ture was refluxed for 4 hr., then allowed to stand overnight. A 10% ammonium chloride solution (100 ml.) was cautiously added, then the mixture was filtered. The solid residue was slurried with ethyl ether and filtered. The collected ether filtrates were washed with water and concentrated to a final volume of 250 ml. and extracted with two 50-ml. portions of 10% hydrochloric acid. The acidic extract was made alkaline with a saturated solution of sodium carbonate and extracted with ethyl ether. The ether extract was washed with water, dried over anhydrous sodium sulfate, filtered, concentrated, and the residue distilled *in vacuo*. The fraction boiling at 102° with a pressure of 0.4 mm. was collected and crystallized on standing: yield 3.1 g., m.p. 41–42°.

Anal. Calcd. for $C_{12}H_{19}NO$: C, 74.56; H, 9.91; N, 7.25. Found: C, 74.61; H, 9.95; N, 7.20.

The infrared spectrum was identical with an authentic sample of XIV prepared by another way as described below. The mixed melting points of samples of XIV obtained by the two different methods were not depressed.

2-METHYLAMINOMETHYL-2-PHENYL-1-BUTANOL (XIV) FROM ETHYL β-AMINO-α-ETHYL-α-PHENYLPROPIONATE (XV)

β-Carbethoxyamino-α-ethyl-α-phenylpropionic acid (XVI). In a flask fitted with a mechanical stirrer, a thermometer, and a dropping funnel, 20 g. of ethyl β-amino-α-ethyl-α-phenylpropionate[16] (XV) and 100 ml. of anhydrous pyridine were placed. The mixture was cooled to 0°, then 20 g. of ethyl chloroformate were slowly added while stirring. When the addition was complete, the mixture was further stirred at 0° for 1 hr. then cautiously poured into 350 ml. of ice water, acidified with 10% sulfuric acid and extracted with ethyl ether. The ether extract was washed with water until neutral, dried over sodium sulfate, filtered, and concentrated to dryness. The residue was distilled *in vacuo* collecting the fraction boiling at 150° with a pressure of 0.4 mm. Yield 23.1 g.

Anal. Calcd. for $C_{16}H_{23}NO_4$: C, 65.50; H, 7.90; N, 4.77. Found: C, 65.76; H, 7.87; N, 5.00.

2-Methylaminomethyl-2-phenyl-1-butanol (XIV). To a suspension of 15 g. of $LiAlH_4$ in 150 ml. of anhydrous ethyl ether 10 g. of XVI in 100 ml. of anhydrous ethyl ether were slowly added at low temperature. The mixture was refluxed 3 hr., allowed to stand overnight, then cautiously treated with 100 ml. of 10% ammonium chloride. The mixture was filtered, treated with ethyl ether and the ether layer extracted with two 30 ml. portions of 10% hydrochloric acid. The ether layer was discarded; the acid extract was made alkaline with a saturated solution of sodium carbonate, then extracted three times with ether. The combined ether extracts were washed with water, dried over sodium sulfate, concentrated, and the residue was distilled with the technique of Ronco *et al.*[19] Yield 2.77 g. of XIV, b.p. 90° (air bath) with a pressure of 0.2 mm. The distilled product solidified on standing, m.p. 41–42.5°.

2-DIMETHYLAMINOMETHYL-2-PHENYL-1-BUTANOL (XVII) BY REDUCTION OF 3-METHYL-5-ETHYL-5-PHENYLDIHYDRO-1,3-OXAZINE-2,4-DIONE (XIi)

Twenty g. of XIi were reduced with 10 g. of $LiAlH_4$ by the same method described above for the reduction of Ii: 12.55 g. of XVII were obtained, b.p. 95–96° with a pressure of 0.4 mm.; XVII solidified on standing, m.p. 68.5–69°.

Anal. Calcd. for $C_{13}H_{21}NO$: C, 75.31; H, 10.21; N, 6.76. Found: C, 75.30; H, 10.00; N, 6.74.

