which was then distilled with steam. The ether-soluble material from the distillate was extracted with 10% sodium hydroxide, and the alkaline layer was then acidified with 10% sulfuric acid. The oil which separated was collected in ether, and the extract was dried with magnesium sulfate and distilled. *2-Ethylmercaptophenol* (XVI, 10 g., 35% yield, $n_D^{25.5}$ 1.5681) was collected at 59–60°/0.6 mm.

A sample of 2-ethylmercaptophenol (5.57 g., 0.0362 mol.) was benzylated with benzyl chloride by a procedure essentially identical with that described above. 2-Ethylmercaptophenol benzyl ether (XVII, 5.16 g., 58% yield, $n_D^{25.5}$ 1.5960) was collected at 148–149°/1 mm.

Ethylmercaptophenyl benzyl ether was oxidized in hot glacial acetic acid with hydrogen peroxide (30%) by a procedure identical with that described elsewhere in this report. 2-Benzyloxyphenyl ethyl sulfone (XV) was obtained in quantitative yield; m.p. 106–107.5° (from ethanol).

Anal. Calcd. for $C_{15}H_{16}O_3S$: C, 64.95; H, 5.82. Found: C, 64.85; H, 5.70.

Samples of 2-benzyloxyphenyl ethyl sulfone, prepared by procedures (a) and (b) showed no depression of melting point upon admixture. Furthermore, X-ray diffraction patterns of these materials were identical.

Proof of structure of benzo-1,4-oxathiadiene-2-aldehyde (II). *Reduction to 2-methylbenzo-1,4-oxathiadiene* (III). A mixture of benzo-1,4-oxathiadiene aldehyde[3] (II, 2.5 g., 0.014 mol.), hydrazine (8 ml., 95%), triethylene glycol (50 ml.), and pulverized potassium hydroxide (1 g.) was heated at the reflux temperature for 2 hr. Material was then allowed to distill until the temperature of the solution reached 120°.

(a) The aqueous distillate was extracted with ether (100 ml.), the ether was dried with magnesium sulfate and concentrated. The residue (0.5 g., 22% calcd. as C_9H_8OS) was oxidized with 30% hydrogen peroxide (5 ml.) in hot glacial acetic acid. The solid sulfone, obtained from the acetic acid by addition of water, was recrystallized from 95% ethanol. The sulfone weighed 0.4 g. and melted at 161–162.5°. This material caused no depression in melting point when admixed with authentic 2-methylbenzo-1,4-oxathiadiene sulfone (m.p. 162–163°).

(b) In one experiment the residue from the steam distillation was extracted with ether, and the extract was dried and distilled. The organic distillate (b.p. 54–62°/1.3 mm., *ca.* 2 g.) was washed with water and the insoluble oil (1 g.) was oxidized with hydrogen peroxide, as described above. The resulting product was recrystallized from methylene chloride–petroleum ether (60–68°). This procedure afforded a small amount of white solid melting at 63.5–64.5°.

Anal. Calcd. for $C_8H_8O_3S$: C, 52.16; H, 4.37; S, 17.38; M.W. 184.21. Found: C, 52.29, 52.52; H, 4.76, 4.05; S, 16.99, 17.91; M.W. (freezing point of benzene) 203, 203; M.W. (Rast in camphor), 117, 201.

The identity of this material was not established.

MINNEAPOLIS 14, MINN.

[CONTRIBUTION NO. 184 FROM THE RESEARCH CENTER OF THE UNITED STATES RUBBER CO.]

The Chemistry of Maleimide and Its Derivatives.
I. N-Carbamylmaleimide

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F. S. DOVELL, R. J. KELLY, AND C. H. STITELER

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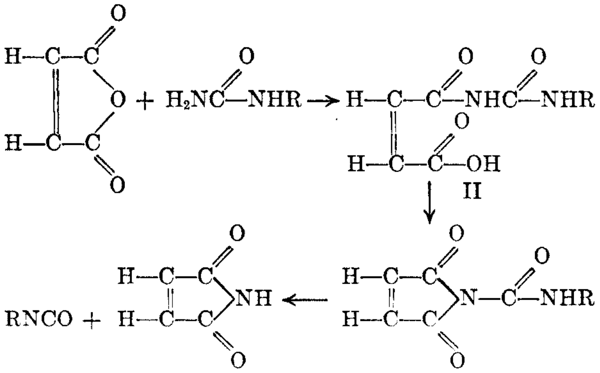
Carefully controlled condensation of maleic anhydride with urea or monosubstituted ureas, and cyclization of the maleuric acids to *N*-carbamylmaleimides followed by decomposition in dimethylformamide provide a practical route to maleimide. *N*-Carbamylmaleimides react with primary and secondary alcohols to yield esters of maleuric acid. *N*-Carbamylmaleimide and the maleurate esters have been copolymerized with several vinyl-type monomers.

