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Benzo-1, 4-thiazino[3, 2-b]tropone 5-Oxides and 5, 5-Dioxides*1

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The oxidation of benzo-1, 4-thiazino[3, 2-b]tropone and its 8-isopropyl derivative with hydrogen peroxide afforded the corresponding 5-oxides or 5, 5-dioxides. The stability of these oxides to heating, acid and alkali was examined. The bromination or nitration of these oxides gave mainly 9-bromo or 9-nitro derivatives. 7- or 9-Aminobenzo-1, 4-thiazino[3, 2-b]tropones were obtained by the reduction of the corresponding nitro compounds.

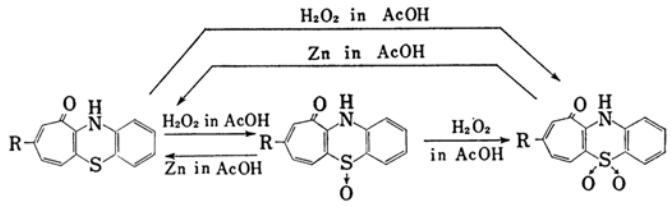
In their previous papers,[1,2] the present authors reported on the synthesis and some electrophilic substitution reactions of benzo-1, 4-thiazino-[3, 2-b]tropones (cyclohepta[b]benzo-1, 4-thiazin-10(11*H*)-ones). This study has now been extended to the oxidation of benzothiazinotropones; the present paper will deal with the formation and with the reactions of sulfoxides and sulfones of benzothiazinotropones.

The hydrogen peroxide oxidation of benzo[b]-tropothiazine (cyclohepta[b]benzo-1, 4-thiazine)[1] (I) yielded an amorphous, unidentified product, whereas the oxidation of benzo-1, 4-thiazino[3, 2-b]tropone (II)[1] with one molar equivalent of hydrogen peroxide in acetic acid easily afforded the corresponding sulfoxide (5-oxide) (III), as has been reported previously.[2] The treatment of III with a further mole of the reagent, or that of II with two molar equivalents of the reagent, gave the corresponding sulfone (5, 5-dioxide) (IV).

*1 Presented at the Local Meeting of the Chemical Society of Japan, Sendai, September, 1960.

1) T. Nozoe, T. Asao and K. Takahashi, This Bulletin **34**, 146 (1961).

2) T. Nozoe, T. Asao and K. Takahashi, ibid., **39**, 1980 (1966).



II R=H III R=H IV R=H
V R=isoPr VI R=isoPr VII R=isoPr

The structure of IV is evident from the presence of bands characteristic of the sulfone group[3] at 1130 and 1189 cm^{-1} in its infrared spectrum. A similar oxidation of 8-isopropylbenzo-1, 4-thiazino-[3, 2-b]tropone (V) gave the corresponding sulfoxide (VI) and sulfone (VII).

The reduction of these oxidation products with zinc in acetic acid regenerated the corresponding thiazinotropones, II or V. These four oxidation products have higher melting points, lower solubilities in organic solvents, and shorter wavelength absorption maxima in the ultraviolet (Fig. 1) region, than do the corresponding starting materials, II or V.

Although II and V are weak bases, their sulfoxides and sulfones have an acidic character, as is shown

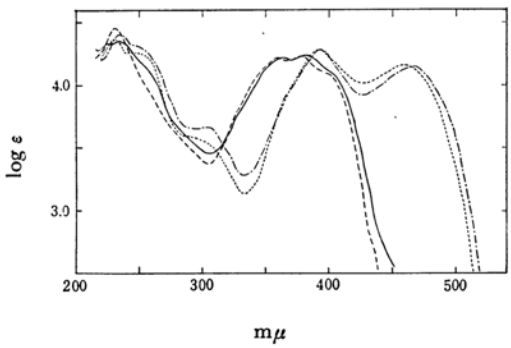


Fig. 1. Ultraviolet absorption spectra of III (—— in MeOH, —·— in 0.1 N NaOH) and IV (---- in MeOH, ····· in 0.1 N NaOH).

by their ultraviolet absorption spectra in an alkaline medium, which exhibit considerable bathochromic shifts as compared with those in methanol. Furthermore, III gave a sodium salt, as orange needles, which can be recrystallized from a 2 N sodium hydroxide solution, but which reverts to the parent acid, III, in water or in polar organic solvents. VI also gave a sodium salt, but it could not be successfully crystallized. Such an acidic character can obviously be attributed to the strong electronegativity of the sulfoxide or the sulfone groups.

