TABLE I

Hydrazone	Mp or bp (mm), °C	Acetylene	Mp or bp (mm), °C	% yield of pure product
$PhCH_2C(=NNH_2)Ph$[a]	57–58	$PhC\equiv CPh$	58–59[j]	43
p-$ClPhCH_2C(=NNH_2)Ph$[a,b]	66–67	p-$ClPhC\equiv CPh$	80–81[j]	55
$PhCH_2C(=NNH_2)CH_2Ph$[a]	35–36 172–174 (0.9)	$PhC\equiv CCH_2Ph$	143–145 (2)[c]	43
$PhCH_2C(=NNH_2)CH_3$[d]	81 (0.17)	$PhC\equiv CCH_3$	71–72 (11)[e]	48
$PhCH_2C(=NNH_2)$-α-naphthyl[f]	77–78	$PhC\equiv C$-α-naphthyl[g]		22
$PhCH_2C(=NNH_2)$-ferrocenyl[h]	122–124	$PhC\equiv C$-ferrocenyl[h]	123–124[i]	15

[a] The hydrazones were prepared essentially as indicated in the experimental section. [b] *p*-Chlorobenzylphenyl ketone was prepared according to the method of S. S. Jenkins [*J. Am. Chem. Soc.*, **56,** 683 (1934)]. [c] T. Jacobs and D. Dankner, *J. Org. Chem.*, **22,** 1424 (1957). [d] Prepared according to the method of J. H. Biel, *et al.* [*J. Am. Chem. Soc.*, **81,** 2805 (1959)]. [e] J. Dudkowski and E. I. Becker, *J. Org. Chem.*, **17,** 204 (1952). [f] Benzyl-α-naphthyl ketone was prepared by the addition of α-naphthonitrile to a benzyl Grignard solution, mp 65–66°; P. Ruggli and M. Reinert [*Helv. Chim. Acta*, **9,** 71 (1926)] reported mp 66–67°. Preparation of the hydrazone required pressure tube conditions for 48 hr at 140°. [g] Molecular weight and ultraviolet spectra were identical with a sample prepared in 85% yield from 1-iodonaphthalene and copper phenylacetylide: R. E. Dessy and S. A. Kandil, *J. Org. Chem.*, **30,** 3857 (1965). [h] The authors wish to thank Dr. M. D. Rausch for generous samples of benzylferrocenyl ketone and ferrocenylphenyl acetylene. [i] P. L. Pauson and W. E. Walts, *J. Chem. Soc.*, 2994 (1963). [j] See ref 3.

Experimental Section

Mercurous trifluoroacetate was prepared according to the method of Swarts[6] and dried for 5–6 hr under vacuum at room temperature. Mallinckrodt anhydrous ether was used as the solvent for the reactions. The hydrazones listed below were stored at 0° and oxidized as soon as possible, since most of them slowly decompose to azines. All hydrazones were characterized by nitrogen analysis. All acetylenes were characterized by correlation of melting point or boiling point and ultraviolet spectra with authentic samples.

Typical Preparation.—Deoxybenzoin hydrazone, when prepared according to the method previously described in the literature, contained a considerable amount of azine.[7] It was alternatively prepared by heating 25 g of deoxybenzoin and 20 g of 99–100% hydrazine hydrate at reflux for 6 hr with stirring to keep the two phases well mixed. On cooling, the reaction mixture was extracted with 100 ml of ether. The ether extract was washed with water and dried over potassium carbonate. The ether was removed under vacuum (to avoid air oxidation to azine) and the residue was recrystallized from alcohol to give colorless needles, mp 57–58° (lit.[7] mp 62°).

Mercurous trifluoroacetate (37.6 g, 0.06 mole) and 100 ml of dry ether were warmed to a slow reflux with stirring. Deoxybenzoin hydrazone (6.30 g, 0.03 mole) in 100 ml of ether was added over a period of 1.5 hr. The reaction mixture was stirred an additional 30 min, filtered, extracted with 5% ammonium hydroxide (to neutralize acid and destroy unreacted mercurous salt), then washed with water, and dried over potassium carbonate. The ether was removed and the residue was dissolved in a minimum amount of 50:50 benzene–petroleum ether (bp 40–60°) and placed on an $8 \times {}^5/_8$ in. column of Woelm neutral alumina, eluting with petroleum ether (bp 40–60°). Diphenylacetylene was present in the first 400 ml of eluent which, after evaporation, yielded 2.3 g (43%) of colorless crystals, mp 58–59° (lit mp 58–60°,[3] 60°[7]).

Deoxybenzoin Monomethylhydrazone.—Deoxybenzoin (19.6 g), 13.8 g of methylhydrazine, and 3 drops of glacial acetic acid were placed in a pressure flask and heated in an oven at 100° for 12 hr. The excess methylhydrazine was extracted with water, and the organic layer was taken up in ether and dried over potassium carbonate. Vacuum distillation yielded 14.6 g (65%) of the monomethylhydrazone,[8] a yellow oil, bp 154–155° (0.3–0.4 mm).

Anal. Calcd: N, 12.49. Found: N, 12.39.