Interest in the chemistry of maleimide (I) and its derivatives, and more particularly in their polymerizability, has been limited by the lack of a practical method of preparing such compounds. Until recently, the synthesis of maleimide was usually effected by chromic acid oxidation of pyrrole[1] or by acid-catalyzed cyclization of maleamide.[2] We have noted that these methods provide low yields and that neither is suitable for the preparation of appreciable amounts of maleimide. In our search for a more satisfactory method, we have devised the synthesis outlined in Chart A wherein the desired compound is obtained by thermal decomposition of the new structure, *N*-carbamylmaleimide (IIIa). Homologs of IIIa such as IIIb, c, and d are also readily available from this sequence of reactions.

CHART A



IIa. R = H
IIb. R = C_6H_5
IIc. R = $n\text{-}C_4H_9$
IId. R = $(CH_3)_3C$

IIIa. R = H
IIIb. R = C_6H_5
IIIc. R = $n\text{-}C_4H_9$
IIId. R = $(CH_3)_3C$

It is the purpose of this paper to describe the synthesis of III and to point out some of its reactions.

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[1] G. Plancher and F. Cattadori, *Atti reale accad. naz. Lincei*, [5] **13**, I, 489 (1904).

[2] I. J. Rinkes, *Rec. trav. chim.*, **48**, 961 (1929).

TABLE I

N-CARBAMYLMALEAMIC ACIDS (II)

R	Yield, %	M.P., (Dec.) °C.	Analyses							
			Carbon		Hydrogen		Nitrogen		Neut. Equiv.	
			Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
H	50–95	161–162[a]					17.72	17.68	158	139 159
C_6H_5	32	162–163[b]	56.3	57.02 57.23	4.26	4.36 4.39	11.95	11.83 11.79	234	232
n-C_4H_9	58	105.5–107.0[c]	50.50	51.29 51.39	6.54	6.75 6.67	13.05	13.03 13.01	214	214
tert-C_4H_9	85	151.5–153.5[c]	50.50	50.54 50.73	6.54	6.64	13.05	13.0	214	210

[a] Recrystallized from acetic acid. [b] Recrystallized from ethyl acetate. [c] Recrystallized from water.

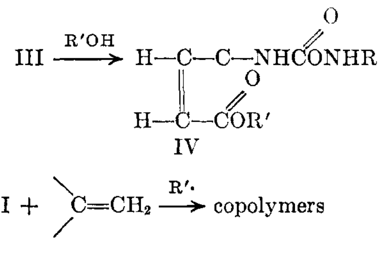
Preparation of N-carbamylmaleimides (III). We have effected a substantial improvement in the method of Dunlap and Phelps[3] for preparing *N*-carbamylmaleamic acid (IIa) by allowing equimolar amounts of maleic anhydride and urea to react in glacial acetic acid solution at 50–60° for twelve hours.[4] Yields became practically quantitative if mother liquors were re-used in subsequent reactions. It was demonstrated that the improvement in rate resulted from a catalytic effect exerted by IIa. A search for other catalysts showed that tertiary amines depressed the yield of IIa, while neither sulfuric acid nor acetate ion had any effect; dichloroacetic acid was a poorer solvent than was acetic acid. Anhydrous conditions were essential since as little as four per cent of water in the solvent completely inhibited the reaction. It was necessary to keep the reaction temperature within the 50–60° range in order to obtain good yields of readily purified product. At higher temperatures, the reaction became so violently exothermic as to be difficult or impossible to control, and carbon dioxide was evolved vigorously. That this gas-evolution resulted from decomposition of the product was indicated by the fact that simply refluxing IIa in acetic acid caused evolution of carbon dioxide. Other possible side-reactions include rearrangement of IIa to *N*-carbamylfumaramic acid, cyclization of IIa to IIIa by maleic anhydride and formation of derivatives of aspartic acid. The products of these possible reactions could seriously complicate the isolation and purification of IIa.

