The Reduction of N-Substituted 3-Aminothianaphthene 1,1-Dioxides by Means of Lithium Aluminum Hydride in the Presence of Aluminum Chloride

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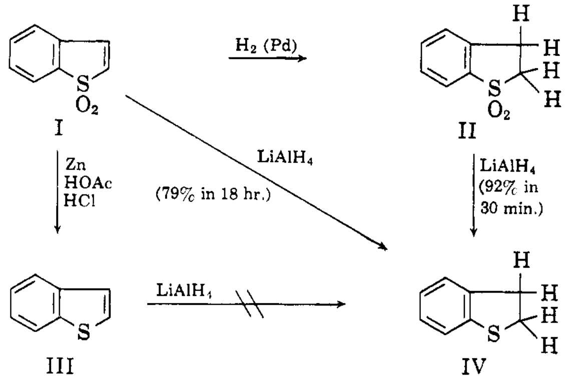
Several N-substituted 3-aminothianaphthene 1,1-dioxides have been reduced with lithium aluminum hydride in the presence of aluminum chloride. While the sulfone group is completely reduced, the extent of reduction of the 2,3-double bond increases with increasing amounts of aluminum chloride and also with decreasing basicity of the N-substituted group in the limited number of compounds used.

The reduction of thianaphthene 1,1-dioxide (I) by lithium aluminum hydride to 2,3-dihydrothianaphthene (IV) is quite slow (79% in 18 hr.), whereas 2,3-dihydrothianaphthene 1,1-dioxide (II) is very quickly reduced to IV (92% in 30 min.).[1] Thianaphthene (III) is not reduced at all by lithium aluminum hydride.[1] V.p.c. analysis in this laboratory of the products of the reduction of I to IV by means of lithium aluminum hydride indicate that no III is formed as an intermediate; *i.e.*, there is complete reduction of the double bond. Bordwell[1] also observed that III is not an intermediate in the reduction of I to IV, and that the first stage is probably a slow reduction of I to II.

SCHEME I



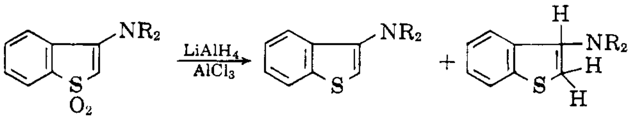
Thus, it is apparent that the 2,3-double bond of a thianaphthene system is reduced by lithium aluminum hydride only when the sulfur has been converted to a sulfone group. It is suggested that this is due to the polarizing action of the sulfone group on the 2,3-double bond making it susceptible to attack by the negatively charged aluminohydride ion. This interpretation agrees with that proposed by Trevoy and Brown.[2]

In this laboratory,[3] N-substituted 3-aminothianaphthene 1,1-dioxides have been reduced by lithium aluminum hydride to give only N-substituted 3-aminothianaphthenes; *i.e.*, there is no reduction of the 2,3-double bond while the sulfone group is reduced. Since these amines differ from I only by the presence of the 3-amino group, it is obvious that this group has the effect of preventing the reduction of the 2,3-double bond. This is probably due to the electron-donor action of the amino nitrogen, which increases the electron density around the 2,3-double bond and thus prevents attack by the aluminohydride ion. Thus the amino group counteracts the polarizing effect of the sulfone group on the 2,3-double bond.

It is interesting to note that other electron-donor groups have a similar effect on the reduction of the 2,3-double bond. Rao[4] reports that the sulfone group is completely reduced and the 2,3-double bond is reduced to varying extents when 2- or 3-alkylthianaphthene 1,1-dioxides are reduced with lithium aluminum hydride. Rao postulates that the incomplete reduction of the 2,3-double bond is due to steric hindrance. It should be noted that groups on the 3-position hindered the reduction much more than did groups in the 2-position.

In this paper are reported results of experiments designed to study the effect of Lewis acid catalysts on the reduction of various 3-aminothianaphthene 1,1-dioxides with lithium aluminum hydride. Only 3-amino compounds were used as substrate, thus enabling some comparison of their effects on the reduction of the 2,3-double bond.