In spite of their great stability to alkali, the sulfoxides, III and VI, are unstable to acids or to heating: when III or VI was heated at a temperature near its melting point for 10—15 min., its color changed from yellow to a reddish brown, decomposition occurred, and II or V was formed in about a 20% yield. Also, the attempted acetylation of III or VI with acetic anhydride at 140°C for one hour resulted in the formation of II or V respectively. The treatment of III or VI with 6 N sulfuric acid resulted in a dark brown coloration and in the formation of small amounts of II or V respectively, together with amorphous, unidentified substances. When heated with 10% hydrobromic acid for 2 hr., III gave II and reddish violet crystals of a halogenated compound (VIII) which has been shown to be the 9-bromo derivative of II.[2] Examples of the reduction and reductive halogenation of sulfoxides by acid have previously been observed with phenothiazine 5-oxide[4] and thianthrene 5-oxide.[5] The fact that VIII was also obtained[2] by the bromination of II is consistent with the mechanism proposed[6] for the reductive halogenation, which involves the initial reduction of the sulfoxide to the sulfide by acid, with the liberation of a mole of free halogen which subsequently attacks the heterocycle. In contrast to the sulfoxides, III and VI, the sulfones, IV and VII, were very stable to heat or to acids. This difference in the stability of sulfoxides and sulfones can be attributed to the difference in their S–O bond energies.[7]

As has already been reported,[1] the attempted alkylation of II or V with alkyl halide was unsuccessful. Since these oxidation products have an acidic character, one would expect alkylations or acylations of the OH or the NH group to be feasible. However, the attempted methylation of III or VI with methyl iodide, or the benzoylation with benzoyl chloride in pyridine, resulted

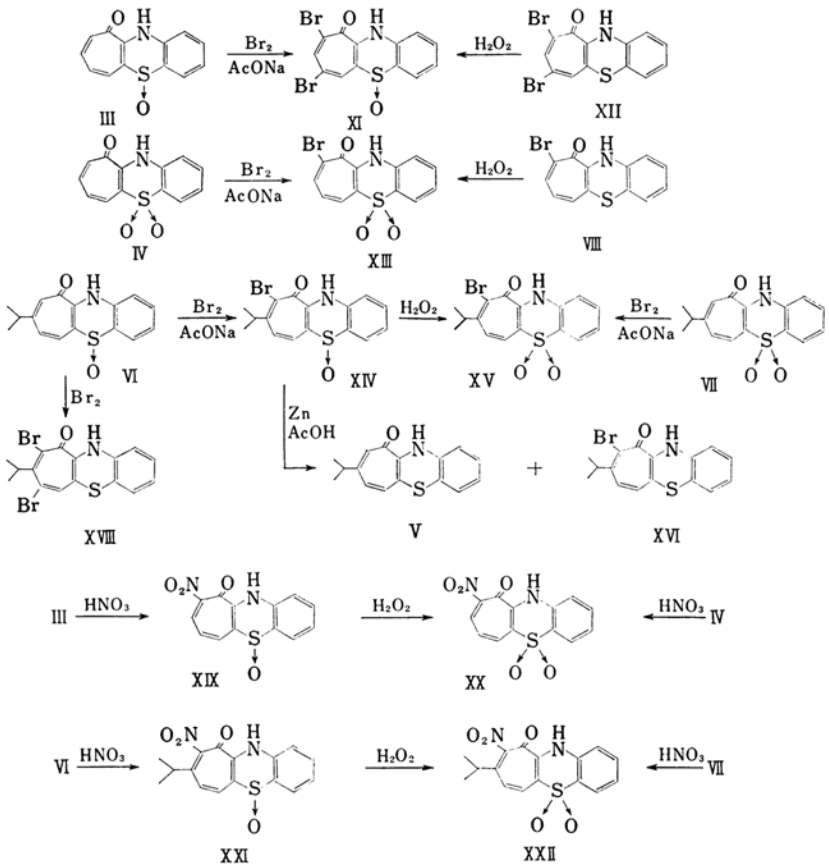
3) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen and Co., London (1958), p. 360.

4) J. A. Smithe, *J. Chem. Soc.*, **95**, 349 (1909); H. J. Page and S. Smiles, ibid., **97**, 1112 (1910); A. C. Schmalz and A. Burges, *J. Am. Chem. Soc.*, **76**, 5455 (1954); E. N. Karaulova and G. D. Galpern, *Zhur. Obschshei. Khim.*, **29**, 3033 (1959); *Chem. Abstr.*, **54**, 12096 (1960).

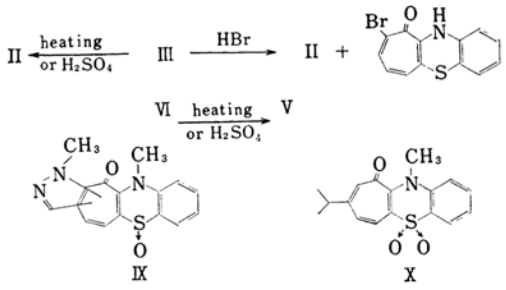
5) H. Gilman and D. R. Swayampati, *J. Am. Chem. Soc.* **77**, 5944 (1955).

