

Pentatomic Heteroaromatic Cations. Note II (1). Chemical Properties of 2-Phenyl-1,3-benzoxathiolium Perchlorate (2).

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The reactions of 2-phenyl-1,3-benzoxathiolium perchlorate with common nucleophilic reagents (water, sodium hydroxide, ethanol, thiophenol, morpholine, phenylmagnesium bromide), with reducing agents (zinc, lithium aluminium hydride) and with manganese dioxide, were studied. In every case the reactions proceed by attack of the reagents at the C-2 position of the cationic system, giving rise either to 1,3-benzoxathiole derivatives or to ring-opening products. The 1,3-benzoxathiolium salts were shown to be suitable intermediates for converting the carboxylic acids into aldehydes and ketones.

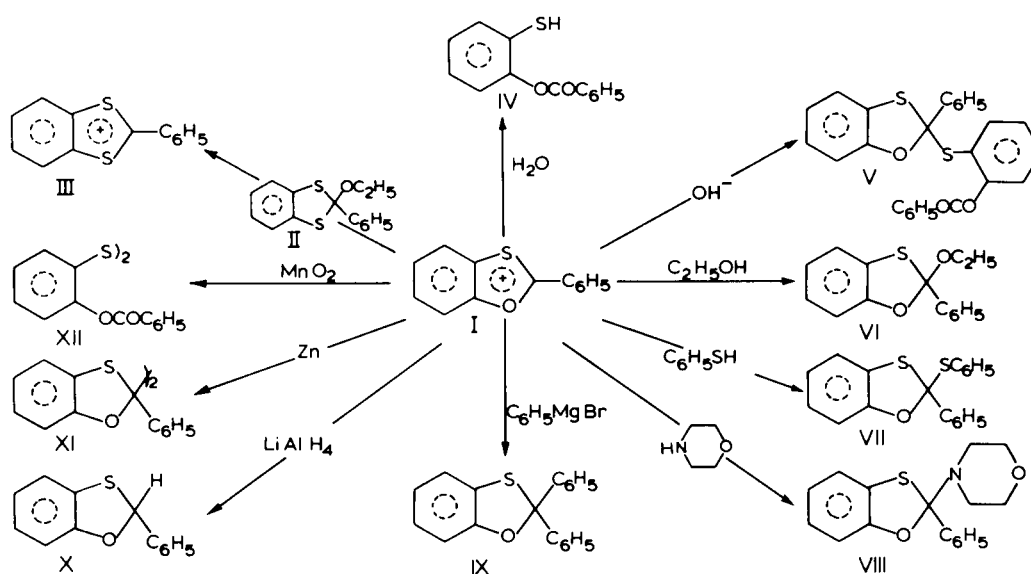
In a previous note (1), the syntheses of 2-phenyl-1,3-benzoxathiolium perchlorate (I) and some of its simple derivatives, were reported. In this work we report some reactions of the perchlorate I with nucleophilic reagents, with reducing agents and with manganese dioxide (Scheme 1).

The chemical properties of the 2-phenyl-1,3-benzoxathiolium cation can be compared with those of 1,3-dithiolium cations (3-5), with some meaningful differences, attributable to the different pair of heteroatoms which are in the heterocycle.

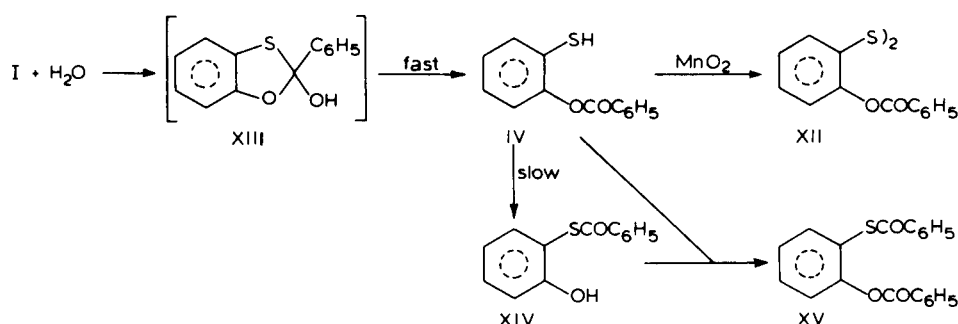
2-Phenyl-1,3-benzoxathiolium perchlorate is very stable and can be kept for many months without appreciable decomposition; however, its stability is lower than that of 2-phenyl-1,3-benzodithiolium perchlorate (III). In fact, by reacting I with 2-ethoxy-2-phenyl-1,3-benzodithiole (II), III and 2-ethoxy-2-phenyl-1,3-benzoxathiole (VI) were obtained in almost quantitative yield. The substitution of one sulfur atom by an oxygen atom evidently destabilizes the corresponding cationic system.