Homologs of IIa (Table I) were prepared from the appropriately substituted ureas. It was discovered that the substituted carbamylmaleamic acids were less stable than the parent compound; *N*-(phenylcarbamyl)-(IIa) and *N*-(*n*-butylcarbamyl)maleamic acid (IIc) underwent partial isomerization to the corresponding fumaramic acid derivatives on protracted warming in aqueous solution. Conversion to the *trans* isomer was avoidable by using organic recrystallization solvents such as ethyl acetate or methanol. IIa was not isomerized in aqueous solution, but it was noted that the melting point of crude IIa was not improved by recrystallization from this solvent. *N*-Carbamylfumaramic acid (Table II) and its homologs were prepared in excellent yield by refluxing II in methanol or acetic acid containing a trace of mineral acid.

The cyclization[5] of IIa was most satisfactorily accomplished by heating a suspension of the compound in two or three times its weight of acetic anhydride at 80–100° until the solid dissolved. The reaction was very slow at lower temperatures, and decomposition of the product to I and cyanuric acid became appreciable above 100°. On cooling, yields in excess of 90% of *N*-carbamylmaleimide (IIIa), m.p. 157–158°, crystallized from solution. It was possible to replace part of the acetic anhydride with acetic acid, but the product then had a lower melting point. Recrystallization of pure IIIa from acetic acid yielded the same material which bore a strong odor of acetic acid and was assumed to be a solvate. Acetic acid could not be completely pumped off the product under vacuum but could be removed by recrystallization from acetic anhydride or nitromethane.

Chemical properties of N-carbamylmaleimide (III). Certain of the chemical reactions of III are outlined in Chart B.

CHART B



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[3] F. L. Dunlap and I. K. Phelps, *Am. Chem. J.*, **19**, 492 (1897).

[4] R. H. Snyder, U. S. Patent **2,717,908**, September 13, 1955.

[5] R. H. Snyder, U. S. Patent **2,788,349**, April 9, 1957.

TABLE II

N-CARBAMYLFUMARAMIC ACIDS

R	M.P., (Dec.) °C.	Analyses Carbon Calcd.	 Carbon Found	 Hydrogen Calcd.	 Hydrogen Found	 Nitrogen Calcd.	 Nitrogen Found	 Neut. Equiv. Calcd.	 Neut. Equiv. Found
H	224					17.7	17.3	158	159
C_6H_5	208–210	56.3	56.9 56.6	4.26	4.33 4.20				
n-C_4H_9	202–204	50.5	50.4 50.8	6.55	6.44 6.66	13.05	13.44 13.48		

TABLE III

N-CARBAMYLMALEIMIDES (III)

R	Yield, %	M.P., °C.	Analyses Carbon Calcd.	 Carbon Found	 Hydrogen Calcd.	 Hydrogen Found	 Nitrogen Calcd.	 Nitrogen Found	 Neut. Equiv. Calcd.	 Neut. Equiv. Found
H	92.5	157–158[a]					20.0	19.7 19.8	140	139
C_6H_5	71	140–141[b]	61.0	61.8 62.1	3.73	3.80 3.88	13.0	13.0 13.1	216	215
n-C_4H_9	74	66.5–68.0[c]	55.1	55.7 55.8	6.16	6.21 6.25	14.3	14.2 14.7	196	211
tert-C_4H_9	23	107–109[c]	55.1	55.6 55.9	6.16	6.10 6.14	14.3	14.3 14.2	196	184

[a] Recrystallized from acetic anhydride. [b] Recrystallized from benzene. [c] Recrystallized from benzene–petroleum ether (b.p. 60–70°).

Thermal decomposition. The literature contains references[6,7] to the successful pyrolysis of *N*-carbamylimides to yield imides and cyanuric acid. IIIa sublimed under vacuum at 150° but decomposed at 180° to yield some I and a large amount of a complex polymer. In the presence of zinc chloride better yields of I were obtained at 130–150°, while the most satisfactory yields (60–80%) were obtained from decompositions run in dimethylformamide at 100°. Reaction periods of about one hour followed by rapid separation of I from the liquors favored higher yields. Homologs of IIIa have been decomposed similarly to produce high yields of isocyanates and very low yields of I.

Reaction of III *with alcohols.*[8,9] III reacted with primary and secondary alcohols, but not with tertiary alcohols or phenols, at 80–100° to yield alkyl *N*-carbamylmaleamates (IV) (Table IV).

