dioxane and poured into excess concentrated ammonia. After the mixture had been allowed to stand overnight, the tan precipitate was collected and dried to give 8.5 g. (94%) of (VII) which melted at 240–241° after one recrystallization from absolute ethanol.

Anal. Calcd. for $C_{10}H_7NO_3S$: S, 14.50. Found: S, 14.23.

2-Acetamido-5,6-methylenedioxybenzothiophene (VIII). The amide prepared in the preceding experiment was subjected to the Hofmann hypobromite reaction according to the procedure of Vogel.[5] Eight grams (0.036 mole) of VII was treated with 30 ml. of a solution made by dissolving 8.4 ml. of bromine in 120 ml. of water containing 30 g. of sodium hydroxide. The mixture was warmed slightly until the reaction started and was then held at 80–90° for 45 min. The resulting suspension was diluted with 25 ml. of water and cooled to room temperature. Twenty milliliters (0.21 mole) of acetic anhydride was added with rapid stirring over a period of 20 min. and then the mixture was warmed at 60° for 0.5 hr. After the solution had been allowed to cool in the refrigerator overnight, the brown precipitate was collected and recrystallized from ethanol. The yield was 6 g. (70%) of red warty aggregates which melted at 241°. A mixed melting point with compound VI was depressed to 208–215°, and one with compound VII was depressed to 223–240°.

Anal. Calcd. for $C_{11}H_9NO_3S$: N, 5.95; S, 13.62. Found: N, 5.83; S, 13.98.

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[5] A. I. Vogel, *Practical Organic Chemistry*, Longmans, Green, Inc., N. Y., 3rd edition, 1956, p. 773.

1-Thiadibenzo[*a,c*][3,6]cyclooctadiene and Other Cyclic *o,o'*-Bridged Diphenylmethanes[1]

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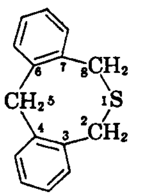
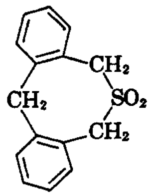
Regarding our studies on the preparation and geometry of various *o,o'*-bridged biphenyls and diphenylmethanes, it appears unlikely that further experimental work along these lines will be undertaken in the near future at this laboratory. Hence, the present data are being published in the hope that they may be of use to other workers, particularly since the stereochemistry of *o,o'*-bridged diphenylmethanes has yet to be demonstrated.

2,2'-Bis(bromomethyl)diphenylmethane, prepared from phthalic anhydride by the complex route of Bergmann and Pelchowicz,[3] was cyclized with methanolic sodium sulfide to the eight-membered ring 1-thiadibenzo[*a,c*][3,6]cyclooctadiene (I) approximately as readily as similar cyclization to the corresponding seven-membered sulfide in the biphenyl series occurred.[4] It was not necessary to use high dilution techniques in order to obtain good yields of the cyclic sulfide.



I



II

Oxidation of the sulfide (I) to the corresponding sulfone (II, 1-thiadibenzo[*a,c*][3,6]cyclooctadiene-1-dioxide) was readily accomplished with hydrogen peroxide in acetic acid. Alkylation of I with excess methyl iodide in ethanol produced a sublimable and water-insoluble coordination complex with an analysis corresponding to two g.-atoms of iodine per mole; the literature has described methyl iodide, haloform, and metal halide coordination complexes of sulfonium salts.[5]

Reduction of 2'-aminobenzophenone-2-carboxylic acid[6] to 2'-aminodiphenylmethane-2-carboxylic acid was accomplished *via* reduction by means of zinc dust (activated by copper) in ammonia.[7] Although stable indefinitely as carboxylate salts, the free 2'-aminodiphenylmethane-2-carboxylic acid cyclized slowly at room temperature (rapidly at 100°) to form the seven-membered ring cyclic lactam, indicating that this amino acid is more stable than 2'-aminobiphenyl-2-carboxylic acid and 2'-aminobiphenyl-2-acetic acid which have never been isolated, both cyclizing spontaneously to their six- and seven-membered cyclic lactams, respectively.[8]

EXPERIMENTAL[9]

1-Thiadibenzo[*a,c*][*3,6*]*cyclooctadiene* (I). A mixture of 10 g. (0.028 mole) of 2,2'-bis(bromomethyl)diphenylmethane,[3] 30 g. of sodium sulfide nonahydrate (0.125 mole), 80 ml. of water, and 1600 ml. of methanol were gently refluxed with stirring for 36 hr. The methanol was distilled and the residue was taken up in 500 ml. of cold water. The water-insoluble product was filtered off and recrystallized from a mixture of alcohol and benzene. The yield was 4.6 g. (72%), m.p. 194–195°.

Anal. Calcd. for $C_{15}H_{14}S$: C, 79.64; H, 6.19; mol. wt. 226. Found: C, 79.39; H, 6.14; mol. wt. 226.

A mercuric chloride coordination complex of the above sulfide was prepared by dissolving 1.00 g. of mercuric chloride in 10 ml. of hot absolute ethanol and adding quickly, with rapid stirring, a solution of 0.86 g. of the sulfide dis-

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[1] Abstracted from the doctoral thesis submitted to Purdue University in 1956 by Donald D. Emrick.

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[3] E. D. Bergmann and Z. Pelchowicz, *J. Am. Chem. Soc.*, **75**, 4281 (1953).

[4] W. E. Truce and D. D. Emrick, *J. Am. Chem. Soc.*, **78**, 6130 (1956).

[5] N. V. Sidgwick, *The Chemical Elements and Their Compounds*, Vol. II, Oxford University Press, London, 1950; *Chem. Zentr.*, **69**, ii, 524 (1898) [Farbenfabriken vorm. Friedr. Bayer & Co., DRP 97207 (1897)].

[6] E. Beckmann and O. Liesche, *Ber.*, **56**, 1 (1923).

[7] E. D. Bergmann and E. Loewenthal, *Bull. soc. chim., France*, **19**, 66 (1952).

[8] L. Oyster and H. Adkins, *J. Am. Chem. Soc.*, **43**, 208 (1921); C. W. Muth, W. L. Sung, and Z. B. Papanastassiou, *J. Am. Chem. Soc.*, **77**, 3393 (1955).

[9] Boiling and melting points reported are uncorrected.

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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(10) F. J. Moore and E. H. Huntress, *J. Am. Chem. Soc.*, **49**, 2618 (1927).

The Synthesis of 2-Mercaptoethanesulfonamide

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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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(2) C. Walling and W. F. Pease, *J. Org. Chem.*, **23**, 478 (1958).

(3) C. H. Schramm, H. Lemaire, and R. H. Karlson, *J. Am. Chem. Soc.*, **77**, 6231 (1955).

(4) C. S. Rondestvedt, Jr., *J. Am. Chem. Soc.*, **76**, 1926 (1954).

(5) P. W. Clutterbuck and J. B. Cohen, *J. Chem. Soc.*, 120 (1922).

(6) H. D. Porter and A. Weisberger, U. S. Patent 2,396,-879, March 19, 1946.