solved in 90 ml. of hot ethanol. Upon cooling, white crystals were obtained, m.p. 262–263°.

Four grams (0.0177 mole) of the above 1-thiadibenzo[*a,c*]-[3,6]cyclooctadiene were refluxed for 36 hr. with 30 ml. of absolute ethanol and 45 ml. (0.72 mole) of methyl iodide. Upon concentrating the reaction mixture down to a volume of 50 ml. with an air jet, white crystals were deposited upon standing overnight at −5°. Recrystallization from absolute ethanol produced white crystals (fluffy needles) which sublimed completely at 215–217°. In a sealed capillary, the crystals melted at 217°. The properties and analysis are consistent with a methyl iodide coordination complex of the sulfonium iodide.[5]

Anal. Calcd. for $C_{17}H_{20}SI_2$: I, 49.8. Found: I, 50.4.

1-Thiadibenzo[a,c][3,6]cyclooctadiene 1-dioxide (II). 1-Thiadibenzo[*a,c*][3,6]cyclooctadiene was prepared on a scale twice that described above. A mixture of 8.9 g. (0.039 mole) of this crude sulfide, 33 ml. (about 0.30 mole) of 30% hydrogen peroxide, and 130 ml. of glacial acetic acid was refluxed for 20 hr. The cooled mixture was poured into a cold solution of 87 g. of sodium hydroxide in 300 ml. of water and the resulting paste was allowed to cool to room temperature. Upon filtering off the crude sulfone and recrystallizing from an 80:20 benzene-toluene mixture, white crystals were obtained; yield 6.3 g. (61%), m.p. 258–259.

Anal. Calcd. for $C_{15}H_{14}SO_2$: C, 69.76; H, 5.43; mol. wt. 258. Found: C, 69.66; H, 5.40; mol. wt. 263.

Beckmann rearrangement of anthraquinone monoxime. The procedure for the reported successful Beckmann rearrangement of anthraquinone monoxime[6] was employed with poor results. A procedure patterned directly after the method used by Moore and Huntress[10] for the rearrangement of fluorenone oxime was employed successfully.

Anthraquinone monoxime (100 g.) was mixed with phosphorus oxychloride (200 ml.). A slurry of 125 g. of phosphorus pentachloride in 300 ml. of phosphorus oxychloride was cautiously added and the mixture was then refluxed for 5 hr. The phosphorus oxychloride (400 ml.) was distilled and the liquid residue was added to excess ice with vigorous stirring. The crude product was filtered off and dried; weight 94 g.; after recrystallization from acetic acid, m.p. 243–244°, literature[6] m.p. 245° for the cyclic amide.

Ninety grams of the cyclic amide from the above Beckmann rearrangement was refluxed with 90 g. of sodium hydroxide in 200 ml. of ethanol and 400 ml. of water for 6 hr. and was then poured into 1000 ml. of water, decolorized with 20 g. of Norite, cooled to 0°, and then acidified to yield yellowish-green crystals of 2′-aminobenzophenone-2-carboxylic acid; weight after recrystallization from 60% ethanol, 75 g.

Beckmann and Liesche[6] reported a melting point of 199° with decomposition and evolution of water to reform the Beckmann rearrangement amide, m.p. 245°. The recrystallized yellow 2′-aminobenzophenone-2-carboxylic acid, if placed in an initially cold melting point bath and then slowly heated, was found to change slowly to a gray solid (presumably the amide) melting at 243–244°. However, if the yellow crystals were placed in a preheated melting point bath at 180° and rapidly heated, it was found that the material melted with vigorous frothing at 191–194°, obviously expelling water; if these melted crystals were then allowed to solidify by standing for some time at room temperature, they were found to then melt at 243.5–244.5°, clearly indicating the conversion to the amide.

2-Aminodiphenylmethane-2-carboxylic acid and its lactam. The procedure of Bergmann and Loewenthal[7] for reducing benzophenone-2,2′-dicarboxylic acid to diphenylmethane-2,2′-dicarboxylic acid was found in this laboratory to be readily applicable to the reduction of the keto group of 2-benzoylbenzoic acid and 2′-aminobenzophenone-2-carboxylic acid.