Oxidation of Deoxybenzoin Monomethylhydrazone.—Deoxybenzoin monomethylhydrazone (2.24 g, 0.01 mole) in 25 ml of dry ether was added dropwise to 12.5 g of mercurous trifluoroacetate in 20 ml of ether. The reaction mixture was worked up as in the case of diphenylacetylene. The first 50 ml of eluent from the alumina column contained 0.07–0.1 g of diphenylacetylene.

Acknowledgments.—The authors wish to acknowledge the encouragement, in the form of a grant, of the Petroleum Research Fund (1086-A4).

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(6) F. Swarts, *Bull. Soc. Chim. Belges*, **48,** 179 (1939).

(7) T. Curtius and A. Blumer, *J. Prakt. Chem.*, [2] **52,** 136 (1895).

(8) T. Kauffmann, *et al.* [*Angew. Chem.*, **72,** 752 (1960)] reported this compound as the product of the addition of sodium methylhydrazide to diphenylacetylene; however, no physical constants are given.

A Simple Preparation for Some Hydroxyphenothiazines[1]

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Various pure 3- and 7-hydroxyphenothiazines were required as intermediates in the synthesis of possible metabolites of the phenothiazine tranquilizing drugs. The few known 3- and 7-hydroxyphenothiazines have been made, with some difficulty, using the following methods: (A) oxidation of phenothiazines and reduction of the resulting phenothiazones;[2,3] (B) dealkylation of alkoxyphenothiazines;[4] and (C) thionation of hydroxydiphenylamines.[5] These syntheses required lengthy preparation of precursors or involved tedious removal of stubborn impurities. In all instances the reaction scale was quite small and with a single exception[4] no yields were reported.

The need for a simpler synthesis for 3- and 7-hydroxyphenothiazines which could be carried out in good yield on a relatively large scale, with minimal formation of troublesome congeners, has led to the improved preparation outlined in Scheme I. To permit easy comparison with the older techniques we have utilized the new procedure in the preparation of the known compounds, 2-chloro-7-hydroxyphenothiazine (VII)[4] and 3-hydroxyphenothiazine (VI).[2,4,5]

Commercial 2-aminobenzenethiol was converted to its zinc salt (I) in 81% yield by a simplification of the

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(1) This investigation was supported by the Psychopharmacology Service Center, National Institutes of Mental Health, Bethesda, Md., under Contract SA-43-ph-3758.

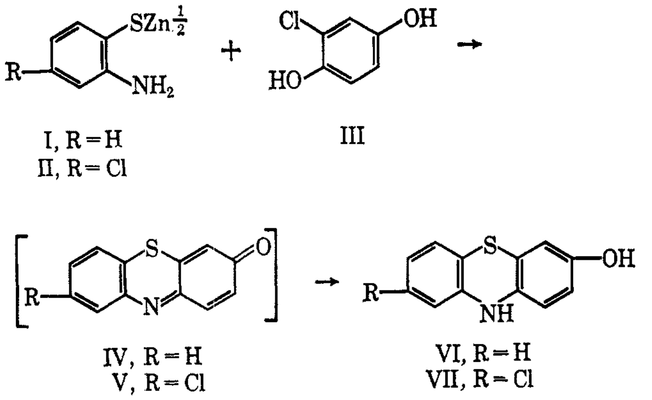
(2) R. P. Harpur, W. E. Swales, and O. F. Denstedt, *Can. J. Res.*, **D28,** 143 (1950).

(3) C. Bodea and M. Raileanu, *Ann.*, **614,** 171 (1958).

(4) P. K. Kadaba and S. P. Massie, *J. Org. Chem.*, **24,** 986 (1959).

(5) D. F. Houston, E. B. Kester, and F. De Eds, *J. Am. Chem. Soc.*, **71,** 3816 (1949).

SCHEME I



method described by Steiger.[6] Reduction of commercial bis(4-chloro-2-nitrophenyl) disulfide in acetic acid with zinc dust and hydrochloric acid provided 84% of the mercaptide II.[7]

Mixtures of the zinc salts I and II and chlorohydroquinone (III) were treated, in aqueous–ethanolic sodium hydroxide, with oxygen. The reaction mixtures, which now contained the phenothiazones IV and V, were simply poured into aqueous sodium hydrosulfite. Routine purification of the resulting precipitates gave a 67% yield of 3-hydroxyphenothiazine (VI) and a 62% yield of 2-chloro-7-hydroxyphenothiazine (VII). The substitution of 3-chlorocatechols for 2-chlorohydroquinone should make accessible various 1- and 9-hydroxyphenothiazines.

Experimental Section[8]

2-Aminobenzenethiol Zinc Salt (I).—To a solution of 8 g (0.2 mole) of sodium hydroxide in 25 ml of water was added 25 g (0.2 mole) of 2-aminobenzenethiol. The volume of the mixture was increased to 250 ml with water, and the mixture was warmed to help effect solution. The solution was filtered to remove a small amount of yellow insoluble material, and the filtrate was poured into a solution of 15 g (0.11 mole) of zinc chloride in 45 ml of glacial acetic acid and 250 ml of water. White solid precipitated immediately as a fine suspension. The suspension was boiled for 15 min to facilitate filtration, and the solid was collected. Drying *in vacuo* at 80–100° provided 25.4 g (81%) of I as white solid, mp >250°.

