enolic nature of the carboxyimides, and therefore allows lactonic oxazine ring formation.

In further studies, the carboxyimides of β-(2-methoxy-4-methylphenyl)glutaric acid and β-(2,4-dimethoxyphenyl)glutaric acid (VIb and c) were prepared and treated with acetic anhydride. The carboxyimides were recovered unchanged indicating the absence of enolization in the case of glutaric acid imides.

EXPERIMENTAL

1-(2-Carbomethoxyphenyl)-4-(4-methoxyphenyl)-6-hydroxy-2-pyridone (IIa). A mixture of 2.2 g. (0.01 mol.) of β-(4-methoxyphenyl)glutaconic anhydride[4] and 5 ml. of methyl anthranilate was heated at reflux temperature in an oil bath for 10 min. After cooling, the red gummy solid was treated with concentrated hydrochloric acid. The solid was collected on a filter and after it had been washed with several portions of cold water, it was air dried. Two recrystallizations from 50% acetic acid gave 3.2 g. (92% yield) of IIa, m.p. 126–130°. An analytical sample was prepared by further recrystallization from ethanol, m.p. 131–132°. It was insoluble in dilute sodium bicarbonate but soluble in dilute sodium hydroxide. The pyridone was recovered from the alkaline solution by acidification with dilute hydrochloric acid.

Anal. Calcd. for $C_{20}H_{17}NO_5$: C, 68.37; H, 4.88; N, 3.99. Found: C, 68.63; H, 5.19; N, 4.10.

1-(2-Carboxyphenyl)-4-(4-methoxyphenyl)-6-hydroxy-2-pyridone (IIIa). The acid (IIIa) was obtained in 63% yield by hydrolysis of the ester (IIa) with ethanolic sodium hydroxide solution. Recrystallization from ethanol gave pure IIIa, m.p. 194–195° (dec.).

Anal. Calcd. for $C_{19}H_{15}NO_5$: C, 67.65; H, 4.48; neut. equiv., 168.7. Found: C, 67.33; H, 4.75; neut. equiv., 171.0.

1-(2-Carboxyphenyl)-4-(4-methoxyphenyl)-6-hydroxy-2-pyridone lactone (IVa). A mixture of 6.7 g. (0.02 mol.) of IIIa and 20 ml. acetic anhydride was refluxed for 1 hr. The contents of the reaction flask was stirred into an excess of cold water (*ca.* 50 ml.) and the solid that separated was collected on a filter. It was washed with water, 5%-sodium bicarbonate solution, and again with water. The dry solid was recrystallized three times from alcohol to afford 2.6 g. (42% yield) of IVa as white needles, m.p. 85–86.5°.

Anal. Calcd. for $C_{19}H_{13}NO_4$: C, 71.47; H, 4.10. Found: C, 71.11; H, 4.45.

1-(2-Carbomethoxyphenyl)-4-(2-methoxy-4-methylphenyl)-6-hydroxy-2-pyridone (IIb). The procedure used in making this compound was the same described for IIa. From 5.8 g. (0.025 mol.) of β-(2-methoxy-4-methylphenyl)glutaconic anhydride,[5] 8.2 g. (90% yield) of IIb was obtained as dull white crystals, m.p. 175–176°.

Anal. Calcd. for $C_{21}H_{19}NO_5$: C, 69.03; H, 5.24; N, 3.83. Found: C, 69.34; H, 5.12; N, 4.02.

1-(2-Carboxyphenyl)-4-(2-methoxy-4-methylphenyl)-6-hydroxy-2-pyridone (IIIb). This acid was prepared by alkaline hydrolysis of IIb. From 3.6 g. (0.01 mol.) of IIb, 1.9 g. (54% yield) of the acid (IIIb) was obtained, m.p. 214–216° (dec.).

Anal. Calcd. for $C_{20}H_{17}NO_5$: C, 68.37; H, 4.88; neut. equiv., 175.6. Found: C, 68.18; H, 5.01; neut. equiv., 172.4.

1-(2-Carboxyphenyl)-4-(2-methoxy-4-methylphenyl)-6-hydroxy-2-pyridone lactone (IVb). Treatment of IIIb with acetic anhydride by the procedure outlined for IVa, gave IVb in 47% yield, m.p. 163–164.5°.

