[CONTRIBUTION FROM RESEARCH DEPARTMENT, STANDARD OIL COMPANY (INDIANA)]

The Action of Lithium Aluminum Hydride on Organic Disulfides

BY ROBERT C. ARNOLD, ARTHUR P. LIEN AND ROBERT M. ALM

Lithium aluminum hydride has been well characterized as a powerful reducing agent for many types of organic compounds. For example, it is effective in reducing aldehydes and ketones to alcohols,[1] organic acids and their derivatives to alcohols,[1,1a] nitriles to amines,[1] and alkyl chlorides to hydrocarbons.[1b] However, its action on organic disulfides has not been noted in the literature.

We have found that lithium aluminum hydride reduces organic disulfides rapidly and smoothly to give high yields of the corresponding mercaptans. This reaction is interesting in that the disulfide molecule is split at the sulfur–sulfur linkage to form a lithium–aluminum complex while the hydrogen of the hydride is liberated as a gas. Mercaptans are obtained on hydrolysis of the complex with dilute acid.

Although the reaction rate of disulfides with lithium aluminum hydride is dependent on the structure of the groups attached to sulfur, conditions have been found that give essentially quantitative reduction in all cases. Methods reviewed by Ball[2] for the quantitative determination of disulfides are not entirely satisfactory, especially in cases where only very small amounts of disulfides are present. It is possible that the lithium aluminum hydride reaction might be used, not only for disulfide reduction *per se*, but also as the basis for a quantitative procedure for determining disulfides. The analytical application of this reaction is being investigated.

Trevoy and Brown[3] have suggested a common reaction mechanism for lithium aluminum hydride reduction of compounds having electronegative elements—such as oxygen, nitrogen or halogen—attached to carbon. Their mechanism proposed a nucleophilic displacement on carbon by complex hydride ions. If disulfides reacted according to such a mechanism, hydrocarbons would be formed rather than the observed mercaptans. The reduction of disulfides, proceeding by scission of a sulfur–sulfur bond, therefore must involve a different reaction mechanism from that proposed by Trevoy and Brown for compounds having carbon attached to oxygen, nitrogen or halogen.

Experimental

Materials.—Lithium aluminum hydride was purchased from Metal Hydrides, Inc., Beverly, Massachusetts. At the time the present investigation was made, it had an activity of about 93%, as determined by measurement of hydrogen liberated from a known amount of hydride on reaction with water. Diethyl ether was treated with metallic sodium or was distilled from lithium aluminum hydride to remove moisture. Tetrahydrofuran was treated with sodium hydroxide pellets to remove peroxides and was dried in the same manner as ethyl ether. The source of the various disulfides is indicated in Table I; unless otherwise indicated, they were used without further purification.

Procedure.—The experimental procedure used in this work is illustrated by the following example, in which di-*n*-butyl disulfide was reduced to *n*-butyl mercaptan.

(a) **Preparation of Disulfide.**—Di-*n*-butyl disulfide was prepared by oxidizing *n*-butyl mercaptan (Eastman Kodak Co.) following the procedure of Ritter and Sharpe.[4] Fractionation of the *n*-butyl mercaptan through a 20-plate column packed with glass helices gave a center cut boiling at 97.0–97.4° (760 mm.). This material was then oxidized at a reaction temperature of 15° with 30% hydrogen peroxide in glacial acetic acid. Distillation of the product gave di-*n*-butyl disulfide, b. p. 102.0–102.4° (10 mm.), along with a small amount of unreacted mercaptan.

(b) **Reduction of Disulfide.**—Lithium aluminum hydride, 13.17 g. (0.348 mole), was placed in a carefully dried 1-liter, 3-necked flask equipped with a reflux condenser and a mercury sealed stirrer. Dry solvent was introduced by distilling 500 ml. of ethyl ether from a solution of lithium aluminum hydride directly into the reaction flask. The previously prepared di-*n*-butyl disulfide, 81.30 g. (0.457 mole), was then added dropwise to the ether solution of lithium aluminum hydride over a period of about one-half hour. The disulfide reacted vigorously with the hydride and liberated hydrogen gas, which was taken off the top of the reflux condenser through a Dry Ice-cooled trap, to remove entrained ether, and was collected in a 5-gal. carboy by water displacement. Following the addition of disulfide, the reaction mixture was refluxed for twenty minutes, after which no further reaction was indicated by hydrogen evolution. The volume of hydrogen collected was 0.456 mole. Excess lithium alumium hydride was destroyed by the slow addition of water to the reaction mixture cooled to 0°. During hydrolysis, an additional 0.372 mole of hydrogen was liberated.