Higher reaction temperatures were found to cause undesirable decomposition. In the case of methanol and ethanol, the reaction was complete in about thirty minutes even at room temperature, but higher primary alcohols and all glycols and secondary alcohols reacted more sluggishly, 25 to 30% yields of ester resulting from several hours of heating in the recommended temperature range. However, electrophilic substances sharply accelerated the reaction and provided excellent yields of the esters in an hour or two at 80–100° whether the reaction was run in excess alcohol or an inert medium such as dioxane, acetonitrile or petroleum ether (b.p. 60–70°). Zinc chloride, cadmium chloride, and ferric chloride catalyzed the acylation smoothly, but aluminum chloride catalyzed the acylation reaction and then isomerized[10] the products to alkyl *N*-carbamylfumaramates. As compared to their *cis*-isomers, the fumaramates were higher melting, less soluble, and had an ultraviolet absorption maximum in the 220 millimicron region which was not observed in the case of the *cis*-isomers.

Copolymerization of III *and* IV *with vinyl monomers.* Both III and IV copolymerized readily with such monomers as styrene, vinyl acetate, and butadiene. The *N*-carbamylfumaramates have not proved to be useful monomers because of their very poor solubility in most organic liquids.

EXPERIMENTAL[11]

Melting points are uncorrected.

N-Carbamylmaleamic acid (IIa). A stoppered flask containing 1000 g. of glacial acetic acid, 300 g. (5.0 mol.) of

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[6] A. Piutti, *Ann*, **214**, 17 (1892); *Gazz. Chim. ital.*, **12**, 169 (1892).

[7] C. S. Smith and C. J. Cavallitto, *J. Am. Chem. Soc.*, **61**, 2218 (1939).

[8] Amines and mercaptans also react with III, but ring-opening and addition to the double bond are frequently concurrent, resulting in complex products.

[9] R. H. Snyder and P. O. Tawney, U. S. Patent **2,854,-438**, Sept. 20, 1958.

[10] R. J. Kelly and C. E. Bryan, U. S. Patent **2,809,190**, Oct. 8, 1957.

[11] Analyses were performed by the Analytical Research Department of the Research Center or by the Schwartzkopf Microanalytical Laboratory, Woodside, N. Y.

TABLE IV

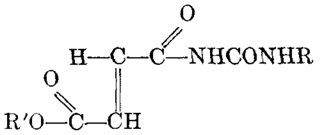
ALKYL *N*-CARBAMYLMALEAMATES (IV)

R	R′	Yield, %	M.P., °C.	Analyses Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Nitrogen Calcd.	Nitrogen Found
H	Methyl	88.6	113–114					16.29	16.36
H	Ethyl	70	111–112					15.05	15.01 14.84
H	*i*-Propyl	75.5	113–114					14.00	13.95 13.97
H	*n*-Butyl	47	96–99					13.09	13.25 13.33
H	Allyl		109–111					14.13	14.02 13.99
H	Benzyl	50	130–131					11.28	11.25
H	β-Hydroxyethyl	60	131–131.5					13.85	13.59 13.71
H	β-Chloroethyl	66	116–119					12.68	12.62 12.84
H	N-Morpholinyl-ethyl	74	121.5–122.5					15.5	15.3 15.2
H	Ethylene[a]	73	184–186					16.37	16.31 16.26
n-Butyl	Benzyl	78	65.5–66.5	63.1	63.8 63.8	6.58	6.69 6.71	9.20	9.34 9.34
tert-Butyl	Benzyl	90	70–72.5	63.1	63.3 63.2	6.58	6.63 6.63	9.20	9.22 9.14
tert-Butyl	*i*-Propyl	88	96–97	56.2	56.9 57.1	7.81	7.88 7.85	10.90	10.99 10.99
Phenyl	Benzyl	77	131–133.5	66.7	66.7	4.97	4.99	8.63	8.48
Phenyl	*i*-Propyl	61	132–133	60.8	61.4 61.1	5.83	5.72 5.74	10.11	10.17 10.19
H	*n*-Dodecyl	79	119–119.5	62.5	62.3	9.2	9.2	8.6	8.7

[a] bis-Maleurate.