6) H. Gilman and J. Eisch, ibid., **77**, 3862 (1955).

7) D. Barnard, J. M. Fabian and H. D. Koch, *J. Chem. Soc.*, **1949**, 2442.



in the recovery of the starting materials, while the attempted acetylation with acetic anhydride resulted in the recovery of the starting materials or in the formation of decomposition products, II or V.



The reaction of the sodium salt of III with methyl iodide also did not afford any methylated product. However, the treatment of III with a large excess of diazomethane gave a small amount of yellow prisms (IX). From its analysis ($C_{16}H_{13}O_2N_3S$), and from the absence of an N–H stretching vibration band in its infrared spectrum, structure IX with a condensed pyrazole ring may be proposed for the compound. This is also supported by the fact that the reaction of tropones with diazomethane is known to give *N*-methylpyrazolotropones.[8] From the reaction of IV with diazomethane, a small amount of yellow crystals were obtained, but an attempt to purify them was not successful. When treated with diazomethane, VII yielded a small amount of a neutral yellow crystaline compound (X). From its analysis and from its infrared spectrum (no N–H band), X may be thought to be the simple *N*-methyl derivative, 8-isopropyl-11-methylbenzo-1, 4-thiazino[3, 2-b]tropone 5, 5-dioxide.

Sulfoxides or sulfones in the phenothiazine series undergo electrophilic substitution at the same position as does phenothiazine itself[9]; it is also known[2] that the bromination of II or V occurs at the 7- and/or the 9-positions, and that nitration occurs at the 7-position. Some electrophilic substitution reactions of the sulfoxides, III and VI, and the sulfones, IV and VII, were investigated for the sake of comparison with the above results.

The action of one molar equivalent of bromine

8) T. Nozoe, T. Mukai and T. Asao, to be published.
9) "Heterocyclic Compounds," Vol. VI, Ed. by R. C. Elderfield, John Wiley & Sons, New York (1957), p. 714.

on III in acetic acid in the presence of sodium acetate gave the dibromide XI, which was also obtained by the oxidation of 7, 9-dibromobenzo-1, 4-thiazino-[3, 2-b]tropone (XII).[2] The reaction of bromine and IV under the same conditions as in III gave monobromosulfone XIII, which was also obtained by the oxidation of 9-bromobenzo-1, 4-thiazino-[3, 2-b]tropone (VIII). Similarly, VI and VII yielded the monobromo compounds, XIV and XV, respectively. The fact that the location of the bromine atoms introduced into both compounds is the same as was established by the hydrogen peroxide oxidation of XIV, which afforded XV in a good yield. In order to determine the position of the bromine atoms, XIV was heated with zinc in acetic acid, thus obtaining two products, one of which was proved to be V. The ultraviolet absorption spectrum of the other product, red violet crystals (XVI), was different from that of 7-bromo-8-isopropylbenzo-1, 4-thiazino[3, 2-b]tropone, but it was similar to that of the 9-chloro derivative reported previously.[2] It is, therefore, clear from the above, and from the elemental analyses, that XVI is 9-bromo-8-isopropylbenzo-1, 4-thiazino-[3, 2-b]tropone; accordingly, XIV and XV are the sulfoxide and the sulfone, respectively, of XVI. When the bromination of VI was carried out without sodium acetate, a small amount of 7, 9-dibromo-8-isopropylbenzo-1, 4-thiazino[3, 2-b]tropone (XVIII) was obtained, together with unidentified products which were presumably formed by the decomposition of the sulfoxide with the hydrogen bromide liberated during the reaction of VI with bromine.

With the expectation that the bromine would be replaced by an ethoxy group, the sulfoxide XIV was heated with sodium ethoxide in a sealed tube; unexpectedly, however, VI was obtained, besides the recovery of the starting material.

The treatment of III in acetic acid with 1.5 molar equivalents of fuming nitric acid afforded a mononitro derivative XIX different from the 7-nitro derivative of III.[2] From the fact that no substitution had occurred in the benzene nucleus (the infrared spectrum of XIX exhibited a band at 770 cm^{-1} which is assigned to the out-of-plane deformation of a 1, 2-disubstituted benzene), and since the bromination of the sulfoxide occurs mainly at the 9-position, XIX is likely to be 9-nitrobenzo-1, 4-thiazino[3, 2 - b]tropone 5-oxide. The nitration of IV yielded a yellow mononitro compound XX, which was also obtained by the oxidation of XIX. It therefore, follows that the nitro group of XX is located at the 9-position.