The reaction mixture was then acidified with 15% sulfuric acid, and the ether layer containing the mercaptan was isolated in a separatory funnel. The ether layer was washed with water, which was then added to the previous aqueous extract. The combined aqueous extracts were saturated with sodium chloride and extracted once with additional ether. The ether layers were combined, washed with water and with saturated salt solution and dried over anhydrous sodium sulfate. Fractionation of the ether solution gave 78.5 g. of mercaptan, b. p. 97–98° (760 mm.), $n^{20}_{\rm D}$ 1.442; the % sulfur as mercaptan, determined by potentiometric titration with silver nitrate, was 35.5%. The physical properties of *n*-butyl mercaptan given by Haines, *et al.*,[5] are: b. p. 97.6° (760 mm.), $n^{20}_{\rm D}$ 1.443; the calculated % sulfur is 35.6. The yield of material boiling at 97–98° was 95.5%. Conversion based on hydrogen liberated was 100%, as will be discussed in the following section.

Results

A summary of the data obtained with several types of disulfides and one trisulfide is presented in Table I.

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(1) Nystrom and Brown, THIS JOURNAL, **69**, 1197 (1947).

(1a) Nystrom and Brown, *ibid.*, **69**, 2548 (1947).

(1b) Nystrom and Brown, *ibid.*, **70**, 3738 (1948).

(2) U. S. Bur. Mines, *Repts. Investigations*, 3591, **45** (1941).

(3) Trevoy and Brown, THIS JOURNAL, **71**, 1675 (1949).

(4) Ritter and Sharpe, *ibid.*, **59**, 2351 (1937).

(5) Haines, *et al.*, U. S. Bur. Mines, Reports Investigations 4060 (1946).

TABLE I

REDUCTION OF DISULFIDES WITH LITHIUM ALUMINUM HYDRIDE

Disulfides	Source	Solvent[a]	Relative reaction rate[b]	% Conversion based on Product isolated	% Conversion based on Hydrogen liberated	Mercaptan formed on hydrolysis	Product identification %S as RSH Found	Product identification %S as RSH Calcd.	$n^{20}D$ Obs.	$n^{20}D$ Lit.[5]
Di-*n*-butyl	Synthesized	E	Rapid	96	100	*n*-Butyl	35.3	35.6	1.442	1.443
n-Butyl-*t*-butyl	Synthesized	E	Moderate	96	98	*n*-Butyl + *t*-butyl	After rough distillation		1.440 1.419	1.443 1.423
Di-*t*-butyl	Eastman	E	No reaction	0	0	....	..	..	...	...
		F	Slow	..	99	*t*-Butyl	35.6	35.6	1.422	1.423
Di-isoamyl	Eastman	E	Rapid	..	100	Iosamyl	30.4	30.8	...	...
Di-*n*-octyl	Conn. Hard Rubber	E	Rapid	98	99	*n*-Octyl	21.3	21.9	1.454	1.454
Di-phenyl	Eastman	E	Rapid	95	...	Phenyl	29.0	29.1	1.587	1.589
Di-benzyl	Eastman	E	Rapid	95	...	Benzyl	25.8	25.8	1.576	1.576
Di-*t*-dodecyl	Phillips Pet. Co.	F	[c]	..	67[c]	....	..	..	...	...
Trisulfide										
Di-*t*-dodecyl	Synthesized	F	Moderate	..	100	*t*-Dodecyl + hydrogen sulfide	15.0	15.8	...	...

[a] E, Diethyl ether; F, tetrahydrofuran. [b] Rapid, reacts vigorously in ethyl ether; moderate, reacts moderately in ethyl ether; slow, does not react in ethyl ether but reacts readily in tetrahydrofuran at 65°. [c] This reduction was so slow that it was not carried to completion.