TABLE V

ALKYL *N*-CARBAMYLFUMARAMATES



R	R′	M.P., °C.	Nitrogen Analysis Calcd.	Nitrogen Analysis Found
H	Methyl	228–230	16.28	16.18 16.18
H	β-Chloro-ethyl	189.5–190.5	12.68	12.62 12.59

urea and 500 g. (5.1 mol.) of maleic anhydride was heated at 50° for 12 hr. and then left overnight at room temperature. The crystalline product, collected on a filter, washed with 250 ml. of glacial acetic acid and dried at 50°, weighed 405 g. (a 56% yield) and melted at 161–162° (dec.). The mother liquors and washings were recharged with 300 g. of urea and 500 g. of maleic anhydride and heated at 56° for only 5 hr. After standing overnight at room temperature, 620 g. (77% yield) of product, m.p. 159–161° (dec.) was collected. Two successive repetitions of this process produced 83.8 and 97.5% yields of product, m.p. 156–159° (dec.) and 157–160° (dec.) respectively. The average yield was 86%.

N-(n-Butylcarbamyl)maleamic acid (IIc). A mixture of 19.6 g. (0.2 mol.) of maleic anhydride, 23.4 g. (0.2 mol.) of *N*-*n*-butylurea and 50 ml. of acetic acid was heated at 55° for 11 hr. Evaporation of solvent left a viscous residue which, when poured into ice water, yielded 25.0 g. (58%) of a white solid, m.p. 102–105°. Recrystallization from water yielded pure *N*-(*n*-butylcarbamyl)maleamic acid, m.p. 105.5–107.0°.

N-Carbamylmaleimide (IIIa). *N*-Carbamylmaleamic acid (1000 g., 6.3 mol.) was added to 3240 g. of acetic anhydride which had been heated to 90–95°. The suspension was stirred vigorously at 90–97° for 35 min. at which time the solid had dissolved. After a hot filtration the filtrate was cooled to room temperature, and the precipitated solid was filtered off and washed with 150 g. of acetone. After vacuum drying, the product weighed 680 g. (76.7%) and melted 155–158°. A sample recrystallized from acetic anhydride had m.p. 157–158°.

Maleimide (I). A 5-l. flask fitted with a stirrer and thermometer was charged with 1680 g. of dimethylformamide and heated to 90–95° by means of a water bath. Heating was stopped and 840 g. (6.0 mol.) of IIIa was added with stirring. The water bath absorbed heat evolved by the exothermic reaction so that the reaction temperature did not exceed 111°. At the end of the exothermic period, heat was applied to maintain the temperature at 95–99° for a total reaction time of 1 hr. The mixture was cooled to room temperature and left overnight. Precipitated cyanuric acid was filtered off and dimethylformamide was removed from the filtrate under vacuum. The product was then distilled rapidly at 96–105° at 5 millimeters to yield 85.9% of crude maleimide. After recrystallization from ethyl acetate, the product had m.p. 92–94° undepressed by admixture with[12] material obtained by pyrolysis of 3,6-*endo*-methylene-Δ^4-tetrahydrophthalimide.

N-Carbamylfumaramic acid. A solution of 1 g. of IIa in 20 ml. of acetic acid containing a drop of concentrated sulfuric acid was warmed on a steam bath for 20 min. Separa-

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(12) P. O. Tawney, U. S. Patent 2,524,145, Oct. 3, 1950.

tion of the *trans*-acid began soon after the heating started. On cooling, 0.75 g. of product separated and was filtered off.

n-Butyl N-carbamylmaleamate (IV. R = H, R′ = *n*-C_4H_9). A mixture of 1184 g. of *n*-butanol, 560 g. (4.0 mol.) of IIIa, 8 g. of zinc chloride and 150 g. of petroleum ether (b.p. 60–70°) was refluxed at 85° until solution was complete. The solution was filtered and cooled, depositing 782 g. (92%) of the ester, m.p. 96–99°.

Methyl N-carbamylfumaramate. Addition of 0.1 g. of aluminum chloride to 5.0 g. (0.036 mol.) of IIIa in 50 ml. of methanol caused an immediate exothermic reaction and precipitation of a quantitative yield of methyl *N*-carbamylfumaramate, m.p. 228–230°.

Copolymerization of IIIa *with vinyl acetate.* A solution of 10 g. (0.07 mol.) of IIIa, 25 ml. (0.27 mol.) of vinyl acetate and 0.1 g. of benzoyl peroxide in 194 ml. of dioxane was heated at 80° in a water bath for 6 hr. The polymer solution was poured into 1 l. of acetone. After filtration and drying, the polymer weighed 5.5 g. (17% conversion), was soluble in dimethylformamide and, with hydrolysis, in 10% aqueous sodium hydroxide, had intrinsic viscosity 0.13 and analyzed for 57.6% nitrogen. This analysis corresponds to a ratio of IIIa to vinyl acetate of 1:1.2 from a feed ratio of 1:3.8.