2-Amino-4-chlorobenzenethiol Zinc Salt (II).—A mixture of 97 g (0.26 mole) of bis(4-chloro-2-nitrophenyl) disulfide (Aldrich Chemical Co., Milwaukee, Wis.), 2.6 l of glacial acetic acid, and 100 ml of concentrated hydrochloric acid was heated to 60°. External heating was discontinued and zinc dust (200 g, 3.1 g-atoms) was added in portions at a rate which kept the reaction temperature at 60–65°. During zinc addition the mixture turned from yellow to yellow-green and finally to pale pink. When addition was complete, the mixture was maintained at 60° for 1 hr and at reflux temperature for another hour. The crude zinc salt was filtered and dissolved in 2.5 l. of boiling N,N-dimethylformamide, and the solution was filtered to remove unreacted zinc dust.[9] The filtrate was poured into 5 l. of water and the resulting white suspension was allowed to stand at room temperature overnight. Filtration, air drying at room temperature, and final drying *in vacuo* gave 82.6 g (84%) of zinc salt II as a white solid, mp >300°.

2-Chloro-7-hydroxyphenothiazine (VII).—To a mixture of 100 g (0.26 mole) of the pulverized zinc salt II, 75 g (0.52 mole) of chlorohydroquinone (III), and 1 l of alcohol was added a solution of 21 g (0.52 mole) of sodium hydroxide in 175 ml of water. The mixture was heated at reflux and a rapid stream of oxygen was introduced below its surface for 1 hr. Filtration of the hot mixture provided a brown solid and dark brown filtrate. The filtrate was poured into 6 l of cold water containing 90 g of sodium hydrosulfite. The resulting light tan suspension was extracted with ether (three 600-ml portions) and the extracts were dried over a mixture of magnesium sulfate and sodium hydrosulfite. The ether was evaporated under reduced pressure and unreacted chlorohydroquinone was removed by pumping the residue at 120–125° and 0.05 mm. The remaining tan solid (mp 211–216°) was stirred for 0.5 hr with 220 ml of refluxing benzene in a nitrogen atmosphere. The resulting slurry was allowed to cool and was filtered. The solid was dried *in vacuo*, providing 81 g (62%) of VI, mp 223–226° (lit.[4] mp 224–226°). The identity of V was confirmed by infrared and mixture melting point comparison with an authentic sample prepared according to the four-step procedure of Kadaba and Massie.[4]

3-Hydroxyphenothiazine (VI).—The reaction between the zinc salt of 2-aminobenzenethiol (I) and chlorohydroquinone, carried out as described for the synthesis of VII (above), gave a 67% yield of 3-hydroxyphenothiazine, mp 175–177.5°. This material was identical (infrared spectrum and mixture melting point) with an authentic sample of VI made by thionation of 4-hydroxydiphenylamine and obtained as white scales (toluene), mp 177.5–178.5° (lit.[5] mp 170–175°; no yield or analysis reported).

Anal. Calcd for $C_{12}H_9NOS$: C, 66.93; H, 4.19; N, 6.51. Found (authentic sample): C, 67.17; H, 4.16; N, 6.53.

In a sealed, evacuated tube VI melted at 188.5–189°.

Acknowledgment.—The authors gratefully acknowledge the assistance of Sandra Graham and Mary Schlauter in carrying out these preparations.

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[6] N. Steiger, U. S. Patent 2,454,260 (Nov. 16, 1948).

[7] Modification of the method of K. J. Farrington and W. K. Warburton, *Australian J. Chem.*, **8**, 545 (1955).

[8] Microanalysis was performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

[9] The filtered zinc dust should be disposed of immediately. It begins to smoke on standing in air.

Halogenated Ketenes. I. Dichloroketene[1,2]

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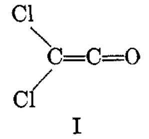
Owing to the rather recent interest in cycloaddition reactions of ketenes with various types of olefins and acetylenic compounds, and also because of the possibilities as a monomer for polymerization, it became of considerable interest to investigate the preparation of dichloroketene (I).



I

Until recently, all dihalogen ketenes were unknown. Difluoroketene[4] has recently been prepared and reportedly distils with ether. It has been reported that this material behaves like ketene and is practically impossible to separate from ether. Staudinger[5] attempted the synthesis of I by the thermal decomposition of the anhydride of dichloromalonic acid and

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[2] Presented at the Southeast-Southwest Regional Meeting of the American Chemical Society, Memphis, Tenn., Dec 1965.

[3] To whom communications concerning this paper should be addressed.

[4] N. N. Yarovenko, S. P. Motornyi, and L. I. Kirenskaya, *Zh. Obsch. Khim.*, **27**, 2796 (1957).

[5] H. Staudinger, E. Anthes, and H. Schneider, *Ber.*, **46**, 3539 (1913).