The stoichiometry of the reaction of lithium aluminum hydride with a disulfide is represented by the equation

$$2RSSR + LiAlH_4 \longrightarrow (RS)_4LiAl + 2H_2 \quad (1)$$

This equation is supported by the data from the example reduction of di-*n*-butyl disulfide. The hydrogen evolution from the reduction of 81.30 g. (0.457 mole) of disulfide amounted to 0.456 mole. Hydrolysis of excess lithium aluminum hydride gave an additional 0.372 mole of hydrogen. This is equivalent to 3.52 g. (0.093 mole) of hydride by the equation[6]

$$LiAlH_4 + 4H_2O \longrightarrow LiAl(OH)_4 + 4H_2 \quad (2)$$

In the reaction, the total available lithium aluminum hydride (corrected to 100% activity) was 13.17 g. × 0.93, or 12.22 g. Therefore, the hydride consumed by the disulfide was 12.22–3.52 g., or 8.70 g. (0.229 mole), compared with a quantity of 8.65 g. (0.228 mole) calculated from Equation (1).

The reaction of lithium aluminum hydride with trisulfides was not investigated as thoroughly as the disulfide reaction. It was observed, however, that acidification of the reaction mixture gave not only mercaptans but also hydrogen sulfide. On this basis, and by analogy with the disulfide reaction, the stoichiometry of trisulfide of reduction is presumed to be

$$2RSSSR + 2LiAlH_4 \longrightarrow (RS)_4LiAl + LiAlS_2 + 4H_2 \quad (3)$$

As no attempt was made to isolate and prove the structure of the reaction products of Equations (1) and (3), the formulas are not intended to represent literally the structure of these materials. However, these formulas are consistent with the observed products of hydrolysis and also with the observed stoichiometric relationships involved in these reactions.

Discussion

The effect of structure of the disulfide on the reaction rate is demonstrated by comparing results obtained using the three isomeric butyl disulfides: As branching around the sulfur–sulfur bond is increased, reduction becomes more difficult. The effect is such that a higher boiling reaction solvent—tetrahydrofuran—was required to reduce di-*t*-butyl disulfide. It appears that tertiary alkyl groups block the sulfur–sulfur linkage and make reduction more difficult.

Increased molecular weight also appears to make reduction more difficult as evidenced by relative reduction rates of di-*t*-dodecyl[7] and di-*t*-butyl disulfides. It was also observed that di-*n*-octyl disulfide reacted less vigorously than di-*n*-butyl disulfide, although both were rapidly reduced according to the classification used in Table I.

The ease of reduction of the one trisulfide tested, di-*t*-dodecyl trisulfide, indicates that lithium aluminum hydride is applicable to trisulfide reduction as well as to disulfide reduction. The blocking effect of tertiary alkyl groups around the trisulfide linkage is much weaker than that around the disulfide linkage, as is shown by the much more rapid reduction of di-*t*-dodecyl trisulfide than of di-*t*-dodecyl disulfide. A possible interpretation of this behavior is that the introduction of a third sulfur atom between the tertiary alkyl groups spreads the tertiary groups so far that they are no longer effective blocking agents.

Lithium aluminum hydride might be used in an

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[6] Finholt, *et al.*, THIS JOURNAL, 71, 1675 (1949).

[7] Supplied by Phillips Petroleum Co.; probably derived from triisobutylene.

indirect method for determining disulfides. It may be possible to use a procedure similar to an active-hydrogen determination,[8] wherein the disulfide would be estimated from the volume of hydrogen liberated on reaction with excess lithium aluminum hydride. This application is being investigated.

Summary

Lithium aluminum hydride in an ether-type solvent is an effective reducing agent for the disulfide linkage in organic molecules. The reduction involves scission of the sulfur-sulfur bond to form a lithium-aluminum complex and to liberate stoichiometrically the hydrogen of the hydride. Mercaptans are obtained by hydrolysis of the complex with dilute acid.

Tertiary alkyl groups attached to the sulfur-sulfur bond slow the reaction rate, but quantitative reduction may be obtained by using higher temperatures and longer reaction times.