The reaction of I with water (Scheme 2) did not stop with the formation of cyclic pseudobase XIII, but immedi-

Scheme 1



Scheme 2



ately gave 2-benzoyloxythiophenol (IV). In fact, the crude residue from the reaction, which was oily and could not be purified by distillation owing to decomposition, showed a strong absorbance at 1745 cm^{-1} ($-O-CO-$) and a weak one at 2600 cm^{-1} ($-SH$); in addition, it quantitatively gave disulfide XII, by oxidation with manganese dioxide. The crude oil, upon standing left at room temperature, solidified, and its ir spectrum showed a strong band at 1690 cm^{-1} ($-S-CO-$) and one at 3455 cm^{-1} ($-OH$), in addition to the bands characteristic of 2-benzoyloxythiophenol. By fractional crystallization, 2-benzoylthiophenol (XIV) was isolated. Compound XIV had a different melting point from the one reported in the literature (6), but its structure was supported by elemental analysis, ir, nmr and mass spectra. Thus, a spontaneous migration of the benzoyl group from oxygen to sulfur had occurred. Furthermore, the crude residue to hydrolysis, chromatographed through silica gel, afforded the disulfide XII from oxidation of IV, and the dibenzoyl derivative XV by intermolecular rearrangement of the benzoyl group.

Hydrolysis of I with sodium hydroxide gave V in high yield. Compound V is evidently produced by the attack of the preliminarily formed 2-benzoyloxythiophenolate on the still unaffected cation. When V was treated with perchloric acid, about an equimolecular quantity of I was obtained; when it was treated with phosphorus oxychloride followed by perchloric acid, two moles of I were obtained.

Reaction of I with ethanol, thiophenol, and morpholine, gave the 1,3-benzoxathiole derivatives VI, VII and VIII, respectively in yields higher than 90%: these nucleophilic reagents attack exclusively the 2-position of the 2-phenyl-1,3-benzoxathiolium cation. The ether VI is a potentially suitable intermediate for the preparation of 2-phenyl-1,3-benzoxathiolium salts; in fact, VI quantitatively regenerated perchlorate I by addition of perchloric acid or trityl perchlorate, and with trityl fluoborate or boron trifluoride-ethyl ether complex it afforded 2-phenyl-1,3-benzoxathiolium fluoborate in similar yield.

Oxidation of perchlorate I with manganese dioxide gave disulfide XII. This can be easily explained by assuming a preliminary hydrolysis of I by water of crystallization held in manganese dioxide and subsequent formation of XIII followed by oxidation.

The reduction of perchlorate I with zinc, afforded dimer XI as a mixture of diastereoisomers (*meso* and *dl*), clearly via the 2-phenyl-1,3-benzoxathiolyl radical (XVI).

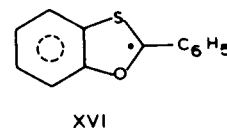


FIGURE 1

Furthermore, reduction of I with lithium aluminium hydride gave 2-phenyl-1,3-benzoxathiole (X) in quantitative yield. Finally, the reaction of I with phenylmagnesium bromide, afforded 2,2-diphenyl-1,3-benzoxathiole (IX) (65%) in addition to dimer XI (25%); evidently formation of the latter proceeds via the radical XVI, by a homolytic side-reaction. It is interesting to observe that IX and X can be quantitatively converted, by acid hydrolysis, into benzophenone and benzaldehyde. On the basis of these and other unpublished results, which will be reported separately, it can be said that the conversion of the carboxylic acids (or some of their derivatives) into aldehydes or ketones, through 1,3-benzoxathiolium salts, gives an alternative method to those already known.

