dide (3.5 g., 1 mol.), lepidine ethiodide (3 g., 1 mol.), triethylamine (1.05 g., 1 mol.) and *n*-propyl alcohol (20 cc.) were refluxed for forty-five minutes. The dye was precipitated by adding ether and the residue treated with sodium perchlorate solution; yield 23%. After two recrystallizations from methyl alcohol (70 cc. per g.) (yield 16%) the beautiful beetle-green tablets melted at 172–174°, dec.

Anal. Calcd. for $C_{19}H_{21}ClN_2O_4$: C, 60.52; H, 5.62. Found: C, 60.51; H, 5.70.

Summary

1. 4-Chloropyridine is known to be unstable and attempts to convert it into 4-iodopyridine alkiodide by heating with methyl or ethyl iodide were unsuccessful. At 0°, however, addition of methyl iodide yields 4-chloropyridine methiodide which is stable.

2. 4-Chloropyridine methiodide is reactive and condensation with γ-picoline metho-*p*-toluenesulfonate yielded 1,1′-dimethyl-4,4′-pyridocyanine (isolated as the perchlorate); it also yielded a 4-pyrido-4′-cyanine.

3. 4-Chloropyridine reacts with phenyl mercaptan to give 4-phenylmercaptopyridine hydrochloride. The alkiodides of the free base condense with quaternary salts of γ-picoline and of lepidine with elimination of phenyl mercaptan to give 1,1′-dialkyl-4,4′-pyridocyanines and 1,1′-dialkyl-4-pyrido-4′-cyanines.

4. The 1,1′-dialkyl-4,4′-pyridocyanine perchlorates are strong photographic sensitizers.

ROCHESTER, N. Y. RECEIVED NOVEMBER 1, 1937

[CONTRIBUTION FROM THE AVERY LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF NEBRASKA]

The Mercuration and Arsenation of Benzothienone

BY ALFRED W. WEITKAMP AND CLIFF S. HAMILTON

The metallation of thiophene and of its alkyl and halogen derivatives has been studied extensively. Mercuration is readily accomplished by reaction at room temperature of thiophene or its derivatives with an alcoholic solution of mercuric chloride buffered with sodium acetate. The presence of so-called meta directing groups seems to inhibit mercuration. With the exception of 2-chloromercuri-5-thenoic acid[1] metallic derivatives of this group were hitherto unknown. Steinkopf[2] reports the failure of 2-nitrothiophene to be mercurated under the above conditions and in this Laboratory it has been shown that benzothienone or phenyl thienyl ketone is not mercurated under the same conditions.

Mercuration.—Under more stringent conditions benzothienone formed a monomercurial, a dimercurial and a double compound consisting of one mole of a monomercurial with one mole of a dimercurial.

The monomercurial, 2-chloromercuri-5-benzothienone, formed almost quantitatively when benzothienone was refluxed with a mixture of equivalent amounts of mercuric chloride and mercuric acetate in glacial acetic acid solution.

$$RH + HgCl_2 + Hg(OAc)_2 = 2R{-}HgCl + 2HOAc$$

Proof of structure was accomplished by converting the mercurial into the corresponding iodo compound, which was shown by means of a mixed melting point to be identical with a sample of 2-iodo-5-benzothienone prepared from 2-iodothiophene and benzoyl chloride by the Friedel–Crafts reaction.

The double compound consisting of one mole of 2-acetoxymercuri-5-benzothienone and one mole of 2,3-diacetoxymercuri-5-benzothienone was formed by fusion of benzothienone with mercuric acetate.

$$2RH + 3Hg(OAc)_2 = R{-}HgOAc\cdot R'{=}(HgOAc)_2 + 3HOAc$$

Analysis indicated a ratio of two atoms of sulfur to three atoms of mercury. Cleavage with iodine and potassium iodide gave a gummy mixture from which 2-iodo-5-benzothienone was isolated by prolonged fractional crystallization, proving the presence and identity of the monomercurial.

A dimercurial was obtained from the double compound by refluxing with excess mercuric acetate in methyl cellosolve solution.

$$R{-}HgOAc\cdot R'{=}(HgOAc)_2 + Hg(OAc)_2 = 2R'{=}(HgOAc)_2 + HOAc$$

Cleavage of the dimercurial with iodine and potassium iodide gave a diiodide which was a viscous, gummy oil. The position taken by the second entering substituent could not be anticipated, but by analogy with the mercuration of

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[1] Steinkopf, *Ann.*, **413**, 330–3 (1917).