Similarly, the nitration of VI and VII afforded the sulfoxide XXI and the sulfone XXII of 8-isopropyl-9-nitrobenzo-1, 4-thiazino[3,2-b]tropone respectively; the latter was also obtained by the oxidation of XXI. As a result of the effect of the nitro group, the ultraviolet spectra of XIX and

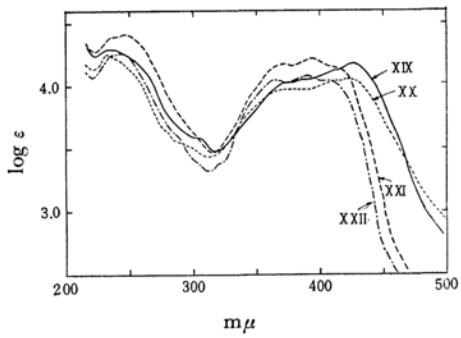


Fig. 2. Ultraviolet absorption spectra of XIX, XX, XXI and XXII in MeOH.

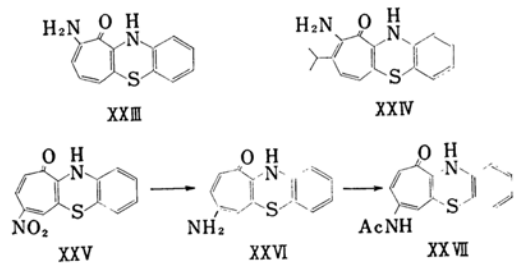
XX (Fig. 2) show considerable bathochromic shifts in comparison with those of III and IV. However, the spectra of the 8-isopropyl homologs (XXI and XXII) show only a small shift in comparison with those of VI and VII. This difference may be attributed to the decrease in the coplanarity of the nitro group and the benzothiazinotropone ring due to steric interference by the isopropyl groups at the position adjacent to the nitro groups in XXI and XXII.

The apparent reactivities of these sulfoxides and sulfones to the electrophilic reagents are greater than those of the benzothiazinotropones. It is considered that this is due to the greater electron density on the rings of the benzothiazinotropone 5-oxides or 5, 5-dioxides because of the easier deprotonation from N–H than on those of benzothiazinotropones.

It has been demonstrated[2] that the nitration of II or V introduces a nitro group at the 7-position, and that it simultaneously causes the oxidation of the sulfur atoms. In view of the nitration experiments described above, it is clear that, in the former cases, the nitration of the benzothiazinotropone rings occurs initially, and that this is followed by the oxidation of the nitrated products.

It has become clear from the above experiments that the bromination of sulfoxides and sulfones of benzothiazinotropone gives 7, 9-dibromo or 9-bromo derivatives, while their nitration produces 9-nitro derivatives exclusively.

When XIX and XXI were heated with zinc in acetic acid, 9-aminobenzo-1, 4-thiazino[3, 2-b]tropone (XXIII) and its 8-isopropyl homolog XXIV,



respectively, were obtained in good yields. The attempted reduction of 7-nitrobenzo-1, 4-thiazino-[3, 2-b]tropone (XXV)[2] by a similar method furnished a resinous product. However, the catalytic reduction of XXV in the presence of Pd-C gave an unstable 7-amino derivative (XXIV), the acetylation of which yielded 7-acetamidobenzo-1, 4-thiazino[3, 2-b]tropone (XXVII).[2]

Experimental*2

Benzo-1, 4-thiazino[3, 2-b]tropone 5-Oxide (III).—A solution of benzo-1, 4-thiazino[3, 2-b]tropone (II) (500 mg.) and hydrogen peroxide*3 (0.24 ml.) in acetic acid was allowed to stand at room temperature for a week. When water was then added to the solution, 490 mg. of yellow needles, m. p. 202°C, were obtained by filtration. Recrystallization from ethanol gave III as yellow needles, m. p. 207°C; a mixed m. p. determination with authentic III[2] showed no depression.

λ_{max}^{MeOH} mμ (log ε): 234 (4.42), 365 (4.22), 380 (4.22).

$\lambda_{max}^{0.1\ N\ NaOH}$ mμ (log ε): 233 (4.38), 393 (4.29), 466 (4.15).

Sodium salt: orange needles; m. p. 223—225°C (decomp.).

Found: C, 55.12; H, 3.19; N, 4.51. Calcd. for $C_{13}H_8O_2NSNa \cdot H_2O$: C, 55.12; H, 3.56; N, 4.95%.

Benzo-1, 4-thiazino[3, 2-b]tropone 5, 5-Dioxide (IV).—a) A solution of II (500 mg.) and hydrogen peroxide (0.7 ml.) in acetic acid (3 ml.) was allowed to stand for a week at room temperature. The crystals (490 mg.) which separated out were collected by filtration. Recrystallization from chloroform-methanol afforded yellow crystals (IV), m. p. 266°C.

Found: C, 60.30; H, 3.35; N, 5.48. Calcd. for $C_{14}H_9O_3NS$: C, 60.23; H, 3.50; N, 5.40%.

λ_{max}^{MeOH} mμ (log ε): 232 (4.44), 358 (4.20), 380 (4.21).