EXPERIMENTAL

2-Phenyl-1,3-benzodithiolium Perchlorate (III).

Compound III was prepared from 1,2-benzenedithiol (7) and benzoic acid in the presence of phosphorus oxychloride followed by perchloric acid, by the procedure employed for the synthesis of 5-methyl-1,3-benzodithiolium perchlorate (8). The yield was 81%. After reprecipitation from acetonitrile-ether, the perchlorate had m.p. $232-233^\circ$ dec: [lit. (9) uncharacterized compound]; uv (96%

sulfuric acid): 245 nm ($\log \epsilon = 3.47$), sh., 288 (3.52), 387 (4.33); nmr (deuteriotrifluoroacetic acid): 1.47-2.45 (m).

Anal. Calcd. for $C_{13}H_9ClO_4S_2$: C, 47.49; H, 2.74; S, 19.48. Found: C, 47.35; H, 2.77; S, 19.53.

2-Ethoxy-2-phenyl-1,3-benzodithiole (II).

Compound II was obtained by dissolving 3.28 g. (10 mmoles) of III in 10 ml. of ice-cold absolute ethanol. After neutralization with sodium bicarbonate, the reaction mixture was poured into water and extracted with ether, dried and evaporated to afford 2.52 g. (yield 92%) of II, m.p. 69-70°, from pentane; uv (95% ethanol): 226 nm ($\log \epsilon = 4.64$), 285 (3.10), 294 (3.18), 303 (3.14); nmr (deuteriochloroform): 2.05-2.25 τ and 2.62-3.15 (each m, 2:7), 6.40 (q, 2, CH_2), 8.75 (t, 3, CH_3).

Anal. Calcd. for $C_{15}H_{14}OS_2$: C, 65.69; H, 5.11; S, 23.36. Found: C, 65.62; H, 5.15; S, 23.45.

Reaction of 2-Phenyl-1,3-benzoxathiolium Perchlorate (I) with 2-Ethoxy-2-phenyl-1,3-benzodithiole (II).

To a solution of 0.31 g. (1 mmole) of I in 4 ml. of acetonitrile, 0.27 g. (1 mmole) of 2-ethoxy-2-phenyl-1,3-benzodithiole (II) was added. The mixture was warmed at 50-60° for 2 minutes. After cooling dry ether was added and the crystals which separated were found to be 2-phenyl-1,3-benzodithiolium perchlorate (III), by m.p., uv and nmr spectra. The yield was 0.31 g. (95%). The filtrate was poured into water and extracted with ether, dried and evaporated to afford an oil (yield 94%), which was found to be identical to 2-ethoxy-2-phenyl-1,3-benzoxathiole (VI), by uv and nmr spectra.

Reaction of 2-Phenyl-1,3-benzoxathiolium Perchlorate with Water.

A solution of 3.12 g. (10 mmoles) of perchlorate I in the smallest possible quantity of acetonitrile, was poured slowly into water (150 ml.). The mixture was extracted with ether which was dried and evaporated. The yield was 2.18 g. The ir spectrum of the crude residue which was immediately recorded in carbon tetrachloride showed SH absorption at 2600 cm^{-1} and OCO absorption at 1745; nmr (deuteriochloroform): 1.70-1.90 τ and 2.42-3.12 (each m, 2:7), 6.71 (s, SH).

A mixture of 0.5 g. of this crude residue and 3 g. of manganese dioxide (10) in 20 ml. of acetonitrile, was refluxed for 10 minutes. After removal of inorganic material, the solvent was evaporated to afford in quantitative yield, 2,2'-dibenzoyloxydiphenyl disulfide (XII), m.p. 88-89°, from petroleum ether. The m.p. and spectra were identical with those of a sample prepared independently by a Schotten-Baumann reaction from 2,2'-dihydroxydiphenyl disulfide (II) and benzoyl chloride; ir (carbon tetrachloride): 1745 cm^{-1} (OCO); uv (95% ethanol): 232 nm ($\log \epsilon = 4.69$), 271 (3.87), sh., 280 (3.78), sh.; nmr (deuteriochloroform): 1.58-1.80 τ , 2.12-2.48 and 2.55-2.75 (each m, 2:4:3).