The infrared spectrum was identical with an authentic sample of the product prepared by another way described hereunder.[18] The mixed melting point of samples of XVII obtained by the two different methods was not depressed.

2-DIMETHYLAMINOMETHYL-2-PHENYL-1-BUTANOL (XVII) FROM α-CARBETOXY-α-PHENYL BUTYRYL CHLORIDE (XVIII)[18]

N,N-Dimethyl-α-carbetoxy-α-phenylbutyramide (XIX). A 17.5% benzene solution of dimethylamine (100 ml.) was added to 30 g. of α-carbetoxy-α-phenylbutyryl chloride (XVIII).[2] After 15 min. the solution was treated with water, acidified with hydrochloric acid, and extracted with ethyl ether. The ether extract was evaporated to dryness and the residue crystallized from ligroin. Yield 28 g., m.p. 52–55°.

2-Dimethylaminomethyl-2-phenyl-1-butanol (XVII). Into a suspension of 17.4 g. of $LiAlH_4$ in 150 ml. of anhydrous ethyl ether a solution of 15 g. of XIX in 90 ml. of anhydrous ethyl ether was gradually dropped without exceeding 25–27°. The mixture was refluxed 1.5 hr. and poured cautiously after cooling into 2 volumes of cold water. The mixture was extracted with ethyl ether and the organic layer evaporated to dryness *in vacuo*. The residual oil was distilled *in vacuo* collecting the fraction boiling at 95–96° with 0.4 mm. Yield 9 g. of XVII. The product crystallized on standing, m.p. 68–69°.

Acknowledgment. We are grateful indebted to Prof. R. Fusco for the very useful discussions on this subject during the experimental work and to Miss. Dr. A. Wittgens for the assistance in the compilation of the manuscript.

MILAN, ITALY

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF AYERST, MCKENNA & HARRISON LTD.]

New Analeptics: 1-(Diphenylmethyl)-2-methyl-2-thiopseudourea Analogs

STANLEY O. WINTHROP AND GREGORY GAVIN

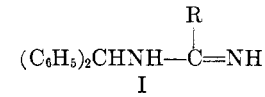
Received June 18, 1959

1-(Diphenylmethyl)pseudoureas, guanidines, and amidines have been prepared as potential analeptics. Analogs of 1-(diphenylmethyl)-2-methyl-2-thiopseudourea where the diphenylmethyl moiety has been replaced by other groupings are also reported. Certain of these compounds possess appreciably analeptic activity.

In a previous paper[1] some 1-(diphenylmethyl)-2-alkyl-2-thiopseudoureas were described and reported to possess analeptic activity. The first member of the series proved to be the most potent with respect to increasing the spontaneous activity of the rat. Since this compound is structurally quite unlike any of the known analeptic drugs, it was of interest to prepare certain of its analogs for pharma-

(1) S. O. Winthrop, S. Sybulski, G. Gavin, and G. A. Grant, *J. Am. Chem. Soc.*, **79**, 3496 (1957).

cological screening. The related cyclized 1-(diphenylmethyl)-2-thiopseudoureas were found to be central nervous system depressants.[2] The present paper deals for the most part with the synthesis of analogs represented by formula I where the methylthio grouping (R) of the pseudothiourea has been replaced with alkoxy, alkylamino, and alkyl groups, yielding pseudoureas, guanidines, and amidines, respectively.



I

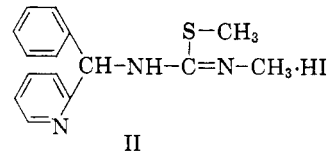
11-Diphenylmethylamine and cyanogen bromide gave (diphenylmethyl)cyanamide, which was then converted to a pseudourea with the appropriate alcohol and one equivalent of hydrogen chloride. In methanol the formation of the pseudourea was considered complete after 24 hr.[3] Progressively longer reaction times were required, however, for the higher alcohols. A modification of this procedure was found to give the desired pseudoureas more readily. (Diphenylmethyl)cyanamide and an excess of hydrogen chloride yielded a product which was assumed to be 1-chloro-*N*-(diphenylmethyl)-formamidine hydrochloride. This latter compound, when heated under reflux for 30 min. in the appropriate alcohol and allowed to stand at room temperature overnight, gave the pseudourea.