$\lambda_{max}^{0.1\ N\ NaOH}$ mμ (log ε): 232(4.35), 394(4.28), 459 (4.15).

b) A solution of III (500 mg.) and hydrogen peroxide (0.5 ml.) in acetic acid (3 ml.) was allowed to stand for 5 days at room temperature. The precipitated crystals were then recrystallized from chloroform-methanol, thus affording 450 mg. of IV, m. p. 266°C.

8-Isopropylbenzo-1, 4-thiazino[3, 2-b]tropone 5-Oxide (VI).—A solution of V (243 mg.) and hydrogen peroxide (0.11 ml.) in acetic acid (5 ml.) was allowed to stand at room temperature for 3 days. The solution was then diluted with water and extracted with chloroform. When the solvent was removed from the extract, and the residue was recrystallized from dilute methanol, VI (200 mg.) was afforded as yellow prisms, m. p. 174°C. This showed no depression of melting point on admixture with an authentic sample,[2] and their ultraviolet and infrared spectra are identical.

λ_{max}^{MeOH} mμ (log ε): 237(4.43), 363(4.20), 382(4.23).

$\lambda_{max}^{0.1\ N\ NaOH}$ mμ (log ε): 235(4.34), 250(4.30), 393 (4.21), 460 (4.06).

8-Isopropylbenzo-1, 4-thiazino[3, 2-b]tropone 5, 5-Dioxide (VII).—a) A solution of V (100 mg.) and hydrogen peroxide (0.1 ml.) in acetic acid (1 ml.) was allowed to stand at room temperature for a week. The precipitated crystals (86 mg.) were then recrystallized from methanol to give yellow crystals (VII), m. p. 195°C.

Found: C, 63.74; H, 5.10; N, 4.53. Calcd. for $C_{16}H_{15}O_3NS$: C, 63.78; H, 5.02; N, 4.65%.

λ_{max}^{MeOH} mμ (log ε): 234 (4.56); 360 (4.23), 377 (4.25).

b) A solution of VI (100 mg.) and hydrogen peroxide (0.1 ml.) in acetic acid (1 ml.) was allowed to stand for 5 days at room temperature. The precipitated crystals were then recrystallized from methanol to yield 80 mg. of VII, m. p. 195°C.

The Reductions of III, IV, VI and VII.—a) A mixture of III (65 mg.), acetic acid (3 ml.) and zinc (194 mg.) was heated at about 90°C for one hour. The excess of zinc was then filtered off, and the filtrate was diluted with water (20 ml.) and extracted three times with benzene. The solvent was removed, and the residue was recrystallized from methanol, thus affording 27 mg. of red needles, m. p. 158—160°C. This showed no depression of melting point on admixture with II.

b) A mixture of IV (100 mg.), acetic acid (5 ml.) and zinc (250 mg.) was heated at about 90°C for 2 hr. The excess of zinc was then filtered off, water was added, and the solution was extracted with benzene. The extract was chromatographed on alumina and then recrystallized from methanol to afford 20 mg. of II.

c) A mixture of VI (100 mg.), acetic acid (2.5 ml.) and zinc (100 mg.) was heated at about 90°C for one hour. When the mixture was then worked up as has been described above, 30 mg. of V, m. p. 94°C, were obtained.

The Thermal Decompositions of III and VI.—a) 5-Oxide (III) (25 mg.) was heated at around its melting point in a test tube for 10 min. The yellow color then gradually turned red. The resulting oil was dissolved in benzene and passed through an alumina column. From the effluent, 10 mg. of red crystals, m. p. 158°C, were obtained. The melting point of these crystals was not depressed by their admixture with II.

b) After VI (25 mg.) had been heated at around its melting point for about 10 min., the resultant red oil was distilled at 120°C/2 mmHg; 5 mg. of red crystals, m. p. 92°C, were thus obtained which showed no depression of melting point on admixture with V.

The Action of Acetic Anhydride to VI.—A solution of VI (150 mg.) in acetic anhydride (5 ml.) was heated at 140°C for one hour. Water was then added to the solution was extracted with benzene, and the extract was dried and passed through an alumina column. Red crystals (30 mg.), m. p. 92°C, were obtained, which showed no depression of melting point on admixture with V.

The Effect of 6 N Sulfuric Acid on III and VI.—a) By adding 6 N sulfuric acid to 5-oxide (III) (50 mg.), the compound was dissolved at once, and the color of the solution turned from brown to dark red. After being allowed to stand overnight, the solution was diluted with water, extracted with benzene, and purified by passing it through an alumina column; this gave 10 mg. of II.

b) After a solution of VI dissolved in 6 N sulfuric acid had been allowed to stand overnight, water was added, it was extracted with benzene, and the extract was passed through an alumina column; thus a small amount of V was afforded.

The Reaction of III with Hydrobromic Acid.—

*2 All melting points are uncorrected.

