Dehydrogenation and Dealkanation of Some Secondary and Tertiary Amines with Sulfur[1]

BY CHARLES M. ROSSER[2] AND JOHN J. RITTER

The dehydrogenation of secondary anilines with sulfur at elevated temperatures has been reported previously from this Laboratory.[3] In the penultimate step in a series of reactions producing camphor from alpha pinene, isobornylaniline was dehydrogenated with sulfur to camphor anil in good yield. Camphor anil has been reported[4] also to be formed in a similar dealkanation by the action of sulfur on the tertiary amine, methylbornylaniline. Vesterberg[5] and later Ruzicka and his co-workers[6] used sulfur successfully to dehydrogenate abietic acid and sesquiterpenes. There appears to be no report of its use for the dehydrogenation of amines to anils except for the above cases, although it is very probable that the formation of benzthiazole and its derivatives by the action of sulfur on alkylanilines proceeds through an intermediate stage similar to the above dehydrogenation and dealkanation.

It is the purpose of the present work to study the action of sulfur on a series of alkyl and/or aryl secondary and tertiary amines of the types, $PhNHCHR_2$ and $PhNRCHR_2$, and to determine some of the simple factors involved. One further object of the study is the preparation of true acetone anil by such methods, as its identity has been a matter of some dispute.[7-9]

The reactions studied may be illustrated by the equations

$$PhNHCHR_2 + S \longrightarrow PhN{=}CR_2 + H_2S \quad (I)$$
$$PhNRCHR_2 + S \longrightarrow PhN{=}CR_2 + RSH \quad (II)$$
$$PhN(COCH_3)CHR_2 + S \longrightarrow PhN{=}CR_2 + CH_3COSH \quad (III)$$

and significant concurrent reactions may be shown by the equations

$$PhN{=}CR_2 + H_2S \longrightarrow PhNH_2 + S{=}CR_2 \quad (A)$$
$$2RSH + PhN{=}CR_2 \rightleftharpoons RSSR + PhNHCHR_2 \quad (B)$$
$$PhN(CH_2R)CHR_2 + S \longrightarrow PhN{=}CHR + R_2CHSH \quad (C)$$
$$2PhN{=}C(CH_3)_2 \longrightarrow PhN{=}C(CH_3)CH_2C(CH_3)_2NHPh \quad (D)$$

Phenylbenzhydrylamine (R equals phenyl) was dehydrogenated with sulfur (equation I) to benzophenone anil in 65% yield. α-Phenylpropylaniline (R_2 equals phenyl and ethyl) was dehydrogenated to propiophenone anil in 30% yields. Isobornyl-p-dimethylaminoaniline (CR_2 equals camphane ring) gave camphor-p-dimethylaminoanil in 50% yield. Isopropylaniline (R equals methyl) gave a negligible yield of acetone anil upon dehydrogenation.

Acetone anil was prepared by the dealkanation (equation II) of methylisopropylaniline, ethylisopropylaniline, and diisopropylaniline with sulfur. Acetone anil prepared in this manner proved to be substantially the same as the product reported by Claisen.[10]

Several significant concurrent reactions were found to take place. Hydrogen sulfide may react to split the anil initially formed to amine and thioketone (equation A). The low yields of the anils indicate their degree of stability to this type of scission. Benzophenone anil was found to be partially split by hydrogen sulfide under the conditions of the dehydrogenation, even though it is stable toward hydrolysis by water at 180°.

It has been found that the mercaptan formed in the dealkanation according to equation II may react with the anil initially formed, reducing it to an alkylaniline (equation B). The mercaptan is oxidized to the disulfide. The latter has been shown also to react reversibly with an alkylaniline, dehydrogenating it to an anil. The disulfide is reduced to the mercaptan.

It has been observed that the dealkanation proceeds according to equation II only if the groups attached to the nitrogen are identical. When R (on nitrogen) equals a methyl or an ethyl grouping, a concurrent dealkanation takes place (equation C) to yield a Schiff base and an isoalkyl mercaptan. This reaction may introduce further side

(1) From a dissertation presented by Charles M. Rosser to the Faculty of the Graduate School of New York University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1935. Presented at the Chapel Hill meeting of the American Chemical Society, April, 1937.