A direct displacement of the methylthio grouping by alkoxy was also considered as a possible method of synthesis. A reaction of this type was recently reported[4] wherein 2-(methylthio)-2-imidazoline on treatment with sodium alkoxides gave the desired 2-alkoxy-2-imidazolines. 1-(Diphenylmethyl)-2-methyl-2-thiopseudourea and sodium ethoxide were heated under reflux in ethanol. However, no pseudourea could be identified from the reaction mixture, the major product being (diphenylmethyl)-cyanamide.

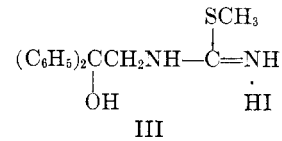
The pseudourea salts were stable, high melting, crystalline solids. They were generally considerably more water-soluble than the corresponding thiopseudoureas. The free bases were easily prepared, found to be stable, and could be used for the preparation of other salts.

The amidines and guanidines were prepared by standard procedures described in the chemical literature. 1,1-Diphenylmethylamine and an ester of an imidic acid, hydrochloride gave the former compounds, while an alkylamine hydrochloride and (diphenylmethyl)cyanamide produced the latter.

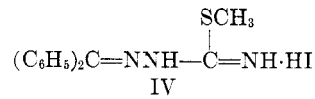
Analogs were also prepared wherein the diphenylmethyl moiety is replaced by other closely related groupings. The replacement of a benzene ring with a pyridine ring has on occasion resulted in enhancement of pharmacological activity. 2-(α-Aminobenzyl)pyridine was prepared by the zinc in acetic acid reduction of phenyl-2-pyridyl ketone, oxime. The fusion of the ammonium salt of thiocyanic acid with 2-(α-aminobenzyl)pyridine, dihydrochloride, proved to be unsatisfactory. The free base with the methyl ester of isothiocyanic acid readily gave 1-(α-2-pyridylbenzyl)-3-methyl-2-thiourea, which was converted with iodomethane to the thiopseudourea (II).



II



III



IV

1-(2,2-Diphenyl-2-hydroxyethyl)-2-thiourea, prepared by fusion of the appropriate amine hydrochloride with the ammonium salt of thiocyanic acid, on treatment with iodomethane gave the thiopseudourea (III). The thiosemicarbazone of benzophenone on methylation gave benzophenone 3-methyl-3-thioisosemicarbazone hydriodide (IV).

Pharmacological activity. The compounds were screened for their effect on the spontaneous activity of the rat by the method of Chappel and coworkers.[5] The pseudoureas (Table I) were found to have appreciable central stimulant activity but were more toxic than the corresponding thiopseudoureas. The amidines and guanidines were convulsants at high doses while the pyridine analog (II) retained the activity of the parent compound. The other compounds were devoid of significant pharmacological activity. The stimulant activity and acute toxicity for some of these compounds are compared with *dl*-amphetamine sulfate in Table II. Detailed results will be reported elsewhere.

EXPERIMENTAL[7]

(*Diphenylmethyl*)*cyanamide.* Cyanogen bromide (40 g., 0.38 mol.) dissolved in 250 ml. of ethyl acetate was added dropwise with stirring and cooling to 1,1-diphenylmethylamine (117 g., 0.75 mol.) in 750 ml. of ethyl acetate. When the addition was complete and the exothermic reaction had subsided, the reaction mixture was heated at reflux for an additional hour. The 1,1-diphenylmethylamine, hydro-

(2) S. O. Winthrop and G. Gavin, *Can. J. Chem.*, **36**, 879 (1958).

(3) R. H. McKee, *Am. Chem. J.*, **42**, 1 (1909).

(4) C. K. Cain, J. Kleis, and G. I. Poos, *J. Org. Chem.*, **22**, 1283 (1957).