*3 The concentration of hydrogen peroxide used in all these experiments was 35%.

A solution of III (200 mg.) in 48% hydrobromic acid (2 ml.) was heated at about 90°C for 30 min. Water (30 ml.) was then added, the solution was extracted with chloroform, and the extract was washed with water and submitted to alumina chromatography. The first elution gave 40 mg. of red crystals, m. p. 158°C, after being recrystallized from methanol; undepressed on admixture with benzo-1, 4-thiazino[3, 2-b]tropone (II). The latter elution afforded 35 mg. of violet plates, m. p. 221°C; undepressed by admixture with 9-bromobenzo-1, 4-thiazino[3, 2-b]tropone (VIII).

The Reaction of III with Diazomethane.—To a solution of III (50 mg.) in methanol (30 ml.), 50 ml. of an ethereal solution of diazomethane prepared from 5 g. of *N*-nitrosomethylurea was added under cooling with ice; the mixture was then allowed to stand for 36 hr. in an ice box. After the insoluble starting material had been collected by filtration, the filtrate was evaporated to leave a red oil; this oil was dissolved in benzene and passed through an alumina column. From the effluent, 46 mg. of yellow prisms (IX), m. p. 194°C, were obtained after recrystallization from methanol.

Found: C, 61.56; H, 4.18; N, 12.95. Calcd. for $C_{16}H_{13}O_2N_3S$: C, 61,73; H, 4.21; N, 13.50%.

λ_{max}^{MeOH} mμ (log ε): 267 (4.26), 354 (4.03), 420 (3.84).

A considerable amount of a yellowish oily product was obtained besides IX, but it could not be purified.

The Reaction of VII with Diazomethane.—To a suspension of VII (100 mg.) in methanol (6 ml.), 10 ml. of an ethereal solution of diazomethane prepared from 1 g. of *N*-nitrosomethylurea was added under cooling by ice; the mixture was then kept in an ice box for 40 hr. The undissolved starting material was filtered off, and the residue obtained by removing the solvent from the filtrate was dissolved in chloroform and passed through an alumina column. From the effluent, 45 mg. of yellow crystals (X), m. p. 159—160°C, were obtained after recrystallization from methanol.

Found: C, 64.63; H, 5.37; N, 3.83. Calcd. for $C_{17}H_{17}O_3NS$: C, 64.75; H, 5.43; N, 4.44%.

λ_{max}^{MeOH} mμ (log ε): 236 (4.44), 368 (4.18).

7, 9-Dibromobenzo-1, 4-thiazino[3, 2-b]tropone 5-Oxide (XI).—a) To a stirred solution of III (200 mg.) and sodium acetate (74 mg.) in acetic acid (2 ml.) a solution of bromine (144 mg.) in acetic acid (1 ml.) was added under cooling by ice; the solution was then kept overnight in an ice box. The crystals (137 mg.) which separated out were collected, and recrystallized from chloroform-ethanol to afford orange plates (XI), m. p. 249°C (decomp.).

Found: C, 39.20; H, 1.96; N, 3.24. Calcd. for $C_{13}H_7O_2NSBr_2$: C, 38.94; H, 1.76; N, 3.49%.

λ_{max}^{MeOH} mμ (log ε): 236 (4.27), 268 (4.30), 380 (4.29).

b) A solution of 7, 9-dibromobenzo-1, 4-thiazino-[3, 2-b]tropone (XII) (60 mg.) and hydrogen peroxide (0.04 ml.) in acetic acid (4 ml.) was allowed to stand for 62 hr. at about 30°C. The crystals which separated out were filtered off and recrystallized from chloroform-ethanol to afford XI, m. p. 246°C (decomp.). The ultraviolet and infrared spectra of this compound are identical with those of the compound obtained in procedure a).

9-Bromobenzo-1, 4-thiazino[3, 2-b]tropone 5, 5-Dioxide (XIII).—a) To a stirred solution of IV (209 mg.) and sodium acetate (70 mg.) in a mixture of acetic acid (2 ml.) and chloroform (1.5 ml.), a solution of bromine (138 mg.) in acetic acid (1 ml.) was added under cooling by ice; the solution was then kept overnight in an ice box. The crystals which separated out were filtered and recrystallized from a large amount of acetic acid to give 150 mg. of yellow crystals (XIII), m. p. over 300°C.

Found: C, 46.31; H, 2.37; N, 4.16. Calcd. for $C_{13}H_8O_3NSBr$: C, 46.19; H, 2.39; N, 4.14%.

λ_{max}^{MeOH} mμ (log ε): 233 (4.28), 366 (4.18).

b) A solution of VIII (72 mg.) and hydrogen peroxide (0.2 ml.) in acetic acid (3 ml.) was allowed to stand for 5 days at about 30°C. Crystals (71 mg.), m. p. over 300°C, were obtained by filtration, followed by recrystallization from acetic acid. The ultraviolet and infrared spectra of this compound are identical with those of the compound obtained in a).

