acetate in 15 ml. of water, and 1 ml. of acetic acid. The mixture was heated for four hours. Cooling yielded 0.49 g. of the crystalline diacetoxymercurithianaphthene.[9] *Anal.* Calcd. for $C_{12}H_{10}O_4SHg_2$: S, 4.92. Found: S, 4.75.

**Recovery of Thianaphthene.**—The mercury derivative was steam distilled with excess 3 *M* hydrochloric acid. Crystalline thianaphthene, m.p. 29.5–30.0°, was obtained in the distillate. Pure thianaphthene melts at 31.34°.[10] A mixture of equal amounts of the recovered natural product and an authentic synthetic sample melted at 30.0–30.5°. The percentage recovery of pure thianaphthene from D was not determined in this particular case. However, from mixtures of known amounts of thianaphthene and naphthalene, which simulated the composition of fraction D, the recovery of pure thianaphthene was about 60%.

## Discussion

Santa Maria Valley crude oil does not contain free sulfur and does not evolve significant quantities of hydrogen sulfide until a temperature plateau of 266° is reached.[11] Also, possible thianaphthene precursors are known to be thermally stable at even higher temperatures. On the basis of these facts and recent observations,[2] it seems that the thianaphthene isolated was present in the virgin crude and was not formed during the distillation.

The separation procedure depends upon the use of naphthalene picrate as a carrier for the isomorphic thianaphthene picrate. In separate experiments it was shown that coprecipitation of these picrates from ethanol, using a mixture of 1% thianaphthene with 99% naphthalene, gave a 90% yield of thianaphthene picrate but only an 18% yield of naphthalene picrate. The precipitation of thianaphthene picrate in the absence of naphthalene would have required thirty times as much thianaphthene. The greater solubility of naphthalene picrate in 95% ethanol (37 g. per l. at 30°) assists the preferential precipitation of the isomorphic thianaphthene picrate (13 g. per l. at 30°).

The fact that only the picrates of thianaphthene and naphthalene are formed in fraction D is somewhat surprising. However, a series of sulfur compounds (thiophenes, sulfides, cyclic sulfides) and alkyl aromatics, which are representative of materials that could be in fraction C, did not form crystalline picrates under the conditions used.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CANISIUS COLLEGE]

# Complex Metal Hydride Reactions. I. Lithium Aluminum Hydride Reduction of Heterocyclic Nuclei[1]

BY NORMAN G. GAYLORD[2a] AND DANIEL J. KAY[2a,b]

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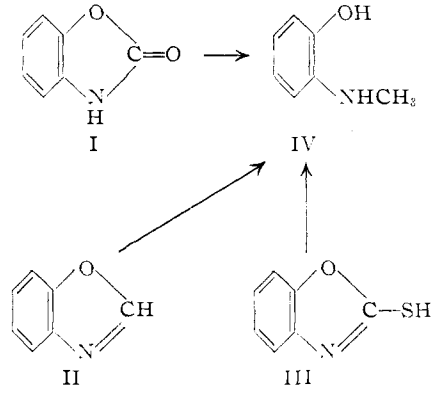
2-Benzoxazolinone and benzoxazole in ether solution and 2-benzoxazolethiol in tetrahydrofuran are reduced with lithium aluminum hydride to *o*-methylaminophenol, identified as the N-benzoyl derivative. 2-Benzimidazolethiol is not reduced in either ether or tetrahydrofuran solution. While the reduction of 2,5-diphenyloxazole in ether solution is unsuccessful, reduction in tetrahydrofuran gives 2-benzylamino-1-phenylethanol.

It has been reported[3] that an –NCO– grouping and an –NCS– grouping, normally not considered to be functional groups *per se*, are cleaved by lithium aluminum hydride (LAH) at the carbon–oxygen and carbon–sulfur bonds, respectively. The present investigation was undertaken to determine the applicability of this generalization to various heterocyclic nuclei.

The reduction of 2-benzoxazolinone (I) with LAH in ether solution gave *o*-methylaminophenol (IV), isolated in 57% yield as the N-benzoyl derivative V. The reduction of benzoxazole (II) in ether solution gave 59% of IV, isolated as V. The reduction of I with LAH involves initially the normal cleavage of the lactone group to yield a glycol. Subsequent cleavage of the –NCO– group yields the N-methyl compound, analogous to the reduction of carbamates.[3] The reduction of II, on the other hand, initially involves the reduction of the carbon–nitrogen double bond, followed by cleavage of the –NCO– grouping.