(2) Present address, Sylvania Industrial Corporation, Fredericksburg, Va.

(3) Ritter, THIS JOURNAL, 55, 3322 (1933).

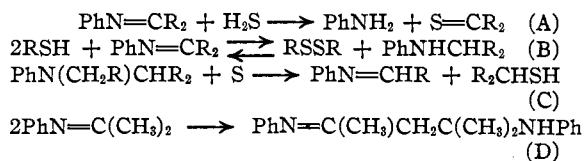(4) Mottern, Doctor of Philosophy Thesis, New York University, 1933.

(5) Vesterberg, Ber., 36, 4200 (1903).

(6) Ruzicka and co-workers, Helv. Chim. Acta, 4, 505 (1921); 5, 345 (1922).

(7) Knoevenagel, Ber., 54B, 1722 (1921).

(8) Reddelien and Thurm, ibid., 65B, 1511 (1932).

(9) Murray and Short, THIS JOURNAL, 55, 2805 (1933).

(10) Claisen, Ber., 29, 2932 (1896).

reactions since the Schiff bases react readily with sulfur to form thioamides, benzthiazoles and hydrogen sulfide. From the series of groups studied (hydrogen, methyl, ethyl, and isopropyl), it was observed that the smaller the group, the more easily it was removed from the nitrogen by the sulfur.

Acetone anil was found to undergo spontaneous aldolization to anilinomesityl oxide anil (equation D) under the conditions of the dealkanation. This offers an insight into the mode of formation of the trimethyldihydroquinoline mistakenly supposed by Knoevenagel[7] to be true acetone anil. Cyclization of anilinomesityl oxide anil with elimination of one aniline may yield either of the two isomeric dihydroquinolines suggested by Reddelien and Thurm[8] as representing Knoevenagel's "acetone anil." They are 1,1,3- and 1,3,3-trimethyldihydroquinoline.

In a third type reaction, the acetyl derivatives of secondary amines treated with sulfur yielded ketone anils with elimination of a molecule of aldehyde as thio acid (equation III). Camphor anil and thioacetic acid were formed by the action of sulfur on isobornyl acetanilide.

Experimental Part

Phenylbenzhydrylamine.[11]—One mole (181 g.) of benzalaniline[12] and one mole (181.2 g.) of phenylmagnesium bromide are allowed to react in anhydrous ether following the method of Busch and Rinck to yield phenylbenzhydrylamine (50%), b. p. 233° (20 mm.).

α-Phenylpropylaniline.[13]—One mole (133 g.) of ethylmagnesium bromide and one mole (181 g.) of benzalaniline are allowed to react as above to yield α-phenylpropylaniline (70%), b. p. 172° (9 mm.).

Isobornyl p-Dimethylaminoaniline.—Camphor p-dimethylaminoanil, prepared from camphor and p-dimethylaminoaniline, is reduced catalytically with hydrogen under pressure in glacial acetic acid solution to yield isobornyl-p-dimethylaminoaniline, b. p. 171–173° (1 mm.).

Isopropylaniline.[8]—Isopropylacetanilide, m. p. 38–40°, prepared from sodium acetanilide and isopropyl bromide in boiling xylene, is hydrolyzed in alcoholic solution to yield isopropylaniline, b. p. 87–89° (13 mm.).

Methylisopropylaniline,[14] Ethylisopropylaniline,[15] and Diisopropylaniline.[16]—These amines are prepared by allowing one mole of the alkylaniline to react with one mole of isopropyl bromide or iodide to form the hydrohalide of the tertiary amine. The salts are purified by recrystallization from dilute alcohol and neutralized with alkali to yield the amines. The amines may be purified further by

treatment with acetic anhydride or benzenesulfonyl chloride: methylisopropylaniline, b. p. 215–218° (760 mm.) and 89–92° (14 mm.); ethylisopropylaniline, b. p. 223–225° (760 mm.) and 100–102° (13 mm.); diisopropylaniline, b. p. 225–227° (760 mm.) and 98–100° (13 mm.).