(5) C. I. Chappel, G. A. Grant, S. Archibald, and R. Paquette, *J. Am. Pharm. Assn.*, **46**, 497 (1957).

(6) Handbook of Toxicology, Vol. 1, William S. Spector, W. B. Saunders Co., Philadelphia, Pa. (1956).

(7) All melting points are uncorrected.

TABLE I

PSEUDOUREAS, GUANIDINES, AND AMIDINES $(C_6H_5)_2CHNH-\overset{R}{\underset{|}{C}}=NH.HCl$

R	Yield, %	M.P.[h]	Formula	Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Nitrogen Calcd.	Nitrogen Found	Chlorine Calcd.	Chlorine Found
OCH_3[a,b,d]	67	124–125	$C_{16}H_{17}ClN_2O$					10.12	9.95	12.81	13.02
OCH_2CH_3[c,e]	78	130–131	$C_{16}H_{19}ClN_2O$					9.63	9.50	12.20	12.33
$OCH_2CH_2CH_3$[f]	55	125–126	$C_{17}H_{21}ClN_2O$					9.18	9.13	11.63	11.91
$OCH(CH_3)_2$[e]	79	136–138	$C_{17}H_{21}ClN_2O$					9.18	9.02	11.63	12.03
$NHCH_3$[e]	54	233–234	$C_{15}H_{18}ClN_3$	65.32	65.67	6.59	6.74			12.85	12.32
$NHCH_2CH_3$[e]	50	198–200	$C_{16}H_{20}ClN_3$	66.31	66.67	6.96	7.05	14.50	14.41	12.23	12.58
CH_3[g]	92	286–288	$C_{15}H_{17}ClN_2$	69.10	69.53	6.56	6.53	10.74	10.64	13.60	13.25
CH_2CH_3[g]	53	230–232	$C_{16}H_{19}ClN_2$					10.20	10.16	12.91	12.96

[a] Free base melted at 105–107°; Calcd. for $C_{15}H_{16}N_2O$: C, 74.85; H, 6.71; N, 11.64. Found: C, 75.04; H, 6.61; N, 11.86. [b] Other salts are described in the experimental. [c] Free base melted at 83–84°; calcd. for $C_{16}H_{18}N_2O$: N, 11.01. Found: N, 11.04. [d] Recrystallized from methanol ether. [e] Recrystallized from ethanol ether. [f] Recrystallized from acetone ether. [g] Recrystallized from ethanol. [h] The pseudoureas invariably melted with decomposition.

TABLE II

1-Diphenylmethyl Compounds	DIA_{50} S.C.,[a] Mg./Kg.	$L.D._{50}$ I.P.,[b] Mg./Kg.
2-Methylpseudourea, hydrochloride	13	50
2-Ethylpseudourea, hydrochloride	5	50
2-Methyl-2-thiopseudourea, hydriodide[c]	2.5	92
2-Ethyl-2-thiopseudourea, hydroiodide[c]	12	80
dl-Amphetamine, sulfate	2[d]	12[e]

[a]Subcutaneous dose increasing spontaneous activity of the rat by 50%. [b]Intraperitoneal dose in the mouse causing death in 50% of the animals. [c]See Reference 1. [d]Intraperitoneally. [e]Values as high as 100 mg./kg., have been reported in the literature.[6]

bromide, was filtered off and the filtrate evaporated *in vacuo*, leaving a solid residue. The crude product was purified by dissolving it in a solution of 500 ml. of ethanol and 2500 ml. of 0.5% aqueous sodium hydroxide, boiling the solution for a few minutes, filtering and finally neutralizing with acetic acid to precipitate the product, a white solid, 35 gm., 44%, m.p. 119–121°. One recrystallization from benzene-hexane raised the melting point to 121–122°.

Anal. Calcd. for $C_{14}H_{12}N_2$: C, 80.72; H, 5.82; N, 13.46. Found: C, 80.35; H, 5.78; N, 13.15.