A mixture of 75 g. (0.311 mole) 2′-aminobenzophenone-2-carboxylic acid, 450 ml. of concentrated ammonium hydroxide (sp. gr. 0.90), 150 ml. of water, 210 g. (3.12 g.-atoms) of zinc dust, and 4 ml. of an ammoniacal solution of 1*M* copper sulfate were gently refluxed with vigorous stirring for 20 hr. under a pressure slightly greater than atmospheric. Sodium carbonate solution (180 ml. of 10%) was added and refluxing with stirring was continued for an additional 20 hr. The resulting solution was filtered, the residue being extracted twice with hot 10% sodium carbonate solution. The combined filtrates were decolorized with 10 g. of Norite and acidified to give a crude grayish spongy mass of solid. Recrystallization from 80% ethanol gave nearly white crystals, m.p. 126–127°. The free acid slowly lactamized upon standing at room temperature while heating at 100–120°, or momentary heating to 190°, rapidly caused the formation of the internal seven-membered cyclic lactam of 2′-aminodiphenylmethane-2-carboxylic acid, m.p. 193–194°. The total yield of the free acid and lactam, collectively, was 75%. The experimental molecular weight was found to be 214, compared to a theoretical value of 209 for the monomeric amide.

Anal. Calcd. for $C_{14}H_{11}NO$: C, 80.46; H, 5.28; N, 6.72 Found: C, 80.13; H, 5.06; N, 6.94.

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The Synthesis of 2-Mercaptoethanesulfonamide

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Received July 25, 1960

As part of an investigation of mercaptoalkanesulfonic acids and related compounds,[2,3] the synthesis of 2-mercaptoethanesulfonamide (V) was undertaken. 2-Chloroethanesulfonyl chloride, (VI) available from previous work[2] was used in an attempt to prepare V *via* 2-chloroethanesulfonamide. However, both aqueous and anhydrous ammonia caused reaction of both chlorine atoms of VI. Dehydrochlorination of VI to ethenesulfonyl chloride and subsequent conversion to ethenesulfonamide[4,5] afforded such low yields that the addition of hydrogen sulfide was not attempted.

Conversion of 2-mercaptoethanesulfonic acid (I), also available from previous work,[3] to V requires the protection of the sulfhydryl group. Thioacetoxyethanesulfonyl chloride[6] was treated with dry ammonia but the resulting oil could not be purified. The desired synthesis of V was ac-

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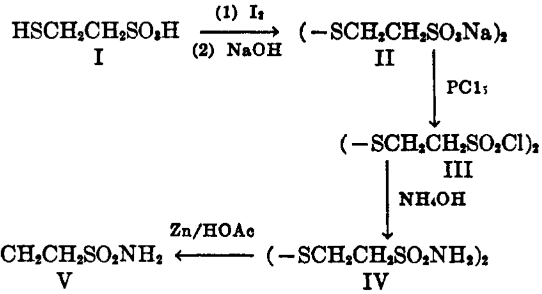
complished by protecting the sulfhydryl group through formation of the disulfide.



$$\begin{tikzcd}
\underset{I}{HSCH_2CH_2SO_3H} \arrow[r, "(1)\ I_2", "(2)\ NaOH"'] & \underset{II}{(-SCH_2CH_2SO_3Na)_2} \arrow[d, "PCl_5"] \\
& \underset{III}{(-SCH_2CH_2SO_2Cl)_2} \arrow[d, "NH_4OH"] \\
\underset{V}{HSCH_2CH_2SO_2NH_2} & \underset{IV}{(-SCH_2CH_2SO_2NH_2)_2} \arrow[l, "Zn/HOAc"']
\end{tikzcd}$$

EXPERIMENTAL

Disodium-3,4-dithia-1,6-hexanedisulfonate (II). Iodine (39 g., 0.31 equivalent) was added to 250 ml. of a stock solution 2-mercaptoethanesulfonic acid (I) containing 54 g. (0.33 equivalent) of solute based on acidimetric titration.[7] A slight amount of iodine color remained undischarged. The disulfonic acid and the hydriodic acid were neutralized with 25.5 g. of sodium hydroxide (0.64 equivalent) in 25 ml. of water. The solution was then diluted with 380 ml. of methanol and treated with 1200 ml. of acetone. A copious precipitate was filtered, washed with acetone, and dried at 70°. It weighed 56.3 g. Recrystallization of 55.0 g. from 50 ml. of water gave 45 g. of wet crystals (not washed) which dried to 35.2 g. of (II) (65% yield).

Anal. Calcd. for $C_4H_8Na_2O_6S_4$: mol. wt., 326. Found[8]; 328.

