Evaporation of the combined filtrates yielded 1.2 g. (59.1%) of cyclic succinhydrazide, m.p. 267–271°. Recrystallization from ethanol raised the melting point to 277°.

Cyclic Succinhydrazide Diacetate (IX).—A mixture of 0.5 g. (0.0044 mole) of cyclic succinhydrazide and 10 ml. of acetic anhydride was refluxed for 2 hours and the excess acetic anhydride evaporated. The resulting oil was dissolved in about 15 ml. of a 1–4 ethanol–ether mixture and cooled. The diacetate crystallized and was purified from an ethanol–ether mixture to yield 0.41 g. of material, m.p. 130–132°.

Anal. Calcd. for $C_8H_{10}O_4N_2$: C, 48.48; H, 5.05; N, 14.14. Found: C, 48.50; H, 4.92; N, 14.12.

Reduction of Cyclic Succinhydrazide (VIII) to Succinamide (X).—One gram of cyclic succinhydrazide was dissolved in 400 ml. of absolute ethanol and 0.1 g. of Raney nickel catalyst was added. The mixture was then shaken under 70 atmospheres of hydrogen at 140° for 24 hours. The catalyst was removed by filtration, and the clear solution evaporated to a slurry. Filtration yielded 0.6 g. (60%) of succinamide, m.p. 260° dec., lit. value[12] 260° dec. A mixed melting point with an authentic specimen of succinamide was also found to be 260° dec.

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[12] G. F. Morrel, *J. Chem. Soc.*, **105**, 2705 (1914).

LAFAYETTE, INDIANA RECEIVED JANUARY 25, 1951

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

Decarboxylation of α-(Benzenesulfonamido)-carboxylic Acids

BY RICHARD H. WILEY AND N. R. SMITH[1]

A continued study of the base-catalyzed decarboxylation of carboxylic acids has shown that α-(benzenesulfonamido)-propionic acid decarboxylates on refluxing in a pyridine–acetic anhydride mixture to give 58% of the theoretical amount of carbon dioxide, 42% of diphenyl disulfide, and traces of 1,4-dibenzenesulfonyl-3,6-dimethylpiperazinedione-2,5. A possible mechanism for the reaction is discussed.

Recent studies of the decarboxylation reaction have resulted in several discussions of the mechanism of the reactions involved under the influence of acid[2a,b] and of basic catalysts[3–6] and on pyrolysis.[6–9] We wish to report in this paper the unusual formation of diphenyl disulfide in the base-catalysed decarboxylation of α-(benzenesulfonamido)-carboxylic acid and to comment on the possible mechanism of the reaction in terms of a *transitory* carbanion as an intermediate in a β-elimination type of reaction.[10]

When α-(benzenesulfonamido)-propionic acid was refluxed with excess pyridine and acetic anhydride a vigorous evolution of a gas took place. This gas consists only of carbon dioxide and was obtained in 58% of the theoretical amount. Two products have been isolated from the reaction mixture. Diphenyl disulfide was obtained in 42% yield (crude) and traces of a compound thought to be 1,4-dibenzenesulfonyl-3,6-dimethylpiperazinedione-2,5 have been isolated. Although the latter has not been previously described, compounds of this type are known to be formed by the action of acetic anhydride on *p*-toluenesulfonyl derivatives of amino acids.[11] In other experiments it has been shown that benzenesulfonamide, substituted for the acid, gave no diphenyl disulfide on refluxing with excess acetic anhydride and pyridine. Also, on refluxing α-(benzenesulfonamido)-propionic acid with pyridine alone no carbon dioxide was formed. On refluxing with acetic anhydride alone carbon dioxide and a tar, from which none of the disulfide was isolated, were formed.

This reaction may be formulated as a base-catalyzed, β-elimination corresponding to the dehydrohalogenation of β-halo acids. Initial attack by the base at the carbon adjacent to the nitrogen would provide a *transitory* carbanion in a reaction which, as in other β-elimination reactions,[10] is probably truly simultaneous and need not involve independent existence of the carbanion.