Anal. Calcd. for $C_{20}H_{15}NO_4$: C, 72.06; H, 4.54. Found: C, 72.19; H, 4.52.

1-(2-Carbomethoxyphenyl)-4-(2,4-dimethoxyphenyl)-6-hydroxy-2-pyridone (IIc). This ester was prepared from β-(2,4-dimethoxyphenyl)glutaconic anhydride[6] by the procedure used for IIa. The yield of IIc was 93%, m.p. 118–118.5°.

Anal. Calcd. for $C_{21}H_{19}NO_6$: C, 66.13; H, 5.02. Found: C, 65.96; H, 4.76.

1-(2-Carboxyphenyl)-4-(2,4-dimethoxyphenyl)-6-2-hydroxy-pyridone (IIIc). Alkaline hydrolysis of the ester (IIc) gave IIIc in 87% yield, m.p. 170–171° (dec.).

Anal. Calcd. for $C_{20}H_{17}NO_6$: C, 65.39; H, 4.66; neut. equiv., 188.65. Found: C, 65.25; H, 4.50; neut. equiv., 185.20.

1-(2-Carboxyphenyl)-4-(2,4-dimethoxyphenyl)-6-hydroxy-2-pyridone lactone (IVc). This lactone was made from IIIc by treatment with acetic anhydride following the procedure used for IVa. From 3.7 g. (0.01 mol.) of the acid (IIIc), 1.7 g. (48% yield) of IVc was obtained, m.p. 152–153.5°.

Anal. Calcd. for $C_{20}H_{15}NO_5$: C, 68.76; H, 4.33. Found: C, 68.60; H, 4.19.

1-(2-Carbomethoxyphenyl)-4-(2-methoxy-4-methylphenyl)-piperidine-2,6-dione (Vb). A mixture of 2.5 g. (0.01 mol.) of β-(2-methoxy-4-methylphenyl)glutaric acid[7] and 7.5 ml. of methyl anthranilate was heated at reflux temperature for 15 min. The resulting product after processing as in the preparation of IIa, gave 3.2 g. (87% yield) of Vb, m.p. 120–121°.

Anal. Calcd. for $C_{21}H_{21}NO_5$: C, 68.65; H, 5.76. Found: C, 68.44; H, 5.40.

It was found completely insoluble in dilute sodium bicarbonate and dilute sodium hydroxide solution and gave a negative test with ferric chloride.

1-(2-Carboxyphenyl)-4-(2-methoxy-4-methylphenyl)-piperidine-2,6-dione (VIb). This acid was prepared in 57% yield by the alkaline hydrolysis of Vb, m.p. 152–152.5°. It dissolved in dilute sodium bicarbonate solution with effervescence.

Anal. Calcd. for $C_{20}H_{19}NO_5$: neut. equiv., 353.61. Found: neut. equiv., 352.80.

1-(2-Carbomethoxyphenyl)-4-(2,4-dimethoxyphenyl)-piperidine-2,6-dione (Vc). This substance was prepared from β-(2,4-dimethoxyphenyl)glutaric acid[1] and methyl anthranilate by the procedure adopted for making IIa. The yield of Vc was 88%, m.p. 145–145.5°.

Anal. Calcd. for $C_{21}H_{21}NO_6$: C, 65.78; H, 5.52. Found: C, 65.52; H, 5.20.

1-(2-Carboxyphenyl)-4-(2,4-dimethoxyphenyl)-piperidine-2,6-dione (VIc). Alkaline hydrolysis of Vc gave VIc in 46% yield, m.p. 134–136°.

Anal. Calcd. for $C_{20}H_{19}NO_6$: neut. equiv., 369.4. Found: neut. equiv., 368.0.

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(7) D. B. Limaye and R. G. Chitre, *J. Univ. Bombay*, **4**, 101 (1935).