3,4-Dithia-1,6-hexanedisulfonyl chloride (III). A dry mixture of 105 g. of II (0.32 mole) and 149 g. of phosphorus pentachloride (0.72 mole) was allowed to stand until it had turned molten and the heat of reaction had dissipated. Fumes were evolved and 24 g. was lost. An additional 93 g. of phosphorus oxychloride was removed by distillation at reduced pressure. The residue, 137 g., was taken up in 300 ml. of benzene, filtered to remove sodium chloride, and stripped to 95 g. of oily crystals. Filtration and washing with petroleum ether (b.p. 90–120°) gave 45 g. of III melting at 64°–72°. Mixing the mother and wash liquors gave more crystals which were dissolved in hot benzene filtered with Norite, and recovered by the addition of petroleum ether. This crop weighed 20 g. (total yield 0.204 mole, 63%) and melted at 68°–72°.

3,4-Dithia-1,6-hexanedisulfonamide (IV). Dithiahexanesulfonyl chloride (III), 20 g., was added to 200 ml. of concd. ammonium hydroxide with cooling to hold the temperature below 25°. The solid dissolved. The solution was concentrated to 100 ml. at reduced pressure, giving a precipitate which was filtered with great difficulty. The very finely divided powder was recrystallized from alcohol with Norite and again from alcohol to give 3.0 g. of crystals (17% yield) melting 146°–151°. Analysis by reduction showed a purity of 99%.

In another preparation the crude powder was recrystallized from water and three times from alcohol, the last time with Norite, to give platelets melting at 152.5°–154°.

Anal. Calcd. for $C_4H_{12}N_2O_4S_4$: S, 45.74. Found: S, 45.89.

2-Mercaptoethanesulfonamide (V). A solution of 7.0 g. (0.025 mole) of disulfonamide (IV) was prepared in a mixture of 50 ml. of water and 40 ml. of acetic acid at 90°. Eleven grams of 20-mesh zinc were added and the reduction mixture held at 90° for 45 min. The zinc was filtered off and the filtrate made up to 100 ml. Titration of an aliquot showed the presence of 50 mequivalents of mercaptan. Ten grams (63 mequivalents) of mercuric acetate in 20 ml. of water were added and the resulting precipitate was filtered and washed with ethanol. It was suspended in water and hydrogen sulfide passed in until the light colored solid had disappeared. Most of the mercuric sulfide suspension was removed by centrifuging and decantation. The rest was filtered on a Seitz K5 asbestos filter.

The solution of 2-mercaptoethanesulfonamide was concentrated at reduced pressure, leaving a small amount of oil. 1-Propanol was added and the solution again concentrated to an oil. Addition of petroleum ether gave 3.0 g. of crystals (yield 43%) which assayed 96% by iodometric titration.[8] A sharp melting point could not be obtained on this product.

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[7] Iodometric titration showed only 0.31 equivalent of mercaptan. The discrepancy is probably due to disulfide formed in the solution by air oxidation.

[8] Samples of 100 mg. were dissolved in 20 ml. of water and 5 ml. of sulfuric acid. Titration showed the absence of mercaptan. One-half gram of powdered zinc was added and the reaction allowed to proceed for 30 min. (Similar results were obtained after 20 min. or 40 min.) The metallic zinc was removed, and the solutions were titrated with standard tenth normal iodine.

Oxidation of Dialkyl Sulfides with Nitric Acid

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Received June 27, 1960

Many articles in the literature describe the oxidation of organic sulfides and sulfoxides to the corresponding sulfones. Oxidizing agents which are cited[1] are hydrogen peroxide, organic peroxides, per acids, potassium permanganate, sodium hypochlorite, hypochlorous acid, aqueous chlorine, chromic acid, oxygen, ozone, oxides of nitrogen, fuming nitric acid, ruthenium tetroxide,[2] and potassium persulfate.[3] Anodic oxidation also has been used.

For commercial processes, the above oxidizing agents are relatively costly and thus a search for an inexpensive oxidizing agent was undertaken. Nitric acid offers the advantage of economy over most of the other oxidants. Not only is the initial cost low but also the recovery of nitrogen oxides produced during oxidation and passage through a nitric acid tower assures very high recovery of the acid for re-use.

The oxidation of sulfides to corresponding sulfoxides with nitric acid[4,5] has been known to proceed smoothly and in good yield for many years. However, oxidation in high yield of the resulting sulfoxides to sulfones with nitric acid has heretofore not been realized at ordinary pressures.[6,7,8]

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