue which was shown by vapor-phase chromatographic analysis to contain 12.1 g. (0.163 mole) of *n*-butyl alcohol and 12.5 g. (86%) of toluene as well as 0.7 g. of tetrahydrofuran.

A similar experiment with acetone in place of benzyl chloride gave no amount of *n*-butyl alcohol detectable by vapor-phase analysis, as described above.

Cleavage of tetrahydrofuran with a lithium aluminum hydride–aluminum chloride mixture. To a standard solution containing 1.52 g. (0.04 mole) of lithium aluminum hydride in 66 ml. of tetrahydrofuran was added as rapidly as possible with shaking a mixture of 1.78 g. (0.0133 mole) of aluminum chloride in 40 ml. of tetrahydrofuran. During the addition the solution became warm and a white fog (not hydrogen chloride) was produced. After the mixture had been heated under mild reflux for 26 hr. in an oil bath (105–110°),[19] most of the tetrahydrofuran was removed by distillation under reduced pressure (15 mm.) at room temperature over a 30-min. period. The residue was added to dilute sulfuric acid (prepared from 15 ml. of concd. sulfuric acid, 60 g. of ice and 86 ml. of water), and the resulting solution was extracted with three 50-ml. portions of ether. The ether extracts were then extracted with 40 ml. of a 5% sodium bicarbonate solution and two 20-ml. portions of water. The combined aqueous extracts were neutralized and extracted with 30 ml. of ether. After the combined ether layers had been dried over magnesium sulfate, the ether plus some tetrahydrofuran was removed by distillation through a 10-inch, helix-packed column. An analysis of the residue by vapor-phase chromatography showed the presence of 3.96 g. (0.0535 mole) of *n*-butyl alcohol. (In a similar vapor-phase analysis of the distillates, no additional *n*-butyl alcohol was detected.) If it is assumed that 1.78 g. (0.0133 mole) of aluminum chloride can yield 1.6 g. (0.0532 mole) of aluminum hydride and that 1 mole of *n*-butyl alcohol is produced for every mole of aluminum hydride present, 3.95 g. (0.0532 mole) of *n*-butyl alcohol is expected. On this basis, the actual amount of *n*-butyl alcohol obtained was 100.3% of the theoretical amount.

Cleavage of tetrahydrofuran with aluminum hydride. A solution of 1.72 g. (0.04 mole) of lithium aluminum hydride in 100 ml. of dry ether was heated under reflux for 5 hr. and then transferred through a fritted-glass filter into a solution of 1.72 g. (0.0133 mole) of freshly sublimated aluminum chloride in 200 ml. of dry ether. After the mixture had been allowed to stand for 10 min., it was filtered and the ether was removed from the filtrate by distillation under reduced pressure at 0°. To the dry residue was added 100 ml. of tetrahydrofuran, and the resulting solution was heated for 24 hr. at 100°. (The solution then contained a small amount of a gray precipitate.) When the solution was worked up as described above, the vapor-phase chromatographic analysis showed the presence of 2.52 g. (0.034 mole) of *n*-butyl alcohol. With the stated assumptions, this corresponds to a 64% yield.

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[18] H. Felkin, *Bull. soc. chim. France*, [5] **18,** 347 (1951).

[19] After the mixture had been heated for about 2 hr., there was observed a gray voluminous precipitate which was not dissolved by the dilute sulfuric acid during decomposition of the mixture. Wiberg and Gösele[15] observed a similar precipitate from the heating of a solution of aluminum hydride in tetrahydrofuran.

[Contribution from the Department of Chemistry, University of Maryland]

Polymers. III. Synthesis of Optically Active Stereoregular Polyolefins[1-3]

WILLIAM J. BAILEY and EDWIN T. YATES[4]

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Polymerization of optically active 3-methyl-1-pentene, $[\alpha]^{25}_{D}$ +33.49°, with a Ziegler catalyst gave a low melting atactic fraction, $[\alpha]^{23}_{D}$ + 94.9°, and a high melting isotactic fraction, $[\alpha]^{25}_{D}$ − 257°. The high melting fraction, m.p. 271–278°, was insoluble in boiling xylene but soluble in boiling 1,1-ditolylethane and was almost entirely crystalline. In contrast, the polymer from *dl*-3-methyl-1-pentene melted at 229–237°, was soluble in boiling 1,1-diphenylethane, and was composed of equal parts of amorphous and crystalline phases. Copolymerization of a mixture containing 40% *d*-3-methyl-1-pentene and 60% 4-methyl-1-pentene gave a copolymer with $[\alpha]^{26}_{D}$ +112.4°.

In a program to determine the correlation of chemical structure with physical properties of polymers, the effect of symmetry on the crystallinity of polymers has been of particular interest. Earlier

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[1] Previous paper in this series, *J. Org. Chem.*, **24,** 545 (1959).

[2] Presented before the Division of Polymer Chemistry at the 137th Meeting of the American Chemical Society, Cleveland, Ohio, April 1960.

[3] This work was supported in part by a grant from the National Science Foundation.

[4] Office of Naval Research Fellow, 1955–57; Goodyear Tire and Rubber Co. Fellow, 1957; Dunlop Research Fellow, 1957–58.