Benzophenone Anil.[18]—Twenty-six grams of phenylbenzhydrylamine and 3.2 g. of sulfur are heated at 200–225° for five hours to yield benzophenone anil (65%), m. p. 114–115° from alcohol, hydrogen sulfide (90%), and aniline and thiobenzophenone in small amounts. Mixed melting points with known benzophenone anil, m. p. 113–114°, show no lowering. The anil, upon acid hydrolysis, yields aniline (acetyl, m. p. 114°) and benzophenone, m. p. 47–48° from alcohol.

Propiophenone Anil.[18]—Twenty-one grams of α-phenylpropylaniline and 3.2 g. of sulfur are heated at 200–210° for six hours to yield propiophenone anil (30%), b. p. 170–173° (10 mm.), hydrogen sulfide (80%), aniline and sulfur containing tars. The anil, upon acid hydrolysis, yields aniline and propiophenone, b. p. 214–217°.

Camphor p-Dimethylaminoanil.—Twenty-seven and two-tenths grams of isobornyl-p-dimethylaminoaniline and 3.2 g. of sulfur are heated at 210–230° for five hours to yield camphor-p-dimethylaminoanil (50%), orange solid of m. p. 61–62° from absolute alcohol, and hydrogen sulfide (85%). The anil, upon acid hydrolysis, yields camphor and p-dimethylaminoaniline. Mixed melting points with known anil, m. p. 62°, show no lowering.

Acetone Anil.[7–10,17–19]—One hundred and seventy-seven grams of diisopropylaniline and 32 g. of sulfur are heated at 180–210° for five hours. The apparatus is arranged to allow low boiling products to distil as formed. The products include acetone anil (23%), b. p. 85–87° (13 mm.) and 199–202° (760 mm.); isopropylaniline (35%) identified as the N-phenyl, N'-phenyl, N'-isopropyl urea, m. p. 94–95°; isopropyl mercaptan (30%) identified as the 2,4-dinitrophenylisopropyl sulfide, m. p. 94–95°, as reported by Bost.[20] Small amounts of mesityl oxide anil, b. p. 123–126°, aniline and diisopropyl disulfide are also present among the products. The acetone anil, upon acid hydrolysis, yields aniline (acetyl, m. p. 114°) and acetone (p-nitrophenylhydrazone, m. p. 148–149°). Similarly, the mesityl oxide anil yields aniline and mesityl oxide, b. p. 133–136°.

Camphor Anil.—Twenty-seven grams of isobornylacetanilide[4] and 3.2 g. of sulfur are heated at 185–210° for six hours to yield camphor anil (40%), b. p. 118–120° (1 mm.), thioacetic acid (10%), hydrogen sulfide (50%), and unchanged amide (42%).

Dehydrogenation by Disulfides.—Thirteen and one-half grams of isopropylaniline and 15 g. of diisopropyl disulfide, b. p. 172–175°, are heated under reflux for six hours with the apparatus arranged to allow distillation of the mercaptan formed. Isopropyl mercaptan (20%) is recovered and identified as above. Acetone is obtained by acid hydrolysis of the reaction mixture.

Twenty-two and nine-tenths grams of isobornylaniline[3] and 20.6 g. of diamyl disulfide, b. p. 106° (5 mm.), are

(11) Busch and Rinck, *Ber.*, **38**, 1767 (1905).
(12) Bigelow and Eatough, *Org. Synth.*, Coll. Vol. I, **73** (1932).
(13) Reddelien, *Ber.*, **46**, 1597, 2712 (1913); **47**, 1355 (1914).
(14) Thomas and Jones, *J. Chem. Soc.*, **89**, 287 (1906).
(15) Von Braun, *Ber.*, **33**, 2732 (1900).
(16) Zander, *Ann.*, **214**, 170 (1882).

