TABLE I

1,1-Bis(2-BENZOTHIAZOLYLAMINO)-2,2,2-TRICHLOROETHANES

R	M.P.	Formula	% C Calcd.	% C Found	% H Calcd.	% H Found	% N Calcd.	% N Found	% Cl Calcd.	% Cl Found	Yield, %
(a) H	203° (dec.)	$C_{16}H_{11}Cl_3N_4S_2$	44.70	45.20	2.56	2.66	13.03	13.00	24.79	24.65	80
(b) CH_3	180–181° (dec.)	$C_{18}H_{15}Cl_3N_4S_2$	47.21	47.60	3.27	3.34	12.24	12.50	23.27	22.89	51
(c) OCH_3	196–197° (dec.)	$C_{18}H_{15}Cl_3N_4O_2S_2$	44.12	44.30	3.06	3.06	11.44	11.56			82
(d) OC_2H_5	168–169° (dec.)	$C_{20}H_{19}Cl_3N_4O_2S_2$	46.37	46.73	3.67	3.67	10.82	10.73			85
(e) $COO(CH_2)_2-N(C_2H_5)_2$	102–103°	$C_{30}H_{37}Cl_3N_6O_4S_2.2HCl$	45.70	45.93	4.94	4.97	10.65	10.00			75

The analytical samples were: (*a*) recrystallized in colorless needles from benzene; (*b*, *c*, *d*) recrystallized in colorless needles from absolute ethanol–light petroleum (40–60°); (*e*) recrystallized from dry benzene, hygroscopic, decomposes if crystallized from hydroxylic solvents.

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An Unusual Reaction of Propargyl Bromide

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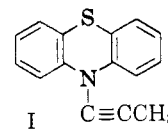
When an attempt to alkylate phenothiazine with propargyl bromide failed using the customary conditions of sodamide in xylene, the procedure was changed to one using sodium hydride in dimethylformamide. Under these conditions, alkylation occurred to give a 70% yield of product which turned out to be *N*-(1-propynyl)phenothiazine (I) instead of the desired isomeric *N*-(2-propynyl)phenothiazine. Support for the assigned structure includes the presence of disubstituted acetylenic absorption at 4.48 microns in the infrared, and the absence of ≡C—H and >C=C=C< absorption in the 3 and 5.1 micron regions, respectively. However, a disturbing feature of the infrared spectrum is the absence of C-methyl absorption at 7.25μ. Instead, two strong bands appear at 6.87μ and 6.96μ, more characteristic of *N*-methyl absorption. In view of the chemical evidence, it is assumed, nevertheless, that this shift is caused by attachment of methyl to the polar $\rangle N-C\equiv C-$ system.



I

Chemical evidence for structure I was obtained by hydrogenation to known *N*-(*n*-propyl)phenothiazine and by hydrolytic cleavage to unsubstituted phenothiazine.

The anomalous course of this reaction can be rationalized by postulating involvement of the dipolar ion, $\overset{+}{C}H_2C\equiv C^-$, of the type proposed by Hennion and co-workers[1-3] to explain some of the hydrolytic and aminolytic reactions of certain

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(3) G. F. Hennion and K. W. Nelson, *J. Am. Chem. Soc.*, **79**, 2142 (1957).

tertiary acetylenic chlorides. Resonance stabilization of this ion by the forms, $H:\overset{\cdot\cdot}{\underset{H}{C}}:C:::C: \rightarrow H:C::C::C: \leftrightarrow H:\overset{\cdot\cdot}{\underset{H}{C}}:C:::C$, explains how nucleophilic attack by nitrogen (of the phenothiazine ring) can occur at the acetylenic carbon if one assumes either subsequent or simultaneous attack of a proton or sodium ion at the methylenic carbon atom.

EXPERIMENTAL

N-(1-Propynyl)phenothiazine (I). To a stirred suspension of 7.2 g. (0.3 mole) of sodium hydride in 600 ml. of dry dimethylformamide, protected by an atmosphere of dry nitrogen, was added, in portions, 60 g. (0.3 mole) of phenothiazine. After warming at 50° for an additional 2 hr., the reaction mixture was heated to 70° and a solution of 35.7 g. (0.3 mole) of propargyl bromide in 50 ml. of dimethylformamide was added dropwise. After heating for an additional 2 hr. at 70°, the mixture was stirred overnight at room temperature.

