cedure,[2] m.p. 164–165°, λ_{max} 6.06 μ. It discolored bromine solutions and gave a precipitate with silver nitrate. It did not depress the melting point of synthetic Vb (see below) and the infrared spectra of the two were identical.

Anal. Calcd. for $(C_8H_{10}NBr)_x$: C, 48.01; 5.04; N, 7.00; Br, 39.94. Found: C, 47.75; H, 5.25; N, 6.84; Br, 39.73.

Reduction of 0.2159 g. of the bromide with hydrogen over platinum in aqueous solution resulted in the uptake of 4.25 mmoles of hydrogen, 98% of theoretical for a molecular weight of 200. Evaporation of the supernatant and recrystallization of the residue from ethanol–ethyl acetate gave colorless needles, m.p. 199.5–201°, undepressed on admixture with an authentic sample of 2-*n*-propylpiperidine hydrobromide (see below). The free amine with *p*-toluenesulfonyl chloride gave a product which was insoluble in acid or base (*i.e.*, sulfonamide of a secondary amine).

2-Propenylpyridine. To 15.6 g. (0.114 mole) of 1-(2-pyridyl)-2-propanol[9] at −10° was added 31.0 g. (0.114 mole) of phosphorus tribromide portionwise with rapid stirring. The orange viscous oil was then stirred for 1 hr. at room temperature after which it was decomposed at ice temperatures by cautious addition of water. The solution was made basic with aqueous sodium hydroxide and extracted with chloroform. Evaporation of the solvent and distillation gave 4.9 g. (43%) of 2-propenylpyridine as a colorless liquid, b.p. 80–82° at 16 mm., n_D^{25} 1.5510, λ_{max} 6.06 μ, (lit.[10] b.p. 70–74° at 15 mm.) and 3.5 g. (16%) of crude 2-propenylpyridine hydrobromide (Vb) which crystallized from benzene-ethanol as colorless needles, m.p. 164–165°. It was identical with a sample prepared by bubbling anhydrous hydrogen bromide through a cold ethereal solution of 2-propenylpyridine.

Anal. Calcd. for $C_8H_{10}NBr$: C, 48.01; H, 5.04; N, 7.00; Br, 39.94. Found: C, 48.22; H, 5.12; N, 7.00; Br, 40.10.

A hot ethanolic solution of 2-propenylpyridine was treated with a saturated ethanolic solution of picric acid. Cooling gave the picrate as yellow plates, m.p. 144–146° (lit.,[10] m.p. 165–166°).

Anal. Calcd. for $C_{14}H_{12}O_7N_4$: C, 48.27; H, 3.47; N, 16.09. Found: C, 48.27; H, 3.37; N, 16.37.

Treatment of an acetone solution of 2-propenylpyridine with a few drops of 48% hydriodic acid solution followed by evaporation to dryness *in vacuo* and recrystallization of the tan solid from ethanol–ethyl acetate gave 2-propenylpyridine hydriodide as pale yellow needles, m.p. 150–151.5°.

Anal. Calcd. for $C_8H_{10}NI$: C, 38.89; H, 4.08; N, 5.67. Found: C, 38.72; H, 4.18; N, 5.86.

A 1.0-g. sample of Vb was heated for 3 hr. at 170–180° in a sealed tube. The residual black solid was recrystallized from benzene-ethanol in 95% yield as colorless needles, m.p. 162.5–164.5°, undepressed on admixture with Vb. The infrared spectra of the two samples were identical.

2-n-Propylpiperidine(coniine). To a slurry of prereduced platinum oxide in water was added 0.3419 g. (1.71 mmoles) of Vb. After 4.5 hr. 7.1 mmoles of hydrogen had been absorbed and the uptake ceased (104% of 4 equivalents). Evaporation of the supernatant and recrystallization of the resulting solid from ethanol-ethyl acetate gave 2-*n*-propylpiperidine hydrobromide as colorless fine needles, m.p. 199–200° (lit.,[11] m.p. 211°).

Anal. Calcd. for $C_8H_{18}NBr$: C, 46.16; H, 8.72; N, 6.73; Br, 38.39. Found: C, 46.24; H, 8.46; N, 6.84; Br, 38.46.

The free base liberated from its salt with sodium carbonate solution, boiled at 164°. It formed a picrate which crystallized from ethanol as yellow needles, m.p. 157.5–159°.