(17) Engler and Heine, *Ber.*, **6**, 642 (1873).
(18) Pauly, *Ann.*, **187**, 222 (1877).
(19) Riehm, *ibid.*, **238**, 4 (1887).
(20) Bost, THIS JOURNAL, **54**, 1985 (1932).

heated at 200–220° for twelve hours to yield amyl mercaptan (30%), b. p. 116–118°, and camphor anil.

Anil Scission by Hydrogen Sulfide.—Dry hydrogen sulfide gas is bubbled through dry benzophenone anil at 220° for two hours. Aniline, unchanged anil, and thiobenzophenone are recovered from the reaction products. The thiobenzophenone fraction, green oil of boiling range 170–175° (14 mm.), proved to be a mixture of the thioketone and the oxyketone into which the former is changed by exposure to moist air.

Summary

Ketone anils have been prepared by the sulfur dehydrogenation of mixed alkyl-aryl secondary amines of the type, Ph-NH-CHR$_2$.

Acetone anil has been prepared by the sulfur dealkanation of tertiary isopropyl anilines of the type, Ph-NR-CH(CH$_3$)$_2$.

Camphor anil has been prepared by the action of sulfur on isobornylacetanilide and also by the dehydrogenating action of alkyl disulfides on isobornylaniline.

Under the reaction conditions, the anils have been found to undergo scission by hydrogen sulfide, spontaneous aldolization, and reduction by mercaptans in a mercaptan–disulfide–anil–amine equilibrium.

The Electron Diffraction Investigation of Seven Chlorobenzenes

BY L. O. BROCKWAY AND K. J. PALMER

Introduction

The effect of conjugation on bond length was demonstrated a few years ago in the case of diacetylene and cyanogen,[1] in which the single carbon bond lying between two triple bonds, as the structures are ordinarily written, is 0.11 Å. shorter than a single bond in an unconjugated system. This bond shortening was explained as the effect of some double bond character introduced by the resonance of the molecules among several electronic structures including some having a double bond in the position of the single bond in the ordinary structure. This effect is well illustrated by the benzene molecule in which resonance chiefly between the two Kekulé structures shortens the single bonds in the individual structures by 0.15 Å.

More recently in an investigation of the chloroethylenes[2] a conjugated system of a similar type was found to exist when a single bond lies between two atoms, one of which has an unshared pair of electrons and the other is connected by a double bond to a third atom. In this case similar resonance possibilities arise; and the carbon–chlorine bonds in the chloroethylenes were found to be from 0.03 to 0.09 Å. shorter than they are in the chloromethanes. At that time it was suggested that in the halogen substituted benzenes also the carbon–halogen bonds would probably be af-

fected; and the present investigation was begun to measure the effect and to test the possible influence of the number and position of the substituent atoms. We are now reporting the results of the electron diffraction investigation of the vapors of hexachlorobenzene, 1,2,4,5-tetrachlorobenzene, 1,3,5-trichlorobenzene, o-, m-, and p-dichlorobenzenes, and monochlorobenzene.

Experimental

The materials used were obtained from the Eastman Kodak Co. Because of their relatively low vapor pressures at room temperature it was necessary to use a sample holder and gas nozzle which could be heated to about 300°. This consisted of a cylinder of monel metal about an inch (2.5 cm.) long and one-half inch (1.27 cm.) in diameter. The upper end was fitted with a removable cap which gave access for charging the holder with the sample. In the cap was a copper plug containing a 0.016″ (0.41-mm.) hole through which the vapor passed to meet the electron beam just above the top surface of the cap. The flow of vapor was controlled by a needle-pointed rod seated into the hole in the copper plug. The lower end of the monel cylinder was closed by a plate through which a sleeve passed for supporting the valve needle. The movement of this needle was controlled from the outside through a siphon connection. A resistance wire wound on the monel cylinder with mica insulation heated the

(1) L. O. Brockway, *Proc. Nat. Acad. Sci.*, **19**, 868 (1933).

(2) L. O. Brockway, J. Y. Beach and L. Pauling, THIS JOURNAL, **57**, 2693, 2705 (1935).