[2] Steinkopf and Bauermeister, *ibid.*, **403**, 50–72 (1914); Steinkopf, Augestad-Jensen and Donat, *ibid.*, **430**, 78–112 (1922).

benzophenone[3] it seemed probable that mercuration had occurred on the benzene nucleus ortho to the carbonyl group. Accordingly, 2-iodo-5-*o*-iodobenzothienone was prepared by an independent synthesis and was found to be a viscous gummy oil, identical in appearance with the product obtained from the mercurial. It was shown to be structurally different by virtue of the fact that it readily formed a crystalline nitration product, whereas the product from the mercurial was not nitrated under identical conditions. The corresponding meta and para diiodides were synthesized and found to be crystalline solids. This established the fact that mercuration had not occurred on the benzene nucleus.

Final proof of structure was obtained by cleaving the dimercurial with bromine and potassium bromide. A crystalline product resulted and was shown by the method of mixed melting points to be identical with 2,3-dibromo-5-benzothienone prepared by Steinkopf[4] from 2,3-dibromothiophene and benzoyl chloride by means of the Friedel–Crafts reaction and also by direct bromination of benzothienone. This identified the dimercurial as 2,3-diacetoxymercuri-5-benzothienone, and at the same time established the constitution of the double compound.

The diiodide obtained from the dimercurial by cleavage with iodine and potassium iodide must be 2,3-diiodo-5-benzothienone and since the blocking of the 3 position prevented nitration it may be concluded that 2-iodo-5-*o*-iodobenzothienone was nitrated in the 3-position. By means of the foregoing reactions, bromination, mercuration and nitration, the 3-position has been shown to possess an appreciable degree of superaromaticity.

Arsenation.—The arsenicals of benzothienone were prepared from 2-chloromercuri-5-benzothienone by action of arsenic trichloride. This method was applied successfully to the mercurials of thiophene and of the alkyl and halogen substituted thiophenes by Finzi[5] and his co-workers.

Attempts to carry out the reaction were made using benzene and xylene as solvents but there was no evidence of reaction even after prolonged heating at the reflux temperature. In the absence of a solvent, however, arsenic trichloride was found to react rapidly at moderate temperatures. At 50–70° the reaction was complete within a few minutes and the yield of arsenicals was quantitative as calculated from the amount of mercuric chloride precipitated. On account of the large excess of arsenic trichloride used, the bulk of the product was the dichloroarsine. An alkali insoluble substance, containing arsenic and melting at 188°, presumably the tertiary arsine, was isolated but in insufficient quantity for satisfactory characterization.

These substituted thiophene arsenicals stand intermediate between benzene arsenicals and α-furan arsenicals in the strength of the carbon–arsenic bond. Scission of arsenic is easily accomplished by dilute mineral acids. Unlike the α-furan arsenicals this carbon–arsenic bond is sufficiently stable to permit hydrolysis to the corresponding arsine-oxide and oxidation to the arsonic acid.

Experimental[6]

2-Chloromercuri-5-benzothienone was prepared in almost quantitative yield by refluxing a solution of 9.5 g. of benzothienone, 8 g. of mercuric acetate and 6.8 g. of mercuric chloride in 100 cc. of glacial acetic acid for one hour. It is soluble in the cellosolves but practically insoluble in the usual organic solvents; bronze leaflets from ethyl cellosolve; m. p. 242°.

Anal. Calcd. for $C_{11}H_7OSClHg$: Hg, 47.41. Found: Hg, 47.29, 47.85.

Sesquiacetoxymercuribenzothienone.—A mixture of 18.8 g. of benzothienone and 48 g. of mercuric acetate was heated on the steam-bath for ten hours. The crude product was washed with acetone and then recrystallized from glacial acetic acid. It is insoluble in most organic solvents, very soluble in the cellosolves and in glacial acetic acid from which it crystallizes in characteristic lenticular plates; m. p. 202°; yield 90%.