1-Chloro-N-(diphenylmethyl)formamidine hydrochloride. (Diphenylmethyl)cyanamide (20.8 g., 0.1 mol.) was dissolved in 600 ml. of ether and hydrogen chloride gas was introduced in excess. The precipitated hydrochloride was filtered off to yield 26 g., 92%, m.p. 178–180° dec. One recrystallization from acetonitrile raised the melting point to 180–181° dec.

Anal. Calcd. for $C_{14}H_{14}Cl_2N_2$: N, 9.97; Cl, 25.25. Found: N, 10.23; Cl, 25.35.

1-(Diphenylmethyl)-2-methylpseudourea hydrochloride. 1-Chloro-*N*-(diphenylmethyl)formamidine hydrochloride (10 g.) was heated under reflux for 30 min. in 100 ml. of methanol and then allowed to stand at room temperature for 16 hr. The methanol was removed *in vacuo* and the oil residue was crystallized from acetone ether to yield 6.7 g., 69%, m.p. 124–125° dec. One recrystallization from methanol ether did not change the melting point (see Table I).

The hydrochloride (2.8 g., 0.01 mol.) was dissolved in 50 ml. of methanol containing 0.59 g. (0.011 mol.) of sodium methoxide. Enough ether was then added to completely precipitate the sodium chloride, which was removed by filtration. The filtrate was evaporated *in vacuo* to yield 2.0 g., 83% of the free base, 1-(diphenylmethyl)-2-methylpseudourea, m.p. 101–104°. Two recrystallizations from hexane raised the melting point to 105–107° (see Table I).

(Diphenylmethyl)-2-methylpseudourea salts. The following salts were prepared by the addition of the appropriate acid to an ether solution of (diphenylmethyl)-2-methylpseudourea: hydrobromide, m.p. 122–123° dec. Calcd. for $C_{15}H_{17}BrN_2O$: N, 8.72; Br, 24.88. Found: N, 8.69; Br, 25.46. Hydriodide, m.p. 117–118° dec. Calcd. for $C_{15}H_{17}IN_2O$: N, 7.62; I, 34.50. Found: N, 7.48; I, 34.42. Maleate, m.p. 157–158° dec. Calcd. for $C_{19}H_{20}N_2O_5$: N, 7.94. Found: N, 7.61.

1-(Diphenylmethyl)-2-propylpseudourea hydrochloride. (Diphenylmethyl)cyanamide (3.6 g., 0.017 mol.) was dissolved in 50 ml. of 1-propanol containing 0.63 g. (0.017 mol.) of hydrogen chloride. The reaction mixture was allowed to stand at room temperature for 1 week. It was then evaporated *in vacuo* and the oil residue was triturated with ether to yield 4.1 g., 79% of product, m.p. 115–119° dec. Two recrystallizations from acetone ether raised the melting point to 125–126° dec. (see Table I).

Reaction of sodium ethoxide with 1-(diphenylmethyl)-2-methyl-2-thiopseudourea, hydrochloride. 1-(Diphenylmethyl)-2-methyl-2-thiopseudourea hydrochloride,[1] (14.6 g., 0.05 mol.) was suspended in 250 ml. of absolute ethanol containing 2.3 g. (0.1 mol.) sodium. The solution was heated under reflux for 16 hr. and the sodium chloride filtered off. The ethanol was removed *in vacuo*, leaving a solid residue which was triturated with water and neutralized with acetic acid to yield 6 g. of (diphenylmethyl)cyanamide, 58%, m.p. 110–118°. One recrystallization from benzene-hexane gave 3.6 g., m.p. 116–118°, whose infrared spectrum was identical with that of (diphenylmethyl)cyanamide.

1-(Diphenylmethyl)-3-methylguanidine hydrochloride. (Diphenylmethyl)cyanamide (8.4 g., 0.04 mol.) and methylamine, hydrochloride (2.8 g., 0.04 mol.) were dissolved in 200 ml. amyl alcohol and heated under reflux for 4 hr. The amyl alcohol was removed *in vacuo* and the oily residue triturated with ether to yield 6.0 g., 54% of product, m.p. 208–211°. Two recrystallizations from ethanol-ether gave an analytically pure material with m.p. 233–234° (see Table I).