The reduction of 2-benzoxazolethiol (III) in ether

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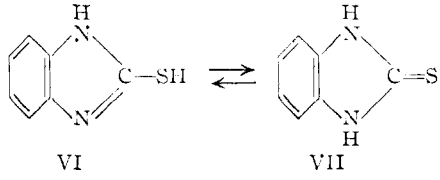
(2) (a) Interchemical Corporation, The Research Laboratories, 432 West 45th Street, New York 36, N. Y.; (b) abstracted from the M.S. thesis of D. J. Kay, Canisius College, June, 1955.

(3) N. G. Gaylord, *Experientia*, **10**, 351 (1954); "Reductions with the Complex Metal Hydrides," Interscience Publishers, New York, N. Y., 1956.

solution gave a 70% recovery of III and a small amount of IV isolated as the N,O-dibenzoyl derivative. In tetrahydrofuran solution, however, reduction followed by benzoylation gave 61% of V. The slight reduction in ether as compared to that in tetrahydrofuran may be due to the partial insolubility of the intermediate complex or an unfavorable position in the equilibrium between the thiol and the tautomeric thione.[4] The change in solvent and the increase in reaction temperature may have resulted in a shift in the equilibrium to the thione or thiocarbamate form. Reduction of the thiolactone, analogous to the reduction of I, to yield the *o*-hydroxymercaptomethylamino derivative would be followed by cleavage of the $-\overset{|}{\underset{|}{N}}\overset{||}{C}\overset{|}{S}-$ grouping to yield IV. It is of interest to note that while III behaves in various reactions as though both tautomeric forms participated,[4a] I behaves as the lactam rather than the lactim.[5]

An examination of the chemistry of *o*-aminophenols has indicated that phenolic acyl groups have a tendency to migrate to the amino group.[6] It is not surprising, therefore, that in this work where equivalent quantities or less of benzoyl chloride were used in the presence of hydrochloric acid, only the N-benzoyl derivative V, was obtained from IV. V was converted to the N,O-dibenzoyl compound by the Schotten–Baumann reaction.

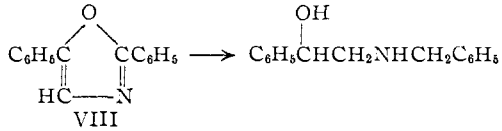
The attempted LAH reduction of 2-benzimidazolethiol (VI) was carried out in refluxing ether, in tetrahydrofuran at 30–40°, and in refluxing tetrahydrofuran. In all cases only unreacted VI was recovered. This may be due to the insolubility of the intermediate complex or the predominance of the tautomeric thione configuration VII.



VI VII

VII is analogous to a cyclic thiourea and it has been reported[3,7] that ureas are not reduced with LAH.

While the attempted reduction of 2,5-diphenyloxazole (VIII) in ether solution resulted in the recovery of VIII, reduction in tetrahydrofuran solution, followed by the addition of hydrogen chloride to the dried solvent extract of the reduction product, gave the hydrochloride of 2-benzylamino-1-phenylethanol in 44.5% yield. Hydrolysis of the salt gave the free base which was converted to the picrate.



VIII

Here, saturation of the carbon–carbon double bond, as in the reduction of ω-nitrostyrenes,[8] accompanies the reduction of the carbon–nitrogen double bond and subsequent cleavage of the $-\overset{|}{\underset{|}{N}}\overset{||}{C}\overset{|}{O}-$ grouping.

## Experimental

**Reduction of 2-Benzoxazolinone (I).**—Powdered I (45 g., 0.33 mole) was added, with stirring, over 30 minutes to a solution of 20 g. of LAH in 500 ml. of ether. The reaction mixture was refluxed for one additional hour and then decomposed, with vigorous agitation, by the dropwise addition of 20 ml. of water over a one-hour period. A total of 90 ml. of 6 *N* hydrochloric acid was added slowly until a strongly acidic reaction mixture was obtained. At this point the ether solution had attained a bright red hue. An additional 200 ml. of water and 200 ml. of ether were added.

Benzoyl chloride (25 g., 0.18 mole) was added dropwise to the two phase reaction mixture while maintaining gentle reflux. The mixture was refluxed for an additional 30 minutes and stirred at room temperature for an equal time. The ether layer was decanted from the insoluble solid phase and, when washed with water, deposited crystalline N-benzoylated material. The insoluble phase was washed with water and a saturated sodium carbonate solution and the aqueous phases were extracted with ether. The combined ether layers were washed with dilute hydrochloric acid and concentrated. The residual solid and the previously isolated N-benzoyl compound were dissolved in alcohol and precipitated with water. After an additional two recrystallizations from an alcohol–water mixture, 33 g. of N-benzoyl-N-methyl-*o*-aminophenol (V) was obtained, m.p. 164° (reported[8] m.p. 160–162°).