Anal. Calcd. for $C_{28}H_{22}O_8S_2Hg_3$: S, 5.57; Hg, 52.24. Found: S, 5.69, 5.68; Hg, 52.49, 52.19.

2,3-Diacetoxymercuri-5-benzothienone was formed when a mixture of 11.5 g. of the preceding mercurial with 6.4 g. of mercuric acetate and 50 cc. of methyl cellosolve was refluxed for three hours. The solution was filtered hot and on cooling the mercurial crystallized out in indefinitely shaped micaceous plates; not melted at 300°; yield, about 60%.

Anal. Calcd. for $C_{15}H_{12}O_5SHg_2$: Hg, 56.88. Found: Hg, 56.45, 56.42.

2-Iodo-5-benzothienone was prepared from 2-iodothiophene by the Friedel–Crafts reaction and from 2-chloromercuri-5-benzothienone by cleavage with iodine.

Method I. Friedel–Crafts Reaction.—To a solution of 10.5 g. of 2-iodothiophene and 7 g. of benzoyl chloride in

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(3) Dimroth, *Ber.*, **35**, 2870 (1902); Grignard and Abelmann, *Bull. soc. chim.*, [4] **19**, 24 (1916).

(4) Steinkopf, Jacob and Penz, *Ann.*, **512**, 156 (1934).

(5) Finzi, *Gazz. chim. ital.*, **45**, II, 280–90(1915); Finzi and Furlotti, *ibid.*, **45**, II, 290–8 (1915); Finzi, *ibid.*, **55**, 824–34 (1925); **60**, 159–65 (1930); **62**, 244–52 (1932).

(6) Halogen and sulfur were determined by the method of Carius, arsenic by the method of Cislak and Hamilton [THIS JOURNAL, **52**, 1195 (1930)] and mercury as the sulfide.

40 cc. of dry benzene maintained at 20–25° was added dropwise with stirring 13 g. of tin tetrachloride. After two hours at room temperature the crystalline addition product was decomposed with water. The benzene solution was washed as free as possible of tin tetrachloride after which benzene was removed with steam and the crude product purified by recrystallization from ethanol; long yellow needles; m. p. 129.5–130°; yield 60%.

Anal. Calcd. for $C_{11}H_7OSI$: I, 40.41. Found: I, 40.23, 40.24.

Method II.—Ten cc. of a solution containing 254 g. of iodine and 498 g. of potassium iodide per liter was added to a suspension of 4.23 g. of 2-chloromercuri-5-benzothienone in 10 cc. of water and the mixture gently warmed until the iodine color had disappeared. The crude product was washed with a little potassium iodide solution and purified as above; yield, quantitative. A mixed melting point showed no depression, thus establishing the identity of these two products and proving the structure of the mercurial.

This procedure was used whenever it was expedient to replace mercury by halogen.

The three isomeric **5-*x*-iodobenzothienones** were prepared from the three iodobenzoyl chlorides and thiophene by the Friedel–Crafts reaction.

Anal. Calcd. for $C_{11}H_7OSI$: I, 40.41. *Ortho.*—Cream-colored needles from ethanol; m. p. 61°; yield 89%. Found: I, 40.40, 40.19. *Meta.*—Glistening leaflets from ethanol; m. p. 48°; yield 75%. Found: I, 40.56, 40.66. *Para.*—Yellow needles from ethanol; m. p. 106.5°; yield 90%. Found: I, 40.33, 40.33.

Mercuration.—Fusion of the above ketones with mercuric acetate and subsequent treatment with calcium chloride in acetone solution yielded the corresponding 2-chloromercuri-5-*x*-iodobenzothienones in about 75% yields.

Anal. Calcd. for $C_{11}H_6OSIHgCl$: Hg, 36.53. *Ortho.*—Fine microscopic needles from methyl cellosolve; m. p. 225°. Found: Hg, 37.41, 37.04. *Meta.*—Microscopic needles from methyl cellosolve; m. p. 252°. Found: Hg, 36.72, 36.96. *Para.*—Microscopic needles from diacetone alcohol; m. p. 285°, with decomposition. Found: Hg, 38.22, 38.08.

The three isomeric **2-iodo-5-*x*-iodobenzothienones** were obtained from the preceding mercurials in almost quantitative yield by the method already outlined for the replacement of mercury by halogen.