2-Methylconidine (IVb). *A.* A solution of 10 g. (0.073 mole) of 1-(2-pyridyl)-2-propanol[9] in 80 ml. of water containing 10 ml. of 6*N* hydrochloric acid and 0.9 g. of platinum dioxide was shaken under 45 lbs. of hydrogen pressure. After 2.5 hr. 107% of 3 equivalents of hydrogen had been absorbed. The catalyst was removed, the solution made basic with 10% sodium hydroxide solution and the amino alcohol extracted with chloroform. Removal of the solvent left 8.5 g. (82%) of 1-(2-piperidyl)-2-propanol as a colorless solid, m.p. 50–52°. It crystallized from hexane as colorless plates, m.p. 56–59° (lit.,[12] m.p. 45–47°).

Anal. Calcd. for $C_8H_{15}NO$: C, 67.10; H, 11.96; N, 9.78. Found: C, 67.36; H, 12.12; N, 10.05.

Heating a solution of 8.0 g. (0.056 mole) of the amino alcohol with 40 ml. of 48% hydrobromic acid for 6 hr. at 160° in a sealed tube followed by addition of base, extraction with chloroform and distillation of the amines gave 1.0 g. (15%) of 2-methylconidine (IVb) as a colorless liquid which darkened on standing, b.p. 67–69° at 51 mm., n_D^{21} 1.4600. It formed a picrate which crystallized from ethanol as yellow needles, m.p. 216–217° (lit.,[4] b.p. 150–153°; picrate m.p. 220–221°).

Anal. Calcd. for $C_{14}H_{16}N_4O_7$: C, 47.45; H, 5.12; N, 15.81. Found: C, 47.65; H, 5.27; N, 15.70.

B. A solution of 2.0 g. (0.014 mole) of the amino alcohol in 30 ml. of 48% hydrobromic acid was heated under reflux for 17 hr. after which the solvent was removed *in vacuo*, leaving a crystalline mass. Recrystallization from ether-ethanol gave 1-(2-piperidyl)-2-bromopropane hydrobromide as colorless fine needles, m.p. 168–169°, in 55% yield (lit.,[13] m.p. 171°).

Heating a heterogeneous solution of 1.85 g. (6.5 mmoles) of the above hydrobromide in 25 ml. of 10% sodium hydroxide solution for 3 hr. under reflux followed by extraction with chloroform afforded 0.50 g. (63%) of crude 2-methylconidine, characterized as its picrate which crystallized from ethanol as yellow needles, m.p. 216.5–217.5° undepressed on admixture with a sample prepared *via* method A above.

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The Metalation of 7H-Benzo[c]phenothiazine with *n*-Butyllithium

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As a part of a continuing investigation on the chemistry of benzophenothiazines,[2,3] we have studied the metalation of 7H-benzo[c]phenothiazine (I). Phenothiazine metalates in the 1-position (adjacent to nitrogen)[4] and 12H-benzo[a]phenothiazine metalates in the unusually high yield of 94% in the 1-position (*peri* to nitrogen).[5] However, the majority of heterocyclic ring systems containing

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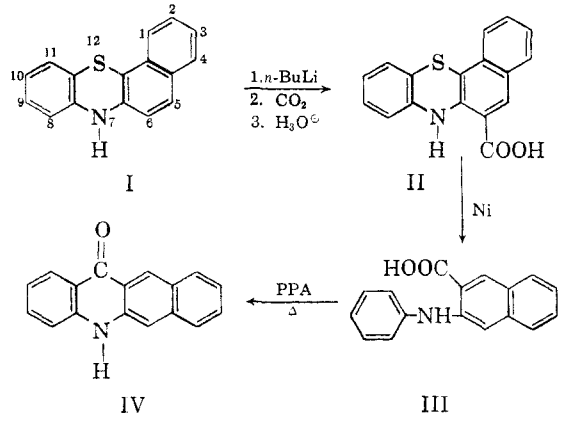
>N—H bonds do not metalate in satisfactory yield (see Reference 5 for specific cases and reference citations).