Anal. Calcd. for $C_{26}H_{18}O_4S_2$: C, 68.12; H, 3.93; S, 13.97. Found: C, 67.88; H, 3.90; S, 14.05.

A part of the crude residue chromatographed through silicagel with benzene as eluant, afforded two products: 2,2'-dibenzoyloxydiphenyl disulfide (XII) and 2-benzoylthiophenyl benzoate (XV), m.p. 67-68°, from ethanol [lit. (6) m.p. 68°]. The ir and nmr spectra were identical with those of the authentic compound. The other part of the crude residue, remaining at room temperature, solidified after 10 days. This solid, crystallized several times from benzene-petroleum ether, afforded 2-benzoylthiophenol (XIV), m.p. 86-87° [lit. (6) m.p. 122°]; mass spectrum: $M^+ = 230$; ir (carbon tetrachloride): 3455 cm^{-1} (OH), 1690 (SCO); uv (95% ethanol): 236 nm ($\log \epsilon = 4.26$), 273 (3.90), 279 (3.89), sh.; nmr

(deuteriochloroform): 1.72-2.05 τ and 2.38-3.08 (each m, 2:7), 3.97 (s, OH).

Anal. Calcd. for $C_{13}H_{10}O_2S$: C, 67.83; H, 4.35; S, 13.91. Found: C, 68.05; H, 4.28; S, 14.00.

Reaction of 2-Phenyl-1,3-benzoxathiolium Perchlorate with Sodium Hydroxide.

A solution of 3.12 g. (10 mmoles) of I in 50 ml. of acetonitrile was poured into 100 ml. of 0.5 N sodium hydroxide. The reaction was immediate and a white precipitate was formed. The usual work-up gave 2.01 g. (yield 91%) of 2-(2'-benzoyloxyphenylthio)-2-phenyl-1,3-benzoxathiole (V), m.p. 117-118°, from petroleum ether; ir (carbon tetrachloride): 1745 cm^{-1} (OCO); uv (95% ethanol): 229 nm ($\log \epsilon = 4.49$), fl.; 281 (3.90); nmr (deuteriochloroform): 1.98-2.18 τ and 2.50-3.22 (each m, 1:8).

Anal. Calcd. for $C_{26}H_{18}O_3S_2$: C, 70.59; H, 4.07; S, 14.48. Found: C, 70.72; H, 4.17; S, 14.38.

To an ice-cold solution of 0.22 g. (0.5 mmole) of V in 2 ml. of acetonitrile, 0.1 ml. of perchloric acid (70%) was added. After precipitation with dry ether, 0.14 g. of I were obtained (yield 90%).

A solution of 0.22 g. (0.5 mmole) of V in 1 ml. of phosphorus oxychloride was warmed for 1 minute. After cooling, 0.1 ml. of perchloric acid (70%) was added, then dry ether. The perchlorate I obtained was 0.27 g. (yield 87%).

2-Ethoxy-2-phenyl-1,3-benzoxathiole (VI).

Compound VI was prepared from 2-phenyl-1,3-benzoxathiolium perchlorate (I), absolute ethanol and sodium bicarbonate by the procedure employed for the synthesis of II (yield 97%). The product was purified by distillation, b.p. 151-152°/0.8 mm Hg; uv (95% ethanol): 241 nm ($\log \epsilon = 3.95$), 288 (3.63), 293 (3.58), sh.; nmr (deuteriochloroform): 2.34-3.12 τ (m, 9, H-aromatic), 6.36 (q, 2, CH_2), 8.69 (t, 3, CH_3).

Anal. Calcd. for $C_{15}H_{14}O_2S$: C, 69.77; H, 5.43; S, 12.40. Found: C, 69.61; H, 5.58; S, 12.51.