N-(Diphenylmethyl)acetamidine hydrochloride. 1,1-Diphenylmethylamine (20.2 g., 0.11 mol.) in 25 ml. of absolute ethanol was added dropwise with stirring to (12.4 g., 0.1 mol.) ethyl ester of acetimidic acid, hydrochloride[8] in 100 ml. of absolute ethanol. Stirring was continued for 3 hr. at room temperature. Enough ether was then added to completely precipitate the product, 24 g., 84%, m.p. 270–280° dec. Three recrystallizations from ethanol gave

(8) H. Gilman, *Org. Syntheses*, **Coll. Vol. I**, 5 (1943).

analytically pure material, m.p. 287–288° dec. (see Table I).

2-(α-Aminobenzyl)pyridine, dihydrochloride.[9] Phenyl-2-pyridyl ketone, oxime, 120 g., (0.06 mol.) was dissolved in 800 ml. of glacial acetic acid containing 30 ml. of water. The solution was brought to reflux and 210 g. (3 mol.) of zinc dust was added portionwise at a rate sufficient to maintain reflux. The addition was complete in 1 hr. and heating was continued for an additional hour. The reaction mixture was then filtered and the filtrate was made strongly alkaline, causing the product to separate. It was taken up in ether, dried over sodium sulfate and the ether was removed *in vacuo*. The oily residue was distilled to yield 69 g., 62%, of a pale yellow liquid, b.p. 159–165° at 3 mm., n_D^{20} 1.5961. On standing 1 day at room temperature it turned dark brown and emitted a strong odor of ammonia.

Anal. Calcd. for $C_{12}H_{12}N_2$: N, 15.22. Found: N, 14.38.

Because of its instability it was converted to a dihydrochloride salt, which was crystallized from ethanol ether, m.p. 242–244° dec.

Anal. Calcd. for $C_{12}H_{14}Cl_2N_2$: C, 56.10; H, 5.46; Cl, 27.55. Found: C, 56.46; H, 6.56; Cl, 27.44.

1-(α-2-Pyridylbenzyl)-3-methyl-2-thiourea. 2-(α-Aminobenzyl)pyridine, 5 g. (0.027 mol.); methyl ester of isothiocyanic acid, 2 g., (0.027 mol.), and 50 ml. of absolute ethanol were heated under reflux for 2 hr. Cooling and addition of ether caused 6 g., 86%, of product, m.p. 165–166° to precipitate. One recrystallization from methanol did not change the melting point.

Anal. Calcd. for $C_{14}H_{15}N_3S$: C, 65.37; H, 5.87; N, 16.30. Found: C, 65.43; H, 5.66; N, 16.24.

1-(α-2-Pyridylbenzyl)-2,3-dimethyl-2-thiopseudourea, hydriodide. 1-(α-2-Pyridylbenzyl)-3-methyl-2-thiourea was converted into its hydriodide by treatment with hydriodic acid in an acetone solution. The hydriodide, 4.1 g., (0.011 mol.), iodimethane, 2.1 g. (0.015 mol.), and 50 ml. of ethanol were heated under reflux for 3 hr. On cooling and addition of ether, 2.7 g., 61%, of product, m.p. 178–180° dec., precipitated. Two recrystallizations from ethanol raised the melting point to 182–183°.

Anal. Calcd. for $C_{15}H_{18}IN_3S$: N, 10.52; S, 8.02. Found: N, 10.30; S, 7.80.

1-(2,2-Diphenyl-2-hydroxyethyl)-2-thiourea. The fusion was carried out in the usual manner in refluxing xylene.[1] α-(Aminoethyl)benzhydrol, hydrochloride,[10] 7.5 g. (0.03 mol.) and the ammonium salt of thiocyanic acid, 2.4 g. (0.03 mol.), gave 3.2 g., 42% of product, m.p. 185–187° dec. One recrystallization from ethanol did not change the melting point.