The aqueous acid extract was treated with excess benzoyl chloride in a 1:1 ether–water system. The N-benzoyl derivative was extracted with ether and purified by precipitation from an alcoholic solution to yield an additional 10 g. of V (total yield 43 g., 57%).

The N-benzoyl derivative was soluble in 10% sodium hydroxide in contrast to the N,O-dibenzoyl compound prepared by heating the N-benzoyl compound with excess benzoyl chloride in the presence of 6 *N* sodium hydroxide. The product on crystallization from alcohol had m.p. 108° (reported[9] m.p. 114–115°).

*Anal.* Calcd. for $C_{21}H_{17}NO_3$: C, 76.13; H, 5.14. Found: C, 75.99; H, 5.01.

**Reduction of Benzoxazole (II).**—A solution of II (25 g., 0.21 mole) in 25 ml. of ether was added dropwise over 40 minutes to a solution of 10 g. of LAH in 400 ml. of ether. The reaction mixture was refluxed for one additional hour and then decomposed by the dropwise addition of 10 ml. of water over a period of 50 minutes. A total of 65 ml. of 6 *N* hydrochloric acid was added slowly with agitation until a strongly acidic reaction mixture was obtained. The resultant bright red solution was diluted with 300 ml. of ether and 100 ml. of water. Benzoyl chloride (30 g., 0.21 mole) was added dropwise to the two phase reaction mixture over a period of 15 minutes while maintaining gentle reflux. The mixture was refluxed for an additional hour and worked up as above to yield 28 g. (59%) of V, m.p. and mixed m.p. 161–162°.

**Reduction of 2-Benzoxazolethiol (III).**—A solution of III (4 g., 0.03 mole) dissolved in 100 ml. of tetrahydrofuran was added over 15 minutes to a solution of 4 g. (0.10 mole) of LAH in 250 ml. of tetrahydrofuran. The reaction mixture was refluxed for an additional 2.5 hours and decomposed with 4 ml. of water added over 30 minutes. Hydrogen sulfide evolution was established by the immediate darkening of wet lead acetate paper positioned at the top of the reflux condenser. A total of 40 ml. of 6 *N* hydrochloric acid was added slowly until the reaction mixture was strongly acidic. Benzoyl chloride (4.5 g., 0.03 mole) was added rapidly to the light green two phase reaction mixture, followed by a one-hour reflux period. The insoluble solid was filtered and washed with ether. A saturated sodium carbonate wash of the combined filtrate and ether washes was followed by

(4) (a) R. D. Desai, R. F. Hunter and A. R. K. Khalidi, *J. Chem. Soc.*, 1186 (1934); (b) L. Katz and M. S. Cohen, *J. Org. Chem.*, **19**, 758 (1954).

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(7) W. Ried and F. Müller, *Chem. Ber.*, **85**, 470 (1952).

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extraction with 50 ml. of 6 *N* sodium hydroxide. The sodium carbonate wash liquors were neutralized with dilute hydrochloric acid to yield 0.5 g. of crude product having m.p. 158°. Further acidification caused precipitation of benzoic acid. Acidification of the alkali extract produced 3 g. of crude product, m.p. 158°. Evaporation of the tetrahydrofuran–ether phase produced 0.2 g. of product, m.p. 158° (total 3.7 g., 61.5% yield). The crude material was crystallized from ethanol to yield V, m.p. and mixed m.p. 160–161°.

**Attempted Reduction of 2-Benzimidazolethiol (VI).**—An attempt to reduce VI with LAH in a refluxing tetrahydrofuran solution for three hours resulted in a 64% recovery of unreacted VI. No reduction product was isolated.

**Reduction of 2,5-Diphenyloxazole (VIII).**—A straw yellow solution of 10 g. (0.45 mole) of VIII in 50 ml. of tetrahydrofuran was added over 40 minutes to a solution of 4 g. of LAH in 200 ml. of tetrahydrofuran. The brick red reaction mixture was refluxed for 3 hours and then decomposed with 4 ml. of water, 4 ml. of 15% sodium hydroxide and 12 ml. of water, in that order. The resultant canary yellow mixture was filtered and the filter cake was washed with tetrahydrofuran. After drying over magnesium sulfate the orange filtrate was treated with gaseous hydrogen chloride for 30 minutes until the solution became light yellow and no further evidence of solid formation was observed. The solid was filtered and washed with ether to yield 5.3 g. (44.5% yield) of the hydrochloride of 2-benzylamino-1-phenylethanol, m.p. 221–223° (reported[10] m.p. 219.5–221.5°).

Several drops of 6 *N* sodium hydroxide were added to a solution of the hydrochloride in hot water. The resultant white solid was filtered, washed with water and air dried. Several recrystallizations from petroleum ether gave the free base, m.p. 102° (reported[10] m.p. 103°).