9-Bromo-8-isopropylbenzo-1, 4-thiazino[3, 2-b]-tropone 5-Oxide (XIV).—To a stirred solution of VI (200 mg.) and sodium acetate (65 mg.) in acetic acid (2 ml.), a solution of bromine (123 mg.) in acetic acid (1 ml.) was added. After it had been stirred for 2 hr., the solution was diluted with water and extracted with chloroform. The residue left by removing the solvent from the extract was crystallized by the addition of methanol. Recrystallization from acetone gave 126 mg. of yellow crystals (XIV), m. p. 224°C (decomp.).

Found: C, 52.83; H, 3.74; N, 3.58. Calcd. for $C_{16}H_{14}O_2NSBr$: C, 52.77; H, 3.87; N, 3.85%.

λ_{max}^{MeOH} mμ (log ε): 255 (4.33), 368 (4.13), 391 (4.11).

9-Bromo-8-isopropylbenzo-1, 4-thiazino[3, 2-b]-tropone 5, 5-Dioxide (XV).—a) To a stirred solution of VII (210 mg.) and sodium acetate (63 mg.) in a mixture of acetic acid (2 ml.) and chloroform (1.5 ml.), a solution of bromine (123 mg.) in acetic acid (1 ml.) was added. When the solution was left standing in an ice box for a day, 224 mg. of crystals were obtained. Recrystallization from a mixture of chloroform and methanol afforded yellow needles (XV), m. p. 272°C (decomp.).

Found: C, 50.40; H, 3.65; N, 3.86. Calcd. for $C_{16}H_{14}O_3NSBr$: C, 50.55; H, 3.71; N, 3.69%.

λ_{max}^{MeOH} mμ (log ε): 252 (4.30), 363 (4.25).

b) A solution of XIV (137 mg.) and hydrogen peroxide (0.1 ml.) in acetic acid (3 ml.) was allowed to stand for 4 days at about 30°C. The crystals which were precipitated were filtered and recrystallized from chloroform-methanol to give yellow needles, m. p. 270°C. The ultraviolet and infrared spectra of this crystals are superimposable upon those of the compound (XIV) obtained in a).

The Reduction of XIV.—A mixture of XIV (200 mg.), zinc (400 mg.) and acetic acid (4 ml.) was heated for 3 hr. at about 90°C. A solid was filtered off, and the filtrate was diluted with water and extracted with chloroform. The residue left by removing the solvent from the extract was dissolved in benzene and passed through an alumina column. From the first effluent, red violet crystals (XVI), m. p. 159—162°C, were obtained; the ultraviolet spectrum of these crystals (λ_{max}^{MeOH} mμ (log ε): 240 (4.38), 277 (4.30), 313 (4.25), 470 (3.83)) closely resembles that of 9-chloro-8-isopropylbenzo-1, 4-thiazino[3, 2-b]tropone.[2] From the latter effluent, red crystals, m. p. 95°C, were obtained; these crystals showed no depression of melting

point on admixture with 8-isopropyl-1,4-thiazino[3,2-b]-tropone (V).

9-Nitrobenzo-1, 4-thiazino[3, 2-b]tropone 5-Oxide (XIX).—To a stirred solution of III (200 mg.) in acetic acid (3 ml.), a solution of fuming nitric acid (80 mg.) in acetic acid (1 ml.) was added drop by drop. After the mixture had been allowed to stand overnight, 83 mg. of crystals were obtained; the recrystallization of these from acetic acid gave yellow crystals (XIX), m. p. 255°C (decomp.).

Found: C, 54.16; H, 2.82; N, 9.55. Calcd. for $C_{13}H_8O_4N_2S$: C, 54.17; H, 2.80; N, 9.72%.

λ_{max}^{MeOH} mμ (log ε): 235 (4.31), 370 (4.03), 427 (4.18).

$\lambda_{max}^{0.1\ N\ NaOH}$ mμ (log ε): 227 (4.29), 400 (3.81), 497 (4.27).

9-Nitrobenzo-1, 4-thiazino[3, 2-b]tropone 5, 5-Dioxide (XX). — a) To a stirred solution of IV (200 mg.) in a mixture of chloroform (1 ml.) and acetic acid (3 ml.), a solution of fuming nitric acid (100 mg.) in acetic acid (1 ml.) was added drop by drop at room temperature. After the mixture had stood for 36 hr. in an ice box, 130 mg. of crystals were obtained. Recrystallization from acetic acid afforded yellow crystals (XX), m. p. over 320°C.

Found: C, 51.20; H, 2.56; N, 9.33. Calcd. for $C_{13}H_8O_5N_2S$: C, 51.32; H, 2.65; N, 9.21%.

λ_{max}^{MeOH} mμ (log ε): 232 (4.25), 380 (3.98), 420 (4.05).