A solution of 0.26 g. (1 mmole) of VI in 1 ml. of acetonitrile, was added to a suspension of 0.34 g. (1 mmole) of trityl perchlorate in 2 ml. of the same solvent. The reaction was immediate and the salt was precipitated by dry ether. The yield was 0.29 g. (93%) of 2-phenyl-1,3-benzoxathiolium perchlorate. After reprecipitation from acetonitrile-ether, the perchlorate had m.p. 197-198° dec.; m.p. and uv spectrum agree with those reported (1); nmr (deuteriotrifluoroacetic acid): 1.52-2.42 (m).

The same product could be obtained in quantitative yield by treatment of an ice-cold solution of 0.26 g. of VI in 2 ml. of acetic anhydride with 0.15 ml. of perchloric acid (70%), then ether.

To a cold solution of 0.26 g. (1 mmole) of VI in 1 ml. of dry ether, 1 ml. of boron/trifluoride-ethyl ether complex was added. 2-Phenyl-1,3-benzoxathiolium fluoborate was obtained in quantitative yield. After reprecipitation from acetonitrile-ether, the m.p. of the salt was 204-205° dec. The uv (in 96% sulfuric acid) and nmr (in deuteriotrifluoroacetic acid) spectra are identical with those of perchlorate I in the same solvents.

Anal. Calcd. for $C_{13}H_9BF_4OS$: C, 52.03; H, 3.00; S, 10.67. Found: C, 51.88; H, 3.09; S, 10.75.

The same product was prepared as described above using VI and trityl fluoborate in acetonitrile, in similar yield.

2-Phenyl-2-phenylthio-1,3-benzoxathiole (VII).

To a suspension of 3.12 g. (10 mmoles) of I in 10 ml. of acetonitrile, 1.10 g. (10 mmoles) of thiophenol was added. After neutralization with sodium bicarbonate, a white precipitate was formed. Ether was added to the reaction mixture, which was washed with

5% sodium hydroxide and then with water. It was dried and evaporated to afford 2.96 g. (yield 92%) of product, m.p. 88-89°, from benzene-petroleum ether; uv (95% ethanol): 247 nm ($\log \epsilon = 4.11$), sh., 288 (3.88), 295 (3.80), sh.; nmr (deuteriochloroform): 2.35-2.92 τ (m).

Anal. Calcd. for $C_{19}H_{14}OS_2$: C, 70.81; H, 4.35; S, 19.88. Found: C, 70.70; H, 4.34; S, 19.92.

2-Morpholino-2-phenyl-1,3-benzoxathiole (VIII).

To a suspension of 3.12 g. (10 mmoles) of I in 10 ml. of acetonitrile, 1.74 g. (20 mmoles) of morpholine was added. The reaction was immediate and the yellow colour of the solution disappeared. This solution was poured into water and extracted with ether, which was dried and evaporated to afford 2.84 g. (yield 95%) of product, m.p. 72-73°, from petroleum ether; uv (95% ethanol): 239 nm ($\log \epsilon = 3.84$), sh., 292 (3.66); nmr (deuteriochloroform): 2.30-2.50 τ , 2.62-2.82 and 2.92-3.25 (each m, 2:3:4), 6.35-6.50 and 6.95-7.70 (each m, each 4H, CH_2 morpholine).

Anal. Calcd. for $C_{17}H_{17}NO_2S$: C, 68.23; H, 5.69; S, 10.70. Found: C, 68.10; H, 5.74; S, 10.80.

Reaction of 2-Phenyl-1,3-benzoxathiolium Perchlorate (I) with Phenylmagnesium Bromide.

To the Grignard reagent prepared from 2.36 g. (15 mmoles) of bromobenzene and 0.36 g. (0.0015 g.-atom) of magnesium turnings in 50 ml. of dry ether, 3.12 g. (10 mmoles) of I was slowly added with vigorous stirring. The reaction was immediate; the mixture was decomposed with a saturated ammonium chloride solution and extracted with ether, which was dried and evaporated. The residue was chromatographed through silica gel with petroleum ether-benzene (9:1) as eluant to afford two products.

1) 2,2-Diphenyl-1,3-benzoxathiole (IX), 1.88 g. (yield 65%), m.p. 74-75°, from petroleum ether; uv (95% ethanol): 290 nm ($\log \epsilon = 3.66$), 297 (3.59), sh.; nmr (deuteriochloroform): 2.17-2.43 τ , 2.57-2.80 and 2.87-3.10 (each m, 2:3:2).