Anal. Calcd. for $C_{11}H_6OSI_2$: I, 57.70. *Ortho.*—An amber, viscous, gummy oil at room temperature; decomposes below the boiling point, sets to a glass but does not crystallize when cooled. Found: I, 56.93, 56.53. *Meta.*—Clusters of yellowish needles from ethanol; m. p. 109°. Found: I, 57.41, 57.50. *Para.*—Yellow needles from ethanol; m. p. 153°. Found: I, 57.80, 57.77.

2-Iodo-3-nitro-5-*o*-iodobenzothienone was prepared by nitration of 2-iodo-5-*o*-iodobenzothienone at 10–15° with a mixture of concd. nitric and concd. sulfuric acids: bronze prisms from methyl alcohol; m. p. 138–139°.

Anal. Calcd. for $C_{11}H_5O_3SNI_2$: I, 52.35. Found: I, 52.69 52.43.

2-Iodo-3-nitro-5-benzothienone was prepared from 2-iodo-5-benzothienone as above. Clusters of yellow needles from methyl alcohol; m. p. 168°.

Anal. Calcd. for $C_{11}H_6O_3SNI$: I, 35.35. Found: I, 35.33, 35.12.

2,3-Diiodo-5-benzothienone was obtained quantitatively from 2,3-diacetoxymercuri-5-benzothienone by cleavage with iodine and potassium iodide. It is a metastable oil which very slowly sets to a crystalline mass, melting in the range 80–90°.

Anal. Calcd. for $C_{11}H_6OSI_2$: I, 57.70. Found: I, 54.08, 54.03.

2-Bromo-5-benzothienone was prepared in almost quantitative yield from 2-chloromercuri-5-benzothienone by cleavage with a solution of bromine and potassium bromide, and in 70% yield by the action of excess bromine on benzothienone in chloroform solution: cream colored, elongated parallelograms from ethanol; m. p. 76°.

Anal. Calcd. for $C_{11}H_7OSBr$: Br, 29.93. Found: Br, 30.06, 29.98.

2,3-Dibromo-5-benzothienone was obtained quantitatively from the corresponding mercurial by cleavage with bromine and potassium bromide, and in 70% yield by action of liquid bromine on 2-bromo-5-benzothienone as cream-colored plates from ethanol; m. p. 80°. This substance was prepared by Steinkopf[4] by direct bromination of benzothienone and from 2,3-dibromothiophene and benzoyl chloride by the Friedel–Crafts reaction.

5-Benzothienone-2-dichloroarsine.—To 8.4 g. of 2-chloromercuri-5-benzothienone was added 20 cc. of arsenic trichloride. The mixture was warmed gently for two to three minutes and cooled, the precipitated mercuric chloride filtered off and arsenic trichloride removed at 15 mm. on the water-bath. The residue was dissolved in hot carbon tetrachloride and on cooling the dichloroarsine separated in greenish-yellow prims; m. p. 113°.

Anal. Calcd. for $C_{11}H_7OSAsCl_2$: Cl, 21.30. Found: Cl, 20.97, 20.97.

5-Benzothienone-2-arsine-oxide was obtained almost quantitatively by dissolving the dichloroarsine in 2 *N* sodium hydroxide and precipitating with dilute hydrochloric acid; white powder; not melted or decomposed below 300°.

Anal. Calcd. for $C_{11}H_7O_2SAs$: As, 26.94. Found: As, 26.85, 26.81.

5-Benzothienone-2-arsonic Acid.—Excess 3% hydrogen peroxide was added to a solution of either the dichloroarsine or the arsine-oxide in 2 *N* sodium hydroxide. The arsonic acid was precipitated quantitatively by acidification with hydrochloric acid. It is insoluble in all of the available organic solvents, including the cellosolves, except ethyl carbitol and fairly soluble in hot water. Pearly, lustrous flakes from hot water; m. p. 360° with decomposition. It loses a molecule of water below 140°.

Anal. Calcd. for $C_{11}H_9O_4SAs$: As, 24.01. Found: As, 24.12, 24.21.

Summary

Benzothienone has been mercurated for the

first time. A monomercurial, a dimercurial and a double compound have been prepared. The structures have been elucidated.

Several new halogen derivatives of benzothienone have been synthesized in the course of this investigation.