Some 2- and 4-Substituted Estrone 3-Methyl Ethers[1a,b]

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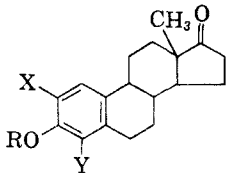
This communication describes the syntheses of several 2- and 4-substituted 1,3,5(10)-estratriene-17-one (estrone) 3-methyl ethers which were required for a biological study of the effect of substi-

tution at these sites on the estrogenic potency of estrone 3-methyl ether.

The positional assignment of substituents in 2-nitroestrone (IIIa) and 4-nitroestrone (IVa) have recently been established from two independent studies.[2-4] Unfortunately, a description of the preparative method failed to include the relative yields of the isomeric mononitroestrones and 2,4-dinitroestrone (Va) from I. Moreover, repetition of this procedure[3] indicated that the mechanical difficulties inherent in the chromatographic separation of IIIa, IVa, and Va would be increased in an extension of the method to the needs of the present study.



I. X = Y = R = H
II. X = Y = H; R = CH_3
IIIa. X = NO_2, Y = R = H
b. X = NO_2, Y = H, R = CH_3
c. X = NH_2, Y = H, R = CH_3
d. X = Cl, Y = H, R = CH_3
e. X = Br, Y = H, R = CH_3
f. X = I, Y = H, R = CH_3
IVa. X = R = H, Y = NO_2
b. X = H, Y = NO_2, R = CH_3
c. X = H, Y = NH_2, R = CH_3
d. X = H, Y = Cl, R = CH_3
e. X = H, Y = Br, R = CH_3
f. X = H, Y = I, R = CH_3
Va. X = Y = NO_2, R = H
b. X = Y = NO_2, R = CH_3
c. X = NH_2, Y = NO_2, R = CH_3

A reinvestigation of this reaction showed, in accord with previous observations[2] that the majority of IVa is deposited from the nitrating medium following the completion of the reaction. However, the use of one equivalent of concentrated nitric acid reduces the formation of the dinitro derivative (Va) to less than 1%.[5] Removal of Va from IIIa and the remaining IVa was accomplished by washing the mixture with aqueous sodium bicarbonate. Fractional crystallization of the residue effected a separation of IIIa from a small quantity of IVa. The mononitroestrones, IIIa and IVa, were, thus, obtained in 38% and 44% yield, respectively.

Methylation of IIIa and IVa, followed by catalytic reduction of the corresponding methyl ethers IIIb and IVb, gave 2-amino- (IIIc) and 4-aminoestrone 3-methyl ether (IVc).[6] The dinitroestrone (Va) was converted to a 2,4-dinitroestrone 3-methyl ether (Vb) in 65% yield with methyl iodide and potassium carbonate in acetone. Partial reduction of Vb with one equivalent of stannous chloride gave 2-amino-4-nitroestrone 3-methyl ether (Vc). The identity of the latter was established by successive diazotization and reduction which yielded a product identical with IVb.

The isomeric aminoestrone 3-methyl ethers (IIIc and IVc) were converted to the corresponding haloestrone 3-methyl ethers [Cl (IIId and IVd), Br (IIIe and IVe), and I (IIIf and IVf)] by conventional Sandmeyer reactions.

EXPERIMENTAL[7]

Nitration of estrone (I). To a solution of 17.28 g. of estrone (0.064 mol.) in 900 ml. of glacial acetic acid at 70–75° was added, all at once with stirring, a solution of 4 ml. of concentrated nitric acid, sp. g. 1.42, in 100 ml. of glacial acetic acid. The clear solution was allowed to cool to room temperature and then stand for 18 hr. during which time 4-nitroestrone (IVa) was deposited, wt. 8.13 g., m.p. 273–276° dec. (lit.[2] 270–280° dec.). The filtrate was evaporated to dryness *in vacuo*, the residue dissolved in 300 ml. of benzene and stirred for 5–6 hr. with 200 ml. of 2% sodium bicarbonate. The aqueous layer was then drawn off and acidified with concentrated hydrochloric acid. The 2,4-dinitroestrone (Va) was then collected, wt. 0.2 g. (yield 1%), m.p. 179–184°. Recrystallization from 95% ethanol gave light yellow plates, m.p. 183–184° (lit.[2] 185–187°).

