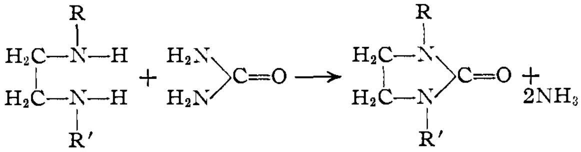
TABLE I

Compound	B. p., °C.	Mm.	M. p., °C.	% yield	N Analyses, % Calcd.	N Analyses, % Found
1,3-Dicyclohexyl-2-iminazolidone	165–166	1	92–94	80	11.19	10.91
1,3-Dibutyl-2-iminazolidone	137–140	3	...	81	14.14	14.36
1,3-Dioctyl-2-iminazolidone	195–200	3	5–6	80	9.02	9.30
1,3-Didodecyl-2-iminazolidone	245–252	2	48–49	76	6.63	6.36
1,3-Dibenzyl-2-iminazolidone	183–186	1	93–94	80	10.53	10.43

which ammonia is rapidly evolved, according to the equation



Although the reaction of urea with amines to produce substituted ureas is well known, the only reaction between diamines and urea previously described was reported by Clarke[1] as a method of preparing polymers of interest as synthetic fibers.

A previous synthesis of 2-imidazolidones was described by Boon,[2] who treated the diamines with phosgene. He reported approximately equal yields of the cyclic urea and of the carbonyl chloride, so that, at best, yields of less than 50% were obtained. In the present investigation, the yield is in general about 80% of the theoretical amount.

Data for the five substances now prepared are shown in Table I. Of these the only one previously reported is the dibenzyl derivative, prepared by Lob[3] from phosgene. In this case our data agree very closely to the physical constants which he reported.

The general procedure for the preparation of these substances is given herewith.

One-tenth mole of the diamine is heated in a glass vessel with 0.125 mole of urea with a free flame until vigorous evolution of ammonia takes place. The heating is continued until this slows down to a negligible rate (ten to fifteen minutes). The product is then vacuum distilled and, if crystalline, is recrystallized from absolute alcohol.

Acknowledgment.—The authors express their appreciation to the F. C. Bersworth Laboratories of Framingham, Massachusetts, for financial support for this research.

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(1) Clarke, British Patent 530,267, Dec. 9, 1940.

(2) Boon, *J. Chem. Soc.*, 307 (1947).

(3) Lob, *Rec. trav. chim.*, **55**, 866 (1936).

DEPARTMENT OF CHEMISTRY
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RECEIVED JUNE 14, 1949

The Reduction of Sulfonyl Chlorides to Mercaptans with Lithium Aluminum Hydride

BY C. S. MARVEL AND P. D. CAESAR

The reduction of aliphatic and aromatic sulfonyl chlorides to mercaptans with lithium aluminum hydride has been realized. There is no previous record of the use of this reagent for a reduction of this type.

The reaction may proceed according to the following stoichiometrical equation, although in the preliminary experiments shown here a two- to threefold excess of lithium aluminum hydride was used to assure a positive reaction. Ethyl ether was employed as the solvent.

$$2RSO_2Cl + 3LiAlH_4 \longrightarrow LiAlCl_2(SR)_2 + 6H_2 + 2LiAlO_2$$

Initial attempts to reduce arylsulfonamides and diarylsulfones, using ethyl ether as a solvent, proved fruitless. It seems probable that use of a higher boiling solvent such as tetrahydrofuran may improve this reaction.

p-Thiocresol and n-Butyl Mercaptan.—These compounds were prepared under the general conditions for lithium aluminum hydride reduction described by Nystrom and Brown.[1] The reductions were carried out at 35° for one and one-half hours.

From 5 g. (0.026 mole) of p-toluenesulfonyl chloride and 4 g. (0.1 mole) of lithium aluminum hydride there was obtained 1.6 g. (50% based on p-toluenesulfonyl chloride) of p-thiocresol, m. p. 42.5–43.5°, alone and when mixed with an authentic sample of p-thiocresol.

From 4 g. (0.025 mole) of 1-butanesulfonyl chloride and 3 g. (0.08 mole) of lithium aluminum hydride there was isolated 2.2 g. (45% based on 1-butanesulfonyl chloride) of mercury n-butyl mercaptide; m. p. 84–85°, reported m. p. 85–86°.[2] This was obtained by distilling the ether, mercaptan and some of the water from the reaction mixture, after decomposition of the lithium aluminum complex, into a suspension of mercuric oxide in alcohol.

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(1) R. F. Nystrom and W. G. Brown, THIS JOURNAL, **69**, 1197 (1947).

(2) E. Wertheim, *ibid.*, **51**, 3661 (1929).

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Proton Exchange between Ammonia and Ammonium Ion in Liquid Ammonia[1]

BY C. J. NYMAN, SI-CHANG FUNG AND H. W. DODGEN

In the explanation of data observed on the exchange of protons between ND_3 and $B_2H_6 \cdot 2NH_3$, it was postulated by Burg[2] that the exchange of protons between ammonia molecules and ammonium ions was rapid. Several properties of the ammonium ion in liquid ammonia caused the authors to consider the possibility of this reaction being slow. The fact that the conductance[3] of the ammonium ion in this solvent is similar to that of lithium indicates that the proton is not nearly so mobile as in aqueous solution. Like-

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(1) This project supported in part by the State College of Washington Committee on Research.

(2) A. B. Burg, THIS JOURNAL, **69**, 747 (1947).