It has been found that the presence of aluminum chloride in the reduction mixture partially negates the effect of the amino group in that the 2,3-double bond is partially reduced. The extent of reduction of the bond is dependent both on the amount of aluminum chloride



V VI VII

TABLE I

PRODUCTS OF REDUCTION OF N-SUBSTITUTED 3-AMINOTHIANAPHTHENE 1,1-DIOXIDES BY MEANS OF LITHIUM ALUMINUM HYDRIDE AND ALUMINUM CHLORIDE

Compd.	Moles of LiAlH$_4$/mole of compd.	Moles of aluminum chloride/ mole of compd.	VII, %	VI, %
3-(1-Piperidinyl)-thianaphthene 1.1-dioxide	6	6	56	44
	6	3	21	79
3-Diethylamino-thianaphthene 1,1-dioxide	6	6	64	36
	6	3	53	47
3-(*n*-Butylamino)-thianaphthene 1,1-dioxide	6	6	100	0
	6	3	100	0

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[1] F. G. Bordwell and W. H. McKellin, *J. Am. Chem. Soc.*, **73**, 2251 (1951).

[2] L. W. Trevoy and W. G. Brown. *ibid.*, **71**, 1675 (1949).

[3] G. Van Zyl. *et. al.*, *J. Org. Chem.*, **26**, 4946 (1961).

[4] D. S. Rao, Abstracts of Papers, 137th meeting of the American Chemical Society, Cleveland, Ohio, 1960, p. 26O.

TABLE II[a]

ELEMENTAL ANALYSIS OF NEW COMPOUNDS PREPARED

Compd.	Carbon, %		Hydrogen, %		Nitrogen, %		Sulfur, %	
	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
3-(1-Piperidinyl)thianaphthene[b]	71.89	72.05	6.91	7.02	6.45	6.31	14.75	14.91
3-Diethylaminothianaphthene[b]	70.24	69.92	7.32	7.35	6.82	6.64	15.61	15.80
3-(*n*-Butylamino)thianaphthene	70.24	70.50	7.32	7.65	6.82	6.81	15.61	15.67
3-(1-Piperidinyl)-2,3-dihydrothianaphthene	71.23	71.12	7.76	7.85	6.39	6.43	14.61	14.63
3-Diethylamino-2,3-dihydrothianaphthene	69.56	69.85	8.21	8.27	6.76	7.05	15.46	15.62
3-(*n*-Butylamino)-2,3-dihydrothianaphthene	69.56	69.40	8.21	8.17	6.76	6.52	15.46	15.75

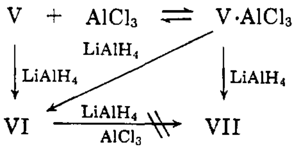
[a] All analyses were performed by Schwarzkopf Microanalytical Laboratory New York, N. Y. [b] See ref. 3.

present and on the nature of the N-substituted group. Table I lists the different amines reduced, the amount of aluminum chloride used, and the composition of the product mixture.

It is postulated that the aluminum chloride, being a Lewis acid, complexes with the amino nitrogen, thus reducing its electron-donor action and allowing partial reduction of the 2,3-double bond. A second possibility which has not been eliminated is complexation of the aluminum chloride with the sulfone oxygens. This might be expected to have similar results as complexation with nitrogen. Possibly both occur.

V.p.c. analysis of the products of the reduction of N-substituted 3-aminothianaphthenes (VI) by means of lithium aluminum hydride and aluminum chloride indicates that, as in the case of thianaphthene itself, the 2,3-double bond cannot be reduced after the sulfone group has been reduced. All evidence thus points toward a mechanism in which reduction must occur at the 2,3-double bond first if this bond is to be reduced. If the sulfone group is reduced first the double bond will not be reduced by lithium aluminum hydride even in the presence of aluminum chloride. Therefore, any N-substituted 3-amino-2,3-dihydrothianaphthene (VII) must result from attack first at the 3-position and then on the sulfone group. Formation of N-substituted 3-aminothianaphthenes (VI) must result from initial attack on the sulfone group after which attack on the 2,3-double bond is precluded.