The action of approximately 2.5 equivalents of *n*-butyllithium on one equivalent of 7H-benzo[c]-phenothiazine (I) yields, subsequent to carbonation with solid carbon dioxide, a monocarboxylic acid derivative II in 41% yield. From the results on metalation of phenothiazine,[4] it was anticipated that metalation had occurred at either the 6- or 8-positions, adjacent to nitrogen. The 6-position was the more likely possibility, as naphthalene appears to metalate somewhat more easily than benzene,[6] (although direct comparisons have apparently not been made), and the preferred point of attack of 2-methoxynaphthalene by *n*-butyllithium is the adjacent β-position of the naphthalene ring.[7]

The structure of the carboxylic acid from metalation (II) was proved by desulfurization of the acid with Raney nickel. The product was a monocarboxy-*N*-phenyl-β-naphthylamine similar in melting point to that reported by Schöpff[8] for *N*-phenyl-3-amino-2-naphthoic acid (III). *N*-Phenyl-3-amino-2-naphthoic acid was synthesized[8] from aniline and 3-hydroxy-2-naphthoic acid and the product was identical in melting point and infrared spectrum with the acid from the desulfurization reaction. Both samples of *N*-phenyl-3-amino-2-naphthoic acid were ring closed with polyphosphoric acid to benzo[b]acridone (IV), which melted in accord with the literature value.[9]



I II III IV

EXPERIMENTAL[10]

7H-Benzo[c]phenothiazine-6-carboxylic acid (II). A solution of 25 g. (0.10 mole) of 7H-benzo[c]phenothiazine[8] in 300 ml. of ether was treated with 200 ml. of an ether solution containing 0.24 mole of *n*-butyllithium. The mixture was stirred and heated under reflux for 24 hr., after which it was cooled in a Dry Ice-acetone bath and small lumps of Dry Ice (large excess) added. The reaction mixture was then allowed to warm to room temperature and hydrolyzed by addition of 150 ml. of water. The ether layer was extracted with 5% aqueous sodium hydroxide solution and the extracts combined with the aqueous layer of the original reaction mixture. Acidification yielded 23.6 g. of tan solid. This was reprecipitated from aqueous sodium hydroxide and recrystallized from a mixture of tetrahydrofuran and ligroin (b.p. 60–80°) with charcoal to yield 12.1 g. (41%) of red-orange needles, m.p. 292–295°, with decomposition. One recrystallization of a small amount of the product from benzene-ligroin and one from acetone-ligroin gave material melting at 300–301° with decomposition. The product was insoluble in warm 5% aqueous sodium bicarbonate solution. An infrared spectrum showed a strong band at 5.97 μ in accord with a carboxyl carbonyl conjugated to an aromatic ring.

Anal. Calcd. for $C_{17}H_{11}NO_2S$: C, 69.60; H, 3.78; N, 4.80, Neut. eq., 293. Found: C, 69.47 and 69.57; H, 3.80 and 3.85; N, 4.86 and 4.54; Neut. eq., 296.

6-Carbomethoxy-7H-benzo[a]phenothiazine. A solution of 0.10 g. (3.4 mmoles) of the carboxylic acid II in ether was treated with an ethereal solution containing excess diazomethane[11] and the mixture allowed to stand overnight in a hood. The 96 mg. (92%) of orange-red crystals remaining melted at 149–150°. Crystallization from petroleum ether (b.p. 30–60°) and from methanol raised the melting point to 150–151°. An infrared spectrum showed a carbonyl band at 5.90 μ.

Anal. Calcd. for $C_{18}H_{13}NO_2S$: C, 70.33; H, 4.26; N, 4.56. Found: C, 70.40 and 70.42; H, 4.25 and 4.30; N, 4.67 and 4.90.

Desulfurization of 7H-benzo[a]phenothiazine-6-carboxylic acid. A solution of 7.0 g. (0.024 mole) of II in 300 ml. of 95% ethanol was stirred and heated under reflux with a suspension of about 80 g. of freshly activated[12] Raney nickel catalyst in 150 ml. of absolute alcohol. After a 30-min. heating period the initial red color of the solution had changed to yellow, but stirring and heating were continued for another 1.5 hr. The catalyst was removed by filtration and the filtrate treated with charcoal and evaporated to a volume of about 20 ml. Addition of a few drops of 5% aqueous hydrochloric acid solution and cooling precipitated 1.6 g. (25%) of yellow crystals melting at 233–236°. Another recrystallization from benzene gave 1.4 g. of product, m.p. 235–237°.

The melting point of this material was identical with that of a sample of *N*-phenyl-3-amino-2-naphthoic acid prepared by the method of Schöpff.[8] A mixture melting point showed no depression and infrared spectra of the two samples were identical.