The benzene fraction was dried over magnesium sulfate and concentrated to a volume of approximately 50 ml. which afforded an additional crop, 0.75 g. of IVa, m.p. 273–276° dec. (total yield 8.88 g., 44%). The filtrate was finally evaporated to dryness *in vacuo* and the residue crystallized from 95% ethanol to give 7.75 g. (38%) yield of 2-nitroestrone (IIIa), m.p. 174–176° (lit.[2] 183.5–184°). A pure sample of IIIa, m.p. 185–186° was obtained in the form of transparent irregular plates by slow crystallization from 95% ethanol. However, the material, m.p. 174–176°, is sufficiently pure to proceed with the methylation step.

4-Nitroestrone 3-methyl ether (IVb). To a solution of 1.58 g. of IVa (0.005 mol.) in 20 ml. of 10% sodium hydroxide, diluted with water to a volume of *ca.* 300 ml. was added portionwise with stirring, along with additional 10% sodium hydroxide, 30 ml. of dimethyl sulfate. The mixture was stirred for 2 hr. at room temperature and then heated to 75° for 0.5 hr. The mixture was cooled and the product collected, wt. 125 g. (75% yield), m.p. 258–259°, $[\alpha]_D^{26}$ +209° (lit.[6] 261°, $[\alpha]_D^{30}$ +212°).

(1) (a) This work was supported in part by an institutional grant to the Detroit Institute of Cancer Research from the American Cancer Society, Southeastern Michigan Division, and in part by research grants p-IR-17J from the American Cancer Society, Inc., and CY-2903 from the National Cancer Institute, Public Health Service. (b) Presented before the Division of Medicinal Chemistry at the 134th Meeting of the American Chemical Society, Chicago, Ill., September 1958.

(2) H. Werbin and C. Holloway, *J. Biol. Chem.*, **223**, 651 (1956).

(3) R. A. Pickering and H. Werbin, *J. Am. Chem. Soc.*, **80**, 680 (1958).

(4) S. Kraychy and T. F. Gallagher, *J. Am. Chem. Soc.*, **79**, 754 (1957).

(5) The original procedure employs, approximately, two equivalents of nitric acid and leads to considerable Va.

(6) After the present study had been completed, S. Kraychy, *J. Am. Chem. Soc.*, **81**, 1702 (1959), reported the conversion of 2-nitro- and 4-nitroestrone to IIIc and IVc by similar methods. The precursory nitroestrones, IIIa and IVa, however, were obtained according to the procedure of Werbin and Holloway.

(7) All melting points are uncorrected. Rotations were determined in a 1-dcm. tube and chloroform was the solvent. Analyses were performed by Micro-Tech Laboratories, Skokie, Ill.

2-Nitroestrone 3-methyl ether (IIIb). A mixture of 3.15 g. of IIIa (0.01 mol.), 100 g. of anhydrous potassium carbonate and 50 ml. of methyl iodide in 200 ml. of acetone was stirred under reflux for 30 hr. The inorganic salts were removed by filtration and the filtrate was evaporated to dryness *in vacuo* to give 3.12 g. (94% yield) of product, m.p. 148–150°. Two recrystallizations from 95% ethanol gave light yellow needles, m.p. 161–162°, $[\alpha]_D^{26}$ +146°. A double melting point, 147° and 157.5–159.5° ($[\alpha]_D^{24}$ +146°) has been recorded for IIIb.[6]

Anal. Calcd. for $C_{19}H_{23}NO_4$: C, 69.27; H, 7.04. Found: C, 68.94; H, 6.91.

2,4-Dinitroestrone 3-methyl ether (Vb). A mixture of 3.60 g. of Va[8] (0.01 mol.), m.p. 184–185°, 100 g. of anhydrous potassium carbonate, and 50 ml. of methyl iodide in 500 ml. of acetone was stirred under reflux for 36 hr. An additional 50 ml. of methyl iodide was added and the mixture refluxed with stirring for another period of 36 hr. The inorganic salts were separated by filtration and the filtrate evaporated to dryness *in vacuo*. The residue was collected, washed with water, and recrystallized from a mixture of acetone, methanol, and water to give 2.45 g. (65% yield) of yellow plates, m.p. 116–117°. Three recrystallizations from ethanol provided an analytical sample, m.p. 119–120°, $[\alpha]_D^{26}$ +179°.