$$C_6H_5SO_2NHCH(CH_3)CO_2H \xrightarrow[-H^+]{\text{Base}}$$

$$[C_6H_5SO_2NH\overset{\curvearrowleft}{-}\ddot{C}H(CH_3)_2CO_2H]^- \xrightarrow{-[C_6H_5SO_2]^-}$$

$$[NH{=}C(CH_3)CO_2H] \xrightarrow{H^+} [CH_3CH{=}NH] + CO_2$$

Once formed, the sulfinite ion can undergo disproportionation, a recognized reaction,[12] but this reaction in which the yield is limited to 33$^1/_3$% is

$$3C_6H_5SO_2H \longrightarrow 2C_6H_5SO_3H + C_6H_5SH$$

insufficient to account for the 42% yield of disulfide

$$C_6H_5SO_2H \longrightarrow 2C_6H_5SO_3H + C_6H_5SH$$

obtained. The sulfinite may be reduced further by the aldimine. Under mild conditions anils[13] and

$$C_6H_5SO_2H + 2CH_3CH{=}NH \longrightarrow C_6H_5SH + 2CH_3CONH_2$$

aldehydes[14] are known to form addition compounds which dissociate at higher temperatures with oxidation–reduction and unclarified decomposition reactions, but there appears to be no exact analogy in the literature for this reaction. The fact that not over 58% of the theoretical amount of carbon diox-

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[1] The authors wish to acknowledge with thanks the grant received from the Research Committee of the College of Arts and Sciences of the University of Louisville in support of this work.

[2] (a) Johnson and Heinz, THIS JOURNAL, **71**, 2913 (1949); (b) Schenkel and Klein, *Helv. Chim. Acta*, **28**, 1211 (1945); Schenkel, *ibid.*, **29**, 436 (1946); Schenkel and Schenkel-Rudin, *ibid.*, **31**, 514 (1948).

[3] Cleland and Niemann, THIS JOURNAL, **71**, 841 (1949).

[4] Cornforth and Elliott, *Science*, **112**, 534 (1950).

[5] (a) Wiley and Borum, THIS JOURNAL, **72**, 1626 (1950); (b) Wiley and Hobson, *ibid.*, **71**, 2429 (1949).

[6] Ashworth, Daffern and Hammick, *J. Chem. Soc.*, 809 (1939).

[7] Sultanov, *J. Gen. Chem.* (*U.S.S.R.*), **16**, 1835 (1946); *C.A.*, **41**, 6223 (1947).

[8] Miller, Cook and Whitmore, THIS JOURNAL, **72**, 2732 (1950).

[9] Arnold, Elmer and Dodson, *ibid.*, **72**, 4359 (1950).

[10] Alexander, "Ionic Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 106.

[11] Wallin, *Acta Universitates Lundensis*, 2 Abt. Abhandl. II, **28**, 12 (1892); Beilstein, "Handbuch der organischen Chemie," Vol. 24, p. 269.

[12] Connor, in Gilman "Organic Chemistry," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 906.

[13] Knoevenagel and Römer, *Ber.*, **56**, 215 (1923).

[14] Bazlen, *ibid.*, **60**, 1470 (1927).

ide is obtained can be accounted for by the formation of the piperazinedione.

Experimental

Decarboxylation.—A typical experimental procedure is described. The ratio of reactants is that previously employed in the synthesis of acetamidoketones from amino acids.[5a] Three grams (0.013 mole) α-(benzenesulfonamido)-propionic acid, m.p. 126°, 5.3 ml. (0.065 mole) of pyridine and 7.4 ml. (0.078 mole) of acetic anhydride were mixed in a 25-ml. distilling flask equipped with a cold finger and a side arm arranged to collect the evolved gases under water saturated with carbon dioxide. The reaction mixture was heated immediately after mixing for 40 minutes under gentle reflux, during which time the evolution of gas practically ceased. The volume of gas, corrected for a small blank, was 170 ml. at S.T.P. or 58% of the theoretical amount of carbon dioxide expected if the acid was completely decarboxylated. This gas gave a precipitate with barium hydroxide and was completely soluble in sodium hydroxide.

The reaction mixture was acidified with an excess of hydrochloric acid and ice and extracted with ether. The combined extracts were washed with dilute acid, water, and then with saturated sodium bicarbonate solution until the latter had removed all acid present. The extracts were then dried and the ether removed under vacuum. The residue was extracted with hot 60° petroleum ether, leaving behind a non-crystalline, resinous material. The extracts were evaporated to a small volume and decanted from a small amount of oily substance. Evaporation of the petroleum ether yielded 0.6 g. (39%) of crude diphenyl disulfide melting above 55°. After recrystallization from ethanol–water, the disulfide melted at 60–61°. The diphenyl disulfide was identified by bromination to 4,4′-dibromodiphenyl disulfide, m.p. 93–94°; reported 93.5°.[15]

When benzenesulfonamide was substituted for the α-(benzenesulfonamido)-propionic acid, no reaction was observed and the starting material was recovered; similarly α-(benzenesulfonamido)-propionic acid, when heated with pyridine alone, gave no carbon dioxide and the starting material was recovered. However, if the α-(benzenesulfonamido)-propionic acid was heated under reflux with acetic anhydride, about 30% of the theoretical amount of carbon dioxide was evolved and a dark tar, which could not be crystallized, remained after evaporation of the solvent. No diphenyl disulfide could be detected even after boiling with pyridine. One reaction which was swept out with carbon dioxide and allowed to stand 30 minutes gave only a 33% yield of carbon dioxide and 20% diphenyl disulfide. The gas evolved was completely soluble in sodium hydroxide.