Copolymerization of methyl N-carbamylmaleamate (IV. R = H, R′ = CH_3) *with styrene.* A mixture of 20 g. (0.192 mol.) of styrene, 20 g. (0.116 mol.) of IV and 0.8 g. of benzoyl peroxide in 40 g. of acetone was heated for 4.75 hr. in a water bath held at 70°. The clear solution, which still contained some undissolved IV, was poured into stirred methanol to precipitate the polymer. The precipitate was filtered off and dried overnight in an evacuated desiccator. The material was then triturated with methanol and again dried overnight in a vacuum desiccator. The product weighed 11.6 g. (29% conversion) and was soluble in dioxane and acetic acid. Nitrogen analysis (6.05, 6.05%) indicated that the monomer ratio (IV:styrene) in the polymer was 1:2.8 from a feed ratio of 1:1.65. The polymer had an intrinsic viscosity in dioxane of 0.11.

Acknowledgment. The following assisted in some of the preparations described: G. H. Brice, F. S. Elkins, A. N. Johnson, M. D. Kellert, and K. A. Leibbrand.

The authors wish to express their appreciation to Dr. F. H. Westheimer of Harvard University and Dr. H. Kwart of the University of Delaware for valuable and stimulating discussions held during the course of research and the preparation of this paper.

WAYNE, N. J.

[CONTRIBUTION FROM THE RESEARCH INSTITUTE OF TEMPLE UNIVERSITY AND THE RESEARCH AND DEVELOPMENT DIVISION SMITH KLINE & FRENCH LABORATORIES]

Synthesis of Phenothiazines. III. Derivatives of Hydroxy- and Mercaptophenothiazines[1]

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Received August 11, 1959

The preparation of seven phenothiazines is reported; they are 2-hydroxy-, 2-benzoyloxy-, 2-methylmercapto-, 2- and 4-trifluoromethylmercapto-, 2-methylsulfonyl-, and 2-trifluoromethylsulfonylphenothiazine. Various new intermediates are described.

The early French work in the phenothiazine field, following the lead of chloropromazine, resulted in the synthesis of the 2-methyl and 2-methoxy derivatives.[4] Further work in France[5] and in Switzerland,[6] as well as independent work in our laboratories, produced the 2-methylmercapto- and 2-methylsulfonyl-phenothiazines. The development of the potent 10-aminoalkyl-2-trifluoromethylphenothiazines[7,8] has led us to study the 10-aminoalkyl-2-trifluoromethylmercapto- and 2-trifluoromethylsulfonylphenothiazines. The present paper describes the preparation of the novel 2-substituted phenothiazine intermediates. The synthesis of a number of 10-alkylated phenothiazines derived from them will be described later.

Many methods for preparing phenothiazines have been reported in the literature.[9] These include: (A) the thionation of an appropriately substituted diphenylamine with sulfur[10] and a catalyst,[11,12] (B) the copper-catalyzed dehydrohalogenation of substituted 2-amino-2′-halodiphenyl sulfides,[13] and (C) the Smiles rearrangement of 2′-amido-2-

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(1) These compounds were prepared at the Research Institute of Temple University under a contract with Smith Kline & French Laboratories. Papers I and II of this series are considered to be those referred to in ref. (7) and (34). (a) To whom inquiries may be addressed.

(2) Research Institute of Temple University.

(3) Smith Kline & French Laboratories.

(4) P. Charpentier, *et al.*, *Compt. rend.*, **235**, 59 (1952).

(5) Rhône-Poulenc, Belgian Patent **552,836** (1957).

(6) J.-P. Bourquin, G. Schwarb, G. Gamboni, R. Fisher, L. Ruesch, S. Guldimann, V. Theus, E. Schenker, and J. Renz, *Helv. Chim. Acta*, **41**, 1061 (1958).

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(9) S. P. Massie, *Chem. Revs.*, **54**, 797 (1954).

(10) A. Bernthsen, *Ber.*, **16**, 2896 (1883).

(11) E. Knoevenagel, *J. prakt. Chem.*, **89**, 11 (1914).

(12) F. Ackermann, German Patent **224,348** (1909).

(13) P. J. C. Buisson, P. Gailliot, and J. Gaudechon, U. S. Patent **2,769,002** (1956).