Anal. Calcd. for $C_{19}H_{22}N_2O_6$: C, 60.94; H, 5.92. Found: C, 60.99; H, 6.09.

2-Aminoestrone 3-methyl ether (IIIc). A solution of 3.2 g. of IIIb (0.0097 mol.) in 150 ml. of 95% ethanol was shaken with (1 teaspoonful) W-2 Raney nickel[9] under 15 lb. of hydrogen for *ca.* 15 min. The catalyst was separated by filtration and the filtrate evaporated to dryness *in vacuo*. The residue was washed into a filter funnel with petroleum ether (65–110°) and sucked dry, wt. 2.36 g. (81% yield), m.p. 160–163°. An analytical sample was obtained in the form of colorless needles on recrystallization from a mixture of ether and petroleum ether (65–110°), m.p. 164–165°, $[\alpha]_D^{26}$ +153° (lit.[6] 160.5–162.5° and 172.5–174.5°, $[\alpha]_D^{28.5}$ +155°).

Anal. Calcd. for $C_{19}H_{25}NO_2$: C, 76.21; H, 8.42. Found: C, 76.50; H, 8.56.

4-Aminoestrone 3-methyl ether (IVc). Application of this same method to IVb gave IVc in 62% yield, m.p. 187–189°. The analytical sample, m.p. 190–191°, $[\alpha]_D^{27}$ +140° (lit.[6] 190.5–191.5°, $[\alpha]_D^{28}$ +149°) was obtained in the form of colorless needles from a mixture of benzene and petroleum ether (65–110°).

Anal. Found: C, 75.68; H, 8.32.

2-Amino-4-nitroestrone 3-methyl ether (Vc). To a solution of 3.74 g. of Vb (0.01 mol.) in 150 ml. of glacial acetic acid at 50° was added all at once with stirring a solution of 6.75 g. of stannous chloride dihydrate (0.03 mol.) in 20 ml. of concentrated hydrochloric acid. The mixture was stirred at room temperature for 3 hr., warmed to 75° for 0.5 hr., then concentrated *in vacuo* to *ca.* one third the original volume. The reaction mixture was made basic with excess 10% sodium hydroxide, the product was, then, collected, and washed with generous quantities of water. The product crystallized from ethanol in the form of yellow plates, wt. 2.51 g. (73% yield), m.p. 200–202°. An analytical sample was obtained by recrystallization from a mixture of ether and petroleum ether (60–110°), m.p. 203–204°, $[\alpha]_D^{26}$ +210°.

Anal. Calcd. for $C_{19}H_{24}N_2O_4$: C, 66.25; H, 7.02. Found: C, 66.21; H, 7.02.

To a solution of 0.5 g. of sodium nitrite (0.007 mol.) in a mixture of 2 ml. of concentrated sulfuric acid and 25 ml. of hypophosphorous acid (50%), cooled to 0°, was added, all at once, a solution of 0.344 g. of Vc (0.001 mol.) in 10 ml. of glacial acetic acid. The temperature of the reaction mixture was maintained at 5 to 10° for 2 hr., then 100 ml. of ice water was added and the vessel refrigerated (5°) for 2 days. The product, which was deposited during this period, was collected, washed with water, and sucked dry, wt. 0.198 g. (60% yield), m.p. 248–250°. Recrystallization from ethanol gave yellow plates, m.p. 258–259°, alone or admixed with an authentic sample of IVb.

2-Chloroestrone 3-methyl ether (IIId). A solution of 299 mg. of IIIc (1 mmol.) in 12 ml. of 2*N* hydrochloric acid was diazotized at 5–10° with a solution of 80 mg. of sodium nitrite (1.15 mmol.) dissolved in 5 ml. of water. The solution was stirred for 0.5 hr. followed by the dropwise addition of 500 mg. of cuprous chloride dissolved in 25 ml. of 0.5*N* hydrochloric acid. The mixture was stirred magnetically at, approximately, room temperature for 24 hr. and the product collected, wt. 200 mg. (63% yield), m.p. 186–190°. Three recrystallizations from a mixture of ether and petroleum ether (30–60°) provided analytical and biological samples in the form of slightly yellow colored needles, m.p. 191–192°, $[\alpha]_D^{26}$ +146°.