One reaction mixture was worked up by direct distillation of the reaction mixture. From this was isolated a 42% yield of diphenyl disulfide and a hard, dark, resinous material was left in the reaction flask. No benzenesulfonic acid could be isolated as its p-toluidine salt from either acid or alkaline extracts obtained from this residue. This residue gave positive qualitative tests for nitrogen and sulfur.

1,4-Dibenzenesulfonyl-3,6-dimethylpiperazinedione-2,5.—In one experiment, the acetic anhydride was added in small portions over a period of 30 minutes. There was obtained a 57% yield of carbon dioxide, which includes air introduced along with the acetic anhydride, a 38% yield of diphenyl disulfide and 0.2 g. of 1,4-dibenzenesulfonyl-3,6-dimethylpiperazinedione-2,5 (7%) m.p. 233–235° (uncor.) after recrystallization from ethanol. This compound gave positive qualitative tests for sulfur and nitrogen. It was insoluble in cold, dilute acid or base, but dissolved readily on boiling with 5% sodium hydroxide.

Anal. Calcd. for $C_{18}H_{16}N_2S_2$: N, 6.66. Found: N, 6.83.

LOUISVILLE 8, KY.

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[15] Bourgeois and Abraham, *Rec. trav. chim.*, **30**, 421 (1911).

[CONTRIBUTION FROM THE NAUGATUCK CHEMICAL DIVISION OF THE U. S. RUBBER CO.]

Some Thiazolylthio Hydroquinones

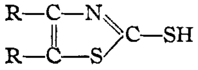
BY THOMAS H. NEWBY AND ELIZABETH C. HOWLETT

2-Mercaptobenzothiazole, 4,5-dimethyl-2-mercaptothiazole and 4-methyl-2-mercaptothiazole were treated with p-benzoquinone to give the corresponding thiazolylthio hydroquinones as shown by ultraviolet spectroscopic curves. The dibenzoates of the new compounds were prepared.

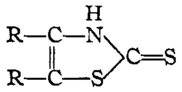
The addition of alkyl and aryl mercaptans to p-benzoquinone to give alkylthio and arylthio hydroquinones is well described in the literature[1]; however, no references to the reaction of thiazole mercaptans with quinone could be found. Inasmuch as alkylthio and arylthio hydroquinones had been found in this Laboratory to be of value as antioxidants, some thiazolylthio hydroquinones were prepared. 2-Mercaptobenzothiazole, 4,5-dimethyl-2-mercaptothiazole and 4-methyl-2-mercaptothiazole were used as starting materials because of cost and availability.

The reaction of mercaptans with p-benzoquinone to give dihydroxyphenyl monothioethers is complicated in many cases by the formation of di- and polythioethers; the initially formed dihydroxyphenyl thioether may or may not be oxidized by p-benzoquinone or air to the quinone thioether. If this oxidation occurs, a second molecule of mercaptan may add and the entire cycle be repeated.[1a]

The reaction of a thiazole mercaptan with p-benzoquinone is further complicated by the fact that thiazole mercaptans may exist in either the thiol (I) or the thione (II) form.



I



II

It is possible, then, for the product to be either a thioether or an aminohydroquinone derivative. Thiourea adds to p-benzoquinone to give a thioether.[2]

The additions of the thiazole mercaptans to p-benzoquinone were accomplished smoothly to give the desired 1:1 reaction products in good yield.

The compound obtained by treating 2-mercaptobenzothiazole with p-benzoquinone was subjected to ultraviolet spectrosopic analysis to determine its structure.[3] The curve obtained in this manner was compared to the curves obtained for authentic samples of 1-methyl-2-thio-1,2-dihydrobenzothiaz-

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[1] (a) J. Troeger and A. Eggert, *J. prakt. Chem.*, **53**, 482 (1896); (b) T. Posner, *Ann.*, **336**, 85 (1904); (c) J. Snell and A. Weissberger, THIS JOURNAL, **61**, 450 (1939); (d) O. Dimroth, L. Kraft and K. Aichinger, *Ann.*, **545**, 124 (1940).

[2] M. Schubert, THIS JOURNAL, **69**, 712 (1947).

[3] Ultraviolet spectroscopic analysis through the courtesy of Mr. J. E. Newell of the U. S. Rubber Company General Laboratories.