The arsenicals of benzothienone have been prepared from 2-chloromercuri-5-benzothienone and some of their properties studied.

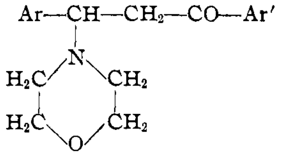
LINCOLN, NEBRASKA RECEIVED SEPTEMBER 27, 1937

[CONTRIBUTION FROM THE ORGANIC CHEMICAL LABORATORY OF THE UNIVERSITY OF FLORIDA]

Derivatives of Morpholine. I. Addition to Conjugate Systems. I.

BY VINCENT E. STEWART AND C. B. POLLARD

α,β-Unsaturated ketones with addition compounds of piperazine have been described by us in previous papers.[1] Similar addition compounds with morpholine instead of piperazine have now been prepared, of the type



Procedure.—The α,β-unsaturated ketone (0.2 mole), prepared as previously described,[1a] was dissolved in a minimum amount of boiling, commercial heptane under reflux. As soon as solution was complete, anhydrous morpholine (0.3 mole = 0.1 mole excess) was added and the solution refluxed for ten hours. In the case of dibenzalacetone the amount of morpholine was doubled (0.6 mole), forming the bisymmetrical compound, no mono-addition product being isolated. The use of an excess of morpholine tended to make the addition more complete and obviated much difficulty in the recrystallization process. The addition compound separated out after standing in the ice-box for several hours. It was filtered, washed with a small amount of alcohol and then with a large amount of water to remove unreacted morpholine, air dried, and recrystallized from commercial heptane three times before being subjected to analysis. The yield of crude product was almost quantitative, although considerable loss was incurred in recrystallization.

The resulting addition compounds are listed in Table I.

TABLE I

Morpholine	M. p. (corr.), °C.	Formula	Analyses, % N Found	Analyses, % N Calcd.
4-Chalcone	80.5- 81.0	$C_{19}H_{21}O_2N$	4.81	4.75
4-(4-Methylchalcone)	90.0- 90.5	$C_{20}H_{23}O_2N$	4.70	4.53
4-(4-Chlorochalcone)	89.5- 90.0	$C_{19}H_{20}O_2NCl$	4.28	4.25
4-(4′-Bromochalcone)	90.0- 90.5	$C_{19}H_{20}O_2NBr$	3.76	3.74
4-(4′-Methylchalcone)	90.0- 90.5	$C_{20}H_{23}O_2N$	4.50	4.53
4,4′-(Dibenzalacetone)-*bis*	99.6-100.2	$C_{25}H_{32}O_3N_2$	6.82	6.86

They are insoluble in cold water, soluble in alcohol and readily soluble in ether, acetone, toluene and halogenated solvents. They are all stable under ordinary conditions. Unlike the piperazine addition compounds, but like the piperidine addition compound reported by Georgi and Schwyzer,[2] they are decomposed by heating with water, yielding morpholine and the α,β-unsaturated ketone. Similarly, dilute hydrochloric acid decomposes them into the hydrochloride of morpholine and the unsaturated ketone.

The following α,β-unsaturated ketones failed to give addition compounds with morpholine under the above conditions: 4-methoxy-4-bromochalcone, 4-methoxy-4′-chlorochalcone, 4-methyl-4′-bromochalcone, 4,4′-dimethylchalcone, cinnamalacetophenone. As was pointed out in a previous paper,[1a] this apparent inertia of certain ketones is probably due to the instability of the addition compounds which prevented their isolation, rather than their failure to add. Thus, in the case of 4,4-dimethylchalcone the crude product was almost pure white, indicating that addition had occurred; yet, upon recrystallization from a variety of solvents, complete decomposition into the reactants took place.

Summary

1. Addition compounds of morpholine with α,β-unsaturated ketones have been prepared and studied.

2. The apparent lack of addition observed with certain ketones is believed to be due to the instability of the addition compounds.

GAINESVILLE, FLORIDA RECEIVED SEPTEMBER 7, 1937

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[1] (a) Stewart and Pollard, THIS JOURNAL **58**, 1980 (1936); (b) **59**, 2006 (1937).

[2] Georgi and Schwyzer *J. prakt. Chem.* **86**, 273–276 (1912).