Anal. Calcd. for $C_{19}H_{23}ClO_2$: C, 71.57; H, 7.27. Found: C, 71.47; H, 7.17.

4-Chloroestrone 3-methyl ether (IVd). The conversion of 1.0 mmol. of IVc to IVd was carried out with the same quantities of reagents and under the same conditions as those described above; yield 220 mg. (69%), m.p. 190–198°. Several recrystallizations from 95% ethanol provided the analytical and biological samples in the form of needles, m.p. 196–197°, $[\alpha]_D^{26}$ +143°.

Anal. Found: C, 71.72; H, 7.40.

2-Bromoestrone 3-methyl ether (IIIe). A solution of 299 mg. (1 mmol.) in 11 ml. of 5% hydrobromic acid was diazotized at 5–10° with a solution of 80 mg. (1.15 mmol.) of sodium nitrite in 5 ml. of water. The solution was stirred for 0.5 hr., followed by the addition of 1.0 g. of cuprous bromide in 32 ml. of 3% hydrobromic acid. The mixture was then stirred at room temperature for 20 hr. and the product collected, wt. 220 mg. (61% yield), m.p. 188–190°. Several recrystallizations from 95% ethanol provided the analytical and biological samples, m.p. 197–198°, $[\alpha]_D^{26}$ +149°.

Anal. Calcd. for $C_{19}H_{23}BrO_2$: C, 62.81; H, 6.38. Found: C, 62.77; H, 6.41.

4-Bromoestrone 3-methyl ether (IVe). The same procedure applied to IVc (1.0 mmol.) gave 200 mg. (55% yield) of IVe, m.p. 183–185°. Several recrystallizations from 95% ethanol provided analytical and biological samples in the form of colorless plates, m.p. 187–188°, $[\alpha]_D^{27}$ +124°.

Anal. Found: C, 63.09; H, 6.47.

2-Iodoestrone 3-methyl ether (IIIf). A solution of 299 mg. of IIIc (1.0 mmol.) in 21 ml. of 0.6*N* hydrochloric acid was diazotized in the usual manner with 80 mg. of sodium nitrite (1.15 mmol.) in 5 ml. of water. The ice cold solution, added dropwise with stirring to a solution of 1.0 g. of potassium iodide (6.0 mmol.) in 30 ml. of water, gave an immediate precipitate. After stirring for 20 hr. at room temperature, the product was collected, wt. 180 mg. (44% yield), m.p. 160–162°. Several recrystallizations from 95% ethanol provided both the analytical and biological samples in the form of colorless needles, m.p. 164–165°, $[\alpha]_D^{27}$ +141°.

Anal. Calcd. for $C_{19}H_{23}IO_2$: C, 55.61; H, 5.65. Found: C, 55.56; H, 5.65.

4-Iodoestrone 3-methyl ether (IVf). The same procedure applied to IVc (1.0 mmol.) gave 220 mg. (54% yield) of IVf, m.p. 210–215°. Recrystallization from acetone provided both the analytical and biological samples in the form of colorless plates, m.p. 219–220°, $[\alpha]_D^{27}$ +102°.

Anal. Found: C, 55.56; H, 5.66.

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(8) The dinitration of I was effected in 66% yield according to the method of Werbin and Holloway (see ref. 2).

(9) E. C. Horning, *Org. Syntheses*, **Coll. Vol. III**, 181 (1955).

Structures of the "Isomers" of 2,3,6,7-Dibenzo-1-thia-4,5-diazacyclohepta-2,4,6-triene-1,1-dioxide[1]

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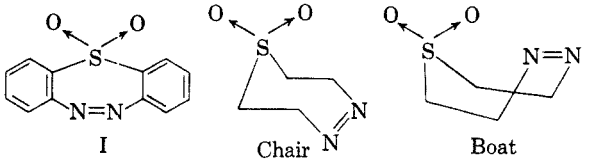
Szmant and Chow[3] originally reported the isolation of three isomers of 2,3,6,7-dibenzo-1-thia-4,5-diazacyclohepta-2,4,6-triene-1,1-dioxide (I). Shortly thereafter one of the compounds was actually found to be the corresponding hydrazo



compound.[4] The two remaining isomers (IA and IB) were assigned structures which differed in the conformation of the center ring, one being a chair and the other a boat form. The more stable isomer was assigned the chair structure.