A portion of the free base was treated with a saturated alcohol solution of picric acid to yield the picrate, recrystallized from alcohol; m.p. 150–151°.

*Anal.* Calcd. for $C_{21}H_{20}N_4O_8$: C, 55.32; H, 4.39. Found: C, 55.66; H, 4.76.

(10) C. L. Browne and R. E. Lutz, *J. Org. Chem.*, **17**, 1187 (1952).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLLEGE OF ARTS AND SCIENCES, UNIVERSITY OF LOUISVILLE]

# Sulfostyrenes.[1] Variable Capacity Di-(*p*-vinylphenyl)-sulfone Cross-linked Sulfostyrene Cation Exchange Polymers from Styrene/Sulfonamidostyrene Copolymers

BY RICHARD H. WILEY AND J. M. SCHMITT

RECEIVED NOVEMBER 4, 1955

Di-(*p*-vinylphenyl)-sulfone has been obtained from di-(*p*-bromoethylphenyl)-sulfone which occurs as a by-product in the previously described *p*-sulfonamidostyrene. Sulfone-free *p*-sulfonamidostyrene has been polymerized and copolymerized with and without added di-(*p*-vinylphenyl)-sulfone as a cross-linking co-monomer. These polymers have been hydrolyzed to a series of cation-exchange sulfostyrene polymers and copolymers with uniformly varied distribution of exchange groups and varying degrees of cross-linkages.

The variable capacity sulfostyrene cation-exchange polymers prepared previously[1] by the nitrous acid hydrolysis of styrene/sulfonamidostyrene copolymers were either cross-linked or highly branched as evidenced by their solvent and alkali insolubility. Because these copolymers are the only available cation-exchange polymers in which the distribution of the exchange units along the chain can be controlled with some degree of predictability and conformity, precise knowledge about their composition is a critical factor in determining the extent of their utility in theoretical studies of selectivity coefficients.[2] The nature and extent of the cross-linking involved in their structure is particularly significant because it is known[3] that the degree of cross-linking is intimately connected with selectivity behavior to the extent that at very low levels of cross-linking selectivity is almost completely lost and that under other conditions reversals of the selectivity coefficients may take place. It is, therefore, highly desirable to have additional data about the character of the cross-linkage or chain branching in the polymers and copolymers of *p*-sulfonamidostyrene and, if possible, to have available a series of variable capacity copolymers with a controlled degree of cross-linkage.

Previously the cross-linkage or branching in these copolymers was attributed to chain transfer reactions involving the N–H linkage of the sulfonamide. Consistent with this was the observation that the hydrolysis of the copolymers did not usually go to completion from which it was inferred that some nitrogen remained in the polymer in linkages other than amino, presumably imino. It has been reported[4] that under some conditions the nitrous acid treatment of sulfonamides leads to the formation of di-(arylsulfonyl)-hydroxylamine, $(ArSO_2)_2NOH$, as a minor by-product. Although this reaction could conceivably lead to cross-linking during hydrolysis of the polymer this possibility seems unlikely since the cross-linking or chain-branching phenomena appear during polymerization as is evidenced by the insolubility of polymers produced under some but not other conditions.

A third possibility leading to cross-linkage in these polymers is that of the presence of traces of di-(*p*-vinylphenyl)-sulfone. This divinyl sulfone would presumably be present as a result of sulfone formation in the preparation of *p*-bromoethylbenzenesulfonyl chloride. The procedure used previously in the preparation of the monomeric *p*-sulfonamidostyrene is not absolutely certain to remove traces of this sulfone. The simple expedient of dissolving the sulfonamide in alkali will, however, per-

(1) Previous papers in this series: (a) R. H. Wiley and S. F. Reed, *J. Phys. Chem.*, **60**, 533 (1956); (b) R. H. Wiley, N. R. Smith and C. C. Ketterer, THIS JOURNAL, **76**, 720 (1954); (c) R. H. Wiley and C. C. Ketterer, *ibid.*, **75**, 4519 (1953).

(2) G. E. Boyd, B. A. Soldano and O. D. Bonner, *J. Phys. Chem.*, **58**, 456 (1954); G. E. Myers and G. E. Boyd, *ibid.*, **60**, 521 (1956).

(3) O. D. Bonner, *ibid.*, **58**, 318 (1954); H. P. Gregor and J. Bregman, *J. Colloid Sci.*, **6**, 323 (1951); D. Reichenberg, K. W. Pepper and D. J. McCawley, *J. Chem. Soc.*, 493 (1951).

(4) O. Hinsberg, *Ber.*, **27**, 598 (1894).