SCHEME II



Owing to competing processes indicated in Scheme II it is impossible with the data now available to ascribe the results of Table I to any specific factors such as basicity of amine or steric hindrance; however there can be no doubt that aluminum chloride facilitates reduction of the 2,3-double bond in V through formation of a complex.

Experimental

Analysis of Reduction Mixtures.—Product mixtures were analyzed by means of gas chromatography on a Burrell Kromo-Tog Model K-2. Columns were packed with 20% Carbowax 4000 on Chromosorb W. Analyses were carried out near 200° using a 90–100 ml./min. flow of helium. The following compounds were synthesized by standard procedures found in the literature in order to obtain pure samples for comparison by v.p.c. analysis. 3-(1-Piperidinyl)thianaphthene 1,1-dioxide, 3-diethylaminothianaphthene 1,1-dioxide, and 3-(*n*-butylamino)-thianaphthene 1,1-dioxide were prepared by the method of Bordwell.[5] 3-(1-Piperidinyl)-2,3-dihyrothianaphthene 1,1-dioxide and 3-diethylamino-2,3-dihydrothianaphthene 1,1-dioxide were also prepared by the method of Bordwell.[6]

3-(*n*-Butylamino)-2,3-dihydrothianaphthene 1,1-Dioxide.—A mixture of 16.6 g. (0.100 mole) of I, 14 g. (0.20 mole) of *n*-butylamine, 0.5 g. of a powdered copper catalyst, and 200 ml. of 96% ethanol was refluxed for 90 min. After filtering out the copper catalyst, the solvent was removed under vacuum and the remaining viscous liquid was treated with 1:1 hydrochloric acid until precipitation started. A quantitative yield of a white precipitate resulted which was recrystallized from ethanol, m.p. 211°.[7]

Reduction of Sulfones.—Each of the above sulfones was reduced with lithium aluminum hydride to the corresponding sulfide. In general, 0.050 mole of sulfone, 0.300 mole of lithium aluminum hydride, and 300–500 ml. of absolute ethyl ether were stirred for 4 hr. at Dry-Ice temperature, 16 hr. at room temperature, and 4 hr. at reflux temperature. Ethyl acetate was added carefully to destroy excess lithium aluminum hydride and the mixture was made basic with 15% sodium hydroxide. After removal of the inorganic salts by filtration the ether was washed with water until neutral and then dried over anhydrous sodium sulfate. The ether was removed under vacuum and the residue was distilled at pressures near 0.1 mm. In all cases this yielded a product pure enough for v.p.c. analysis either with or without an internal standard. Yields varied from 40–80%.

Reduction of N-Substituted 3-Aminothianaphthene 1,1-Dioxides by Means of Lithium Aluminum Hydride and Aluminum Chloride.—The sulfones were reduced in 0.050 *M* quantities with 11.4 g. (0.300 mole) of lithium aluminum hydride and 40 g. (0.30 mole) or 20 g. (0.15 mole) of aluminum chloride in 600 ml. of absolute ethyl ether. The mixtures were treated as in the previous case. Ethyl acetate and water were added carefully to destroy excess lithium aluminum hydride and aluminum chloride, respectively. The mixtures were then made basic with 15% sodium hydroxide and the inorganic salts were filtered and washed with ether. The ether was then washed with water until neutral and then dried over sodium sulfate. The ether was removed under vacuum and the residue was distilled at pressures near 0.1 mm. The products of the reaction were then subjected to analysis by gas chromatography.

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(5) F. G. Bordwell and C. D. Albisetti, Jr., *J. Am. Chem. Soc.*, **70**, 1558 (1948).

(6) F. G. Bordwell and W. H. McKellin, *ibid.*, **72**, 1985 (1950).

(7) This compound could not be purified for analysis. However, the analysis of its reduced derivative (Table II) compared very well with the calculated values.