It can be argued *a priori* that the chair structure represents an exceedingly improbable situation. There is no authentic case known in which both of a pair of conformers such as these can be isolated as separate stable individual substances. The energy barrier for the interconversion of boat and chair forms is estimated to be only about 10 kcal. for cyclohexane,[5] and since the angular deformation necessary to attain planarity appears to be less with a seven-membered ring, the corresponding barrier should be even smaller here. There is still, however, a more serious objection to the chair structure. In the regular chair form illustrated the dihedral angles between either nitrogen and the sulfur are 93°. Since there are benzene rings fused onto positions 2 and 3, and also 6 and 7, these benzene rings would have to be twisted from planarity to an improbable degree. While such a structure might conceivably exist it would certainly not be expected to be more stable than the boat form and yet the isomerization of IB to IA was reported.[3]

An examination of the experimental data reported by Szmant and Chow showed a surprising similarity between the substances IA and IB. The two compounds did not give a mixture melting point depression. The azo compounds IA and IB were reported to oxidize to the corresponding azoxy compounds IIA and IIB, respectively, and the latter pair likewise showed no mixture melting point depression. The isomerization of IB to IA and the various reactions in which IB was converted to derivatives of IA appeared to suggest that IA and IB were actually the same compound and merely samples of different purity.

The chair structure postulated for IA was sufficiently unusual, and the data upon which the structure was based were sufficiently indecisive that the work of Szmant and Chow was repeated. The materials designated by them as IA and IB were isolated without undue difficulty following a modification of their procedure. Compound IA, m.p. 173°, appeared to be a pure substance. Their compound IB, m.p. 126–130°, which did not appear upon close examination of the crystals to be a single substance, was separated by chromatography on alumina into two compounds, IA and the diamine (III) from which I had been prepared, m.p. 148.5°. Szmant and Chow reported[3] that it gave only one band when chromatographed on alumina. This observation was repeated and confirmed. The amine, being colorless, was not visible on the column, and only the azo compound was seen. The other extensive observations of Szmant and Chow on "isomerizations" can be better interpreted as purification. The rapid oxidation of IB relative to IA is not surprising, since the amine would oxidize very easily. Since IB contains about 50% amine, a large amount of oxidant would be consumed, and the rate was apparently not followed far enough to observe a break in the curve. It is clear therefore that only one isomer of I has in fact been previously isolated, that which corresponds in physical properties to the compound labeled IA by the earlier workers. Only the boat form is regarded by the present authors as a reasonable structure for this compound. It follows that the corresponding azoxy compounds IIA and IIB must also be regarded as identical, and possessing the boat structure.

EXPERIMENTAL

2,3,6,7-Dibenzo-1-thia-4,5-diazacyclohepta-2,4,6-triene-1,1-dioxide (I). The preparation was similar to that reported by Szmant and Chow.[3] 2,2′-Diaminodiphenyl disulfide was prepared[5] from benzothiazole, and converted to 2-nitro-2′-aminodiphenyl sulfide,[7] which was acetylated[8] and oxidized[8] to the sulfone. This compound was in turn reduced and hydrolyzed to the diamino sulfone III.[9] 2,2′-Diaminodiphenyl sulfone (III), 4.0 g., phenyliodoso acetate,[10] 4.65 g., and 400 ml. of dry toluene were mixed and allowed to stand at room temperature for 5 days with occasional shaking. The mixture was filtered and the brown precipitate

(1) Supported in part by a research grant from the National Science Foundation.

(2) National Science Foundation Predoctoral Fellow 1956–59.

(3) H. H. Szmant and Y. L. Chow, *J. Am. Chem. Soc.*, **79**, 4382 (1957).

(4) H. H. Szmant and Y. L. Chow, *J. Am. Chem. Soc.*, **79**, 5583 (1957).

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