From the filtration of the products of the recrystallization, 97 mg. of the starting material were recovered.

b) A solution of XIX (100 mg.) and hydrogen peroxide (0.1 ml.) in acetic aicd (2 ml.) was allowed to stand for a week at room temperature. The crystals which separated out were then collected and recrystallized from acetic acid, thus affording yellow crystals (43 mg.), m. p. over 320°C. The ultraviolet and infrared spectra of these crystals are superimposable upon those of XX obtained in a).

8-Isopropyl-9-nitrobenzo-1, 4-thiazino[3, 2-b]tropone 5-Oxide (XXI). — To a stirred solution of VI (570 mg.) in acetic acid (6 ml.) a solution of fuming nitric acid (140 mg.) in acetic acid (1 ml.) was added; the mixture was then allowed to stand in an ice box overnight. When the crystals which separated out were collected and recrystallized from acetic acid, they gave 428 mg. of yellow crystals (XXI), m. p. 263°C (decomp.).

Found: C, 58.23; H, 4.12; N, 8.73. Calcd. for $C_{16}H_{14}O_4N_2S$: C, 58.18; H, 4.27; N, 8.48%.

λ_{max}^{MeOH} mμ (log ε): 223 (4.37), 247 (4.39), 370 (4.15), 395 (4.21).

8-Isopropyl-9-nitrobenzo-1, 4-thiazino[3, 2-b]tropone 5, 5-Dioxide (XXII).—a) To a stirred solution of VII (202 mg.) in a mixture of acetic acid (3 ml.) and chloroform (1 ml.), a solution of fuming nitric acid (90 mg.) in acetic acid (1 ml.) was added; the mixture was then allowed to stand in an ice box for 40 hr. The precipitated crystals (133 mg.) were collected and recrystallized from a large amount of acetic acid to give yellow crystals (XXII), m. p. 320°C (decomp.).

Found: C, 55.22; H, 4.04; N, 7.75. Calcd. for $C_{16}H_{14}O_5N_2S$: C, 55.49; H, 4.08; N, 8.09%.

λ_{max}^{MeOH} mμ (log ε): 243 (4.27), 365 (4.05), 390 (4.07).

b) A mixture of XXI (15 mg.), and hydrogen peroxide (0.05 ml.) in acetic acid (1 ml.) was allowed to stand at room temperature for 4 days. The crystals which separated out were recrystallized from acetic acid to give yellow crystals, m. p. 320°C (decomp.). The ultraviolet and infrared spectra of the crystals are superimposable upon those of XXII obtained in a).

9-Aminobenzo-1, 4-thiazino[3, 2-b]tropone (XXIII).—A mixture of XIX (200 mg.), and zinc (900 mg.) in acetic acid (6 ml.) was heated for 2 hr. at about 90°C. The excess of zinc was then filtered off, and the filtrate was diluted with water and extracted with chloroform. The extract was dried, passed through an alumina column, and eluted with chloroform. From the effluent, orange needles (XXIII) (27 mg.); m. p. 165°C, were obtained after recrystallization from benzene.

Found: C, 64.65; H, 4.37; N, 11.36. Calcd. for $C_{13}H_{10}ON_2S$: C, 64.46; H, 4.16; N, 11.57%.

λ_{max}^{MeOH} mμ (log ε): 238 (4.36), 349 (4.58), 440 (3.79).

9-Amino-8-isopropylbenzo-1, 4-thiazino[3, 2-b]-tropone (XXIV).—Orange needles (XXIV) (27 mg.); m. p. 136°C (from methanol), were obtained by the reduction of XXI (162 mg.) with zinc in acetic acid according to the procedure described above.

Found: C, 67.81; H, 5.77; N, 10.63. Calcd. for $C_{16}H_{16}ON_2S$: C, 67.59; H, 5.67; N, 9.85%.

λ_{max}^{MeOH} mμ (log ε): 239 (4.35), 348 (4.60), 435 (3.77).

The Reduction of 7-Nitrobenzo-1, 4-thiazino[3, 2-b]tropone (XXV).—A mixture of XXV (100 mg.), and 5% Pd-C (10 mg.) in acetic acid (10 mg.) was submitted to catalytic hydrogenation. After 27 ml. of hydrogen had been taken up, the catalyst was filtered off, and the filtrate was diluted with water and extracted with benzene and then with chloroform. The combined extracts gave reddish crystals (XXVI), m. p. 208°C, but they could not be purified. Acetic anhydride was added to the crystals, and the solution was heated gently. The violet needles (50 mg.) which separated out were recrystallized from methanol to afford deep reddish prisms, m. p. 251°C, which were identified with 7-acetamidobenzo-1, 4-thiazino[3, 2-b]tropone[2] (XXVII) by a mixed melting point determination and by a comparison of their ultraviolet and infrared spectra.

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