Most of the solvent was removed by distillation at reduced pressure, and the residue was poured into cold water. Insoluble product was taken up in ether, washed with water, and dried over anhydrous magnesium sulfate. Filtration and removal of the ether by distillation gave an oil (52 g.) which solidified on trituration with hexane. Although purification could be accomplished by recrystallization from hexane, it was conveniently found that passing a benzene solution of the product over a column of alumina gave 48 g. of colorless crystals, m.p. 95–96°.

Anal. Calcd. for $C_{15}H_{11}NS$: C, 75.91; H, 4.67; N, 5.90. Found: C, 75.99; H, 4.70; N, 5.85.

Infrared spectrum (μ): 3.3 (w), 3.37 (w), 3.46 (w), 3.55 (vw), 4.48(m), 5.2 (vw), 5.31 (vw), 5.53 (vw), 5.64 (vw), 6.30 (m), 6.39 (m), 6.77 (m), 6.87 (s), 6.96 (s), 7.18 (vw), 7.28 (vw), 7.58 (s), 7.75 (s), 7.83 (m), 7.97 (s), 8.92 (m), 9.31 (w), 9.68 (m), 10.76 (w), 11.01 (w), 11.21 (w).

Substituting *n*-propyl bromide for the propargyl bromide in the above procedure gave a 65% yield of *N-(n-propyl)-phenothiazine*, b.p. 155–165° (0.8 mm.), m.p. 48–49° (from ethanol) (lit.[4] reports m.p. 49–50°).

Hydrogenation of I. A solution of 10.5 g. of N-(1-propynyl)-phenothiazine (I) in 250 ml. of 95% ethanol was treated with 0.53 g. of platinum oxide catalyst and hydrogenated at 30 lb. pressure and room temperature. After 17 hr., hydrogen absorption was 65% complete. The reaction was then warmed to 60° and reaction was complete in 4 hr. After removal of the catalyst by filtration, the filtrate was concentrated to dryness under reduced pressure. Several portions of benzene were distilled from the residue which was then taken up in 25 ml. of warm absolute ethanol. Heating this solution with charcoal followed by filtering, cooling, and seeding gave, after one more recrystallization from absolute ethanol, 4.2 g. of product, m.p. 47–48°, which did not depress the melting point of *N-(n*-propyl)phenothiazine. Furthermore, the infrared spectrum of the hydrogenation product was qualitatively identical with that of the known reference compound.

Hydrolysis of I. A mixture of 500 mg. of *N*-(1-propynyl)-phenothiazine (I) and 5 ml. of 10% hydrochloric acid was refluxed overnight. However, within 5 min. after the beginning of reflux, the oil turned to a solid. The mixture was concentrated to dryness; the black, crystalline residue was taken up in benzene and dried over anhydrous magnesium sulfate. After removal of the drying agent by filtration, the benzene solution was passed through an alumina column (20 × 1 cm.). Concentration of the eluate gave 295 mg. of yellow crystals, m.p. 174–176°. Recrystallization from benzene gave 195 mg., m.p. 177–179°.

Anal. Calcd. for $C_{12}H_9NS$: C, 72.32; H, 4.55; N, 7.03. Found: C, 72.46; H, 4.64; N, 6.95.

The product did not depress the melting point of an authentic sample of phenothiazine.

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Decarboxylation of 2-Vinylcyclopropane-1,1-dicarboxylic Acid to the Lactone of 4-Hydroxy-5-hexenoic Acid

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The synthesis of one of a series of sulfur compounds being prepared in these laboratories involved 3-cyclopentenecarboxylic acid as an intermediate.[1] This acid should readily be obtainable by hydrolysis and decarboxylation of the product of reaction of 1,4-dibromo-2-butene (I) and diethyl disodiomalonate which Skinner *et al.*[2] have described as diethyl 3-cyclopentene-1,1-dicarboxylate. However, the decarboxylation product obtained by this series of reactions did not possess the properties of the required acid. Its properties and infrared spectrum were in fact those to be expected of a vinyl substituted γ-lactone. Decarboxylation at 200° gave only poor yields of this compound, the majority of the product being a higher boiling material, but heating to 170° under a reduced pressure of nitrogen resulted in considerable improvement in the yields of lactone, presumably due to a decrease in the tendency for polymerization.

In view of the unexpected course of the preparation, a survey of the literature was made and it was then found that Kierstead *et al.*[3] had reported that condensation of 1,4-dibromo-2-butene and the monosodio-derivative of diethyl malonate gave diethyl 2-vinylcyclopropane-1,1-dicarboxylate (II). Investigation showed that our condensation product had an infrared spectrum not inconsistent with

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