(3) E. C. Franklin and C. A. Kraus, *ibid.*, **27**, 191 (1905); *Am. Chem. J.*, **23**, 277 (1900).

wise, the recent observation of Laitinen and Shoemaker[4] on the reversible polarographic reduction of the ammonium ion in liquid ammonia to ammonium amalgam indicates a rather high stability of the N–H bonds in this ion. Burg's postulate has, however, been proven to be correct under the experimental conditions employed. The exchange was followed by observing the disappearance of N^{15} in ammonium chloride which originally contained 13.77% N^{15} in the ammonium ion.

Ammonium nitrate containing 14% N^{15} was purchased from Eastman Kodak Co. and was converted to ammonium chloride by allowing ammonia to distil from a sodium hydroxide solution of the salt into hydrochloric acid. After evaporation the ammonium chloride was further dried at 110°. The ammonia was anhydrous commercial grade material and was dried by condensation on sodium metal before use.

The apparatus and procedure for preparing the liquid ammonia solutions were essentially those described by Laitinen and Nyman.[5] In all experiments described here, 0.2 g. of ammonium chloride was dissolved in 10 cc. of liquid ammonia. Approximately six minutes were required to condense the ammonia in the reaction vessel (a plain glass tube) and to get the salt dissolved completely. When the sample had dissolved completely, the ammonia was evaporated as rapidly as possible. The ammonium chloride was converted to nitrogen gas by passing the vapor over hot cupric oxide. The mass spectrographic analysis for N^{15} was carried out by the Mass Spectrometry Section of the National Bureau of Standards.

Two experiments were carried out at −33° (b. p. of ammonia), and seven minutes were required for the removal of the ammonia after the salt was dissolved. The percentage N^{15} decreased from 13.77 to 0.52 in both instances. In an experiment carried out at −60°, the percentage N^{15} decreased from 13.77 to 0.51, twenty-two minutes being required to evaporate off the ammonia. An additional experiment carried out at −40° for two hours showed a decrease in N^{15} concentration in the ammonium ion from 13.77 to 0.52%. Assuming the exchange to be complete in this time, the results indicate complete exchange in the experiments described previously.

The possibility of this reaction being catalyzed by water was considered, and in one reaction, the following precautions were taken to exclude water. An apparatus was constructed which allowed the sample to be dried *in vacuo* over phosphorus pentoxide and in which the ammonia could be condensed without exposing the sample to the atmosphere. The conditions of this experiment were the same as those at −33°, and the results indicated complete exchange as above.

The two possible mechanisms by which the exchange might occur are

$$\overset{*}{N}H_4^+ + NH_3 \rightleftarrows \overset{*}{N}H_3 + NH_4^+ \text{ and} \qquad (I)$$

$$2NH_3 \rightleftarrows NH_4^+ + NH_2^-. \qquad (II)$$

Because of the rapidity of the exchange, it is impossible to determine by our present procedure which of these two mechanisms is correct. An attempt to study this and similar problems in liquid ammonia by use of radioactive hydrogen is in progress. The improved techniques will allow much closer control of the time, concentration and temperature, and, in addition, will allow more complete exclusion of water.

DEPARTMENT OF CHEMISTRY
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PULLMAN, WASHINGTON
RECEIVED DECEMBER 12, 1949

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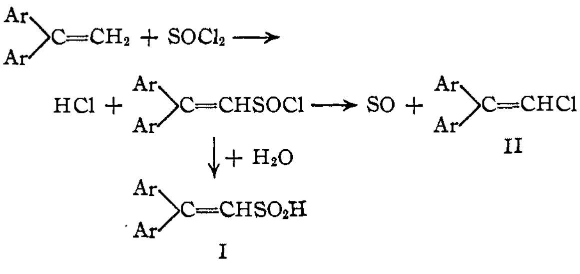
[4] H. A. Laitinen and C. E. Shoemaker, private communication.

[5] H. A. Laitinen and C. J. Nyman, THIS JOURNAL, **70**, 2241 (1948).

On the Reaction of 1,1-Diarylethylenes with Thionyl Chloride

BY SAUL PATAI AND FELIX BERGMANN

1,1-Diarylethylenes are attacked by a number of reagents, which normally do not react with olefinic double bonds, *e. g.*, phosphorus pentachloride[1] and oxalyl chloride.[2] It is a characteristic effect of the strong polarization in 1,1-diarylethylenes that they deform the valency orbitals of the central atom of the above-mentioned reagents towards a cationic state and thus make possible addition to their own negatively charged β-carbon atom. Assuming this to be a general phenomenon, we examined the behavior of diarylethylenes toward other inorganic and organic molecules of similar electronic structure and wish to report here as the first example our results with thionyl chloride. This compound can be considered as a formal analog of phosgene, which has been found previously to react with 1,1-di-(*p*-anisyl)-ethylene.[3] We have been able to isolate from the reaction with 1,1-diphenylethylene the expected 1,1-diphenylethylene-2-sulfinic acid (I) in 17% yield, a reaction which can be represented schematically as



The structure of the sulfinic acid is deduced from the independent synthesis of I from diphenylvinylmagnesium bromide and sulfur dioxide.

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[1] F. Bergmann and Bondi, *Ber.*, **63**, 1158 (1930); **64**, 1455 (1931).

[2] Kharasch, Kane and Brown, THIS JOURNAL, **64**, 333 (1942).

[3] F. Bergmann and co-workers, *ibid.*, **70**, 1612 (1948).