Benzo[b]acridone (IV). A mixture of 200 mg. of *N*-phenyl-3-amino-2-naphthoic acid and approximately 30 ml. of polyphosphoric acid[13] was stirred intermittently and heated to 85–90° for 10 min. An excess of water was added which, after solution of the excess polyphosphoric acid, caused the precipitation of yellow-orange product. This was recrys-

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(13) Provided through the courtesy of Victor Chemical Works, Chicago, Ill.

tallized from 95% ethanol yielding 167 mg. (90%) of yellow-orange leaflets, m.p. 304–305°. The reported value[9] for benzo[b]acridone made in another manner is 303°.

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Reactions of Carbon Monoxide with Thiols, Sulfides, and Disulfides

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The literature on reactions of carbon monoxide with thiols is limited to those in which either acetylene[1] or an olefin[2] is present as a third component. The products are the thiol esters of the carbonylated unsaturate. There are no accounts of the direct reaction of carbon monoxide with thiols or their derivatives.

We now wish to report that carbon monoxide reacts with thiols, disulfides, and sulfides to give thiol esters in accordance with Equations 1–3 in the presence of a cobalt carbonyl catalyst or certain metal oxide catalysts at 250–300° and 100–1000 atm. Results are summarized in Table I.

$$2RSH + CO \longrightarrow RCOSR + H_2S \quad (1)$$

$$RSSR + 2CO \longrightarrow RCOSR + COS \quad (2)$$

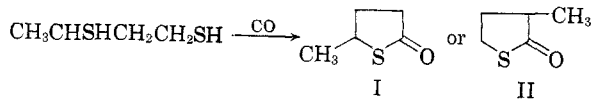
$$RSR + CO \longrightarrow RCOSR \quad (3)$$

$$RSH + CO \longrightarrow RH + COS \quad (4)$$

Carbonylation of thiols. Both aliphatic and aromatic thiols undergo carbonylation according to equation 1 to give thiol esters in yields up to 46% at conversions up to 73%. The catalysts used were dicobalt octacarbonyl and a supported cobalt oxide preparation that presumably was converted to the carbonyl under conditions of the experiment. The temperatures employed were 250–275° at a pressure of 100–1000 atm. of carbon monoxide. The reaction times were two to sixteen hours and the most convenient solvents were benzene and toluene.

No reaction took place between carbon monoxide and thiophenol at 70° in the presence of cobalt carbonyl, nor at 275° with no catalyst. In some runs, carboxylic acids were found. Thus, carbonylation of benzenethiol without solvent gave only benzoic acid. In one benzenethiol run, the gaseous products were collected and found by mass spectrophotometric analysis to contain mainly hydrogen sulfide and carbon oxysulfide.

The carbonylation of 1,3-butanedithiol gave a thiolactone (I or II). The available data do not permit an unequivocal choice between the two possible structures.



I II

Attempted carbonylation of a *gem*-dithiol, 3,5,5-trimethylhexane-1,1-dithiol, at 70° and 150° gave mainly the corresponding monothiol and a small amount of the carboxylic acid. At 250°, the monothiol and the thiol ester derived from the monothiol according to equation 1 were obtained. An attempt to add hydrogen sulfide to an olefin and carbonylate the resulting thiol *in situ* led to only a 1% yield of thiol ester. Benzyl mercaptan was the only thiol which gave products containing no sulfur. 1,2-Diphenylethane and 1,2,3-triphenylpropane were isolated.

An important competing reaction to thiol ester formation apparently was reduction of thiol to hydrocarbon (Equation 4). Attempts were not made to isolate the hydrocarbon in most of the experiments, but in the case of 3,5,5-trimethylhexane-1-thiol approximately as much hydrocarbon was found as thiol ester. With benzothiazole-2-thiol, benzothiazole was the sole product. Similarly, *o*-mercaptobenzoic acid gave benzoic acid.

Carbonylation of disulfides. The conditions for the carbonylation of disulfides were similar to those used for thiols. The cobalt carbonyl–catalyzed reaction of carbon monoxide with *n*-butyl disulfide yielded *n*-butyl thiol-*n*-valerate. Phenyl thiolbenzoate was formed from carbon monoxide and phenyl disulfide using a chromium oxide-on-alumina catalyst, the only catalyst not containing cobalt successfully employed in these reactions. The corresponding sulfides were isolated as by-products.

Carbonylation of sulfides. At 300° and 1000 atm. of carbon monoxide, phenyl sulfide, and *n*-butyl sulfide were converted to thiol esters in small yields using dicobalt octacarbonyl as catalyst. Under the same conditions, phenyl methyl sulfide gave only methyl thiolbenzoate. No evidence for formation of the isomeric phenyl thiolacetate was obtained.

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