Anal. Calcd. for $C_{19}H_{14}OS$: C, 78.62; H, 4.83; S, 11.03. Found: C, 78.68; H, 4.97; S, 11.12.

2) Bis-(2-phenyl-1,3-benzoxathioly) (XII), 0.53 g. (yield 25%) was identical with the mixture of diastereoisomers obtained by reaction between I and zinc, described later.

2-Phenyl-1,3-benzoxathiole (X).

To a suspension of 3.12 g. (10 mmoles) of I in 15 ml. of dry ether, 0.5 g. of lithium aluminium hydride was added. The mixture was stirred for 2 minutes and then poured into a saturated ammonium chloride solution and extracted with ether, which was dried and evaporated to afford 2.05 g. (yield 96%) of product. The product was purified by distillation, b.p. 148-149°/0.7 mm Hg; uv and nmr spectra agree with those reported (1).

Bis-(2-phenyl-1,3-benzoxathioly) (XI).

To a suspension of 3.12 g. (10 mmoles) of I in 10 ml. of acetonitrile, 0.78 g. (0.0012 g.a.) of zinc dust was added with stirring. There was an immediate change from yellow to red, and then to colorless. The reaction mixture was poured into water and extracted with ether which was dried and evaporated to afford 2.00 g. (yield 94%) of product consisting of a mixture of isomers, *meso* and *dl*. Two crystallizations from acetonitrile afforded a pure product, m.p. 174-175°; mass spectrum: $M^+ = 426$; uv (95% ethanol): 242 nm ($\log \epsilon = 4.03$), 292 (3.99), 299 (3.90), sh.; nmr (deuteriochloroform): 2.51-2.62 τ and 2.88-3.12 (each m, 1:1).

Anal. Calcd. for $C_{26}H_{18}O_2S_2$: C, 73.24; H, 4.23; S, 15.02. Found: C, 73.18; H, 4.20; S, 15.10.

After concentration of the mother liquors *in vacuo*, successive recrystallizations from benzene-petroleum ether of the residue, afforded the pure diastereoisomer, m.p. 124-125°; mass spectrum: $M^+ = 426$; the uv spectrum was identical with that of the other diastereoisomer; nmr (deuteriochloroform): 2.51-3.18 τ (m).

Anal. Calcd. for $C_{26}H_{18}O_2S_2$: C, 73.24; H, 4.23; S, 15.02. Found: C, 73.41; H, 4.24; S, 15.07.

Oxidation of 2-Phenyl-1,3-benzoxathiolium Perchlorate (I) with Manganese Dioxide.

A mixture of 3.12 g. of I and 30 g. of manganese dioxide (10) in 50 ml. of acetonitrile, was refluxed for 10 minutes. After removal of inorganic material and evaporation, the residue was crystallized by petroleum ether and afforded 2.04 g. (yield 89%) of 2,2'-dibenzoyloxydiphenyl disulfide (XII), m.p. 88-89°, which was identified by comparison with the previously described authentic sample.

Hydrolysis of 2,2-Diphenyl-1,3-benzoxathiole (IX).

To a solution of 1 g. of IX in 30 ml. of dioxane, 30 ml. of hydrochloric acid (1:1) was added. The mixture was refluxed for 1 hour, then poured into water and extracted with ether. The ether layer was washed with 5% sodium hydroxide and then with water. The solvent was dried and evaporated to afford benzophenone in quantitative yield, m.p. 48-49°, from petroleum ether; m.p., ir and nmr spectra were identical with those of the authentic compound.

Hydrolysis of 2-Phenyl-1,3-benzoxathiole (X).

To a solution of 1 g. of X in 30 ml. of dioxane, 30 ml. of hydrochloric acid (1:1) was added. The mixture was refluxed for 2 hours. Dilution with water, extraction with ether and usual work-up afforded 0.47 g. (yield 96%) of benzaldehyde, b.p. 178-179°; ir and nmr spectra were identical with those of the authentic compound.

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