Anal. Calcd. for $C_{15}H_{16}N_2OS$: C, 66.14; H, 5.92; N, 10.03; S, 11.77. Found: C, 65.72; H, 5.96; N, 10.63; S, 11.90.

1-(2,2-Diphenyl-2-hydroxyethyl)-2-methyl-2-thiopseudourea, hydriodide. The methylation was carried out in the usual manner with iodomethane.[1] 1-(2,2-Diphenyl-2-hydroxyethyl)-2-thiourea, 2.1 g. (0.008 mol.), gave 2.2 g., 69%, of the product, m.p. 150–151° dec. One recrystallization from isopropanol did not change the melting point.

Anal. Calcd. for $C_{16}H_{19}IN_2OS$: N, 6.77; S, 7.74; I, 30.63. Found: N, 6.68; S, 7.60; I, 30.97.

Benzophenone, 3-methyl-3-thioisosemicarbazone, hydriodide. The methylation procedure was identical to that used for the methylation of thioureas with iodomethane.[1] Benzophenone, thiosemicarbazone,[11] 2.6 g. (0.01 mol.), gave 3.7 g., 93%, of product, m.p. 192–194° dec. One recrystallization from isopropanol did not raise the melting point.

Anal. Calcd. for $C_{15}H_{16}IN_3S$: N, 10.58; S, 8.07; I, 31.94. Found: N, 10.59; S, 8.09; I, 31.96.

Acknowledgments. The authors wish to thank Dr. C. I. Chappel of our Laboratories for the pharmacological data, Mr. W. J. Turnbull for the analyses and Dr. Gilles Papineau-Couture and Mrs. J. Jachner for numerous infrared absorption spectra.

MONTREAL, CANADA

(9) 3-(α-Aminobenzyl)pyridine was prepared by La Forge in a similar manner, *J. Am. Chem. Soc.*, **50**, 2487 (1928).

(10) K. Thomas and F. Bettziecke, *Z. Physiol. Chem.*, **140**, 246 (1924).

(11) P. Chabrier and E. Cattelain, *Bull. soc. chim. France*, 48 (1950).

[CONTRIBUTION FROM THE SILICONES DIVISION, UNION CARBIDE CORPORATION]

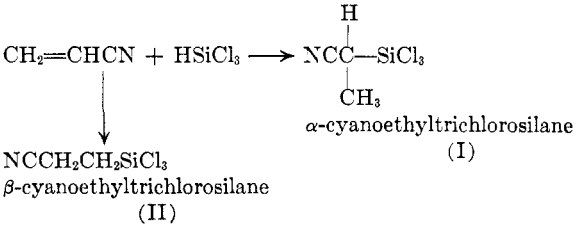
Preparation and Properties of β-Cyanoethyltrichlorosilane[1]

R. A. PIKE, J. E. McMAHON,[2] V. B. JEX,[2a] W. T. BLACK,[2b] AND D. L. BAILEY

Received June 19, 1959

Directive catalysts, organic derivatives of Group V A elements, are described for the addition of trichlorosilane to acrylonitrile, which produce only β-cyanoethyltrichlorosilane. The effect of the cyano group on the rate of hydrolysis of the chlorosilane and heat stability of the corresponding silicone polymer are discussed and the utilization of β-cyanoethyltrichlorosilane as a starting material for the preparation of β-carbethoxyethyl silanes and β-carboxyethyl silicones is illustrated.

Trichlorosilane can add to acrylonitrile with formation of two possible isomeric adducts:



α-cyanoethyltrichlorosilane (I)

β-cyanoethyltrichlorosilane (II)

(1) Presented at the 134th meeting of the American Chemical Society, Division of Organic Chemistry, at Chicago, Ill., Sept. 10, 1958.

(2) (a) Present address: Linde Co., Division of Union Carbide Corp., Tonawanda, N. Y. (b) Patent Department, Union Carbide Corp., 30 East 42nd St., New York, N. Y.