Measurement of liberated hydrogen in lithium aluminum hydride reductions provides the basis for a possible quantitative method for the determination of disulfides.

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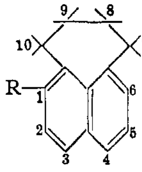
[8] Krynitsky, Johnson and Carhart, THIS JOURNAL, **70**, 486 (1948).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF UTAH]

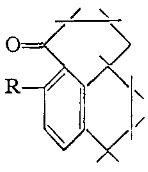
The Synthesis of 1-Hydroxycyclohepta[de]naphthalene[1]

BY RICHARD C. GILMORE, JR., AND W. J. HORTON

The cyclohepta[de]naphthalene ring system, I, has not as yet been reported although a few related compounds are known. von Braun[2] submitted γ-1-tetrylbutyric acid to cyclization and obtained III in low yield. The cyclization of γ-5-methoxy-1-naphthylbutyric acid[3] is almost exclusively toward the peri position. Using phthalic anhydride or succinic anhydride,[4,5] seven-membered ring systems of this type were encountered.

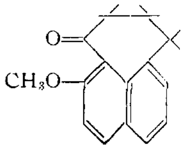


I, R = H
II, R = OH

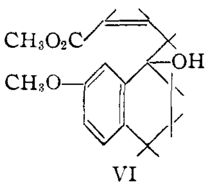


III, R = H
IV, R = OCH_3

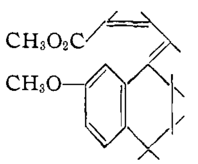
The internal Friedel–Crafts reaction on γ-7-methoxy-1-naphthylbutyryl chloride using stannic chloride gave two different ketones, one of which was converted to a phenanthrene derivative.[6] A keto-cyclohepta[de]naphthalene structure, V, was proposed to account for the second compound.



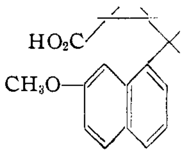
V



VI



VII



VIII

This reaction has been repeated and the pericyclized compound, obtained in 19% yield, has been converted, by reduction of the keto group and demethylation, to 1-hydroxycyclohepta[de]naphthalene, II. In two other independent syntheses of II, compounds were obtained which proved to be identical to the above.

To obtain VIII for the original cyclization, 7-methoxy-1-tetralone[6] and methyl γ-bromocrotonate[7] were treated with zinc and iodine to yield VI. This Reformatsky product was dehydrated to what was assumed to be VII, analogous to a similar case.[8] Reduction, followed by dehydrogenation and saponification, gave VIII, identical to that previously reported.[6]

The reaction of the acid chloride of γ-7-methoxy-1,2,3,4-tetrahydro-1-naphthylbutyric acid for three minutes produced IV in 90% yield.[9] Reduction of the keto group of IV followed by dehydrogenation and demethylation gave II.

A second series of reactions starting with β-methyl naphthyl ether and succinic anhydride gave isomeric β-2-methoxynaphthoylpropionic acids.[10] An improved separation of these isomers gave IX in 25% yield. Reduction of the keto group and cyclization to the 8-position gave

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[1] From the Doctoral Dissertation of Richard C. Gilmore, Jr.

[2] von Braun and Rath, *Ber.*, **60**, 1182 (1927).

[3] Kon and Soper, *J. Chem. Soc.*, 790 (1939).

[4] Fieser and Peters, THIS JOURNAL, **54**, 4347 (1932); Fieser and Fieser, *ibid.*, **55**, 3010 (1933).

[5] Rieche and Frühwald, *Ber.*, **64**, 1603 (1931).

[6] Bachmann and Horton, THIS JOURNAL, **69**, 58 (1947).

[7] Ziegler, Späth, Schaaf, Schumann and Winkelmann, *Ann.*, **551**, 80 (1942).

[8] Stork, THIS JOURNAL, **69**, 2936 (1947).

[9] This is in contrast to von Braun's cyclization[2] using aluminum chloride to produce III in 12% yield. The activating effect of a methoxy group has been noted above.[3]

[10] Short, Stromberg and Wiles, *J. Chem. Soc.*, 319 (1936).