finally distilled *in vacuo:* b.p. (0.5 mm.) 117–119°, yield 39.0 g. (89%). This base was also converted into its *hydrochloride* which was recrystallized from absolute ethanol-ether until its optical rotation was constant: m.p. 224–226°, $[\alpha]^{20}_D$ +7.8° (*c*, 2.536, water).

*Anal.* Calc'd for $C_{11}H_{17}ClN_2O_2$: C, 53.89; H, 7.00; Cl, 14.49. Found: C, 54.09; H, 7.15; Cl, 14.40.

The base was set free from a sample of this hydrochloride: $[\alpha]^{20}_D$ 0.0° (*c*, 6.510, methanol), *picrate* (from methanol), m.p. 131–133°, $[\alpha]^{20}_D$ +43.5° (*c*, 0.987, acetone).

*Anal.* Calc'd for $C_{17}H_{19}N_5O_9$: C, 46.68; H, 4.38; N, 16.01. Found: C, 46.77; H, 4.55; N, 16.17.

*1-(4-Aminophenyl)-2-(N,N-dimethylamino)propane* (XI). The nitro compound X (35.0 g.) was reduced catalytically with Adams' catalyst (1.4 g.) in methanol (1000 ml.): b.p. (0.3 mm.) 104–106° yield 27.0 g. (94%). Recrystallization of this amine was repeated until a constant optical rotation was reached (ether-hexane): m.p. 78–80°, $[\alpha]^{20}_D$ −13.8° (*c*, 1.210, methanol).

*Anal.* Calc'd for $C_{11}H_{18}N_2$: N, 15.72. Found: N, 15.62.

*4,4'-Di-[2-(N,N-dimethylamino)-propyl-1]-thiocarbanilide* (XII). A mixture of 25.0 g. of the amine (XI), carbon disulfide (80 ml.), and benzene (250 ml.) was refluxed for 24 hours and the yellow precipitate was collected on a Büchner funnel (filtrate A). A small portion of this xanthate was further purified for analysis by extracting it with cold acetone: m.p. 103–106°, insoluble in organic solvents, very soluble in water, yellow color reaction with Cu ions, unstable.

*Anal.* Cal'cd for $C_{23}H_{36}S_2N_4$: S, 14.82. Found: S, 14.49.

The suspension of the xanthate in benzene (500 ml.) was refluxed until the generation of $H_2S$ ceased (3 days). Filtrate A was combined with the yellow benzene solution and then was evaporated to dryness under diminished pressure. After several recrystallizations (ether-hexane) the optical rotation was constant: m.p. 116–118°, $[\alpha]^{20}_D$ −16.4° (*c*, 0.750, methanol); yield, 18.0 g. (64%).

*Anal.* Calc'd for $C_{23}H_{34}N_4S$: N, 14.06; S, 8.02. Found: N, 13.93; S, 8.24.

*Carbodiimide* XIII. A mixture of XII (8.0 g.), yellow mercuric oxide (50 g.), and benzene was vigorously stirred and the azeotrope, benzene-water, was distilled off; fresh solvent was added from time to time. After 3 hours the mixture of mercuric sulfide and oxide was filtered and the filtrate was evaporated under reduced pressure. A considerable amount of urea (XIV) was present and was eliminated by repeated addition of hexane to an etheral solution of the mixture. The mother liquor was distilled in small portions, yielding 2.3 g. (31%) of a colorless oil: $[\alpha]^{20}_D$ −6.2° (*c*, 1.499, methanol).

*Anal.* Calc'd for $C_{23}H_{32}N_4$: C, 75.78; H, 8.85; N, 15.37. Found: C, 75.65; H, 8.80; N, 15.13.

*Dipicrate* (from methanol-acetone): m.p. 128–130°.

*Anal.* Calc'd for $C_{35}H_{38}N_{10}O_{14}$: N, 17.03. Found: N, 16.85.

The urea (XIV) was recrystallized from benzene-hexane until the optical rotation was constant: m.p. 181–183° (dimorphous, spontaneous transformation from plates to needles at 150–151°), $[\alpha]^{20}_D$ −6.7° (*c*, 1.128, methanol).

*Anal.* Calc'd for $C_{23}H_{34}N_4O$: C, 72.38; H, 8.96; N, 14.65. Found: C, 72.61; H, 8.80; N, 14.46.

A mixture of 191 mg. of XIII, 500 mg. of anhydrous oxalic acid, and 5 ml. of absolute dioxane was slowly warmed up to 80°. Evolution of gas bubbles, which apparently were a mixture of carbon monoxide and dioxide, took place. Carbon dioxide was shown to be present by precipitation of $BaCO_3$ from a solution of barium hydroxide. Addition of water to the reacted mixture gave a precipitate shown to be the urea XIV.

To a solution of 382 mg. of XIII in 5 ml. of acetone a solution of 194 mg. of glacial acetic acid in 5 ml. of ether was added. The precipitate formed (acetate of XIII) was redissolved by adding more acetone. After standing at room temperature for 3 days, the organic solvent was evaporated *in vacuo* at 30°, the residue was taken up in dilute sodium bicarbonate solution and benzene. In the benzene layer only the urea XIV was found. Similar results were obtained with caprylic, lipoic, and cinnamic acids in a variety of solvents.

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## Synthesis of Dicyclohexylammonium-1-1'-$C^{14}$ Nitrite

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One type of commercial vapor phase corrosion inhibitor is known to be essentially dicyclohexylammonium nitrite. This substance was selected to be synthesized with a radioactive $C^{14}$ atom, in order that the radioactive tracer technique might be applied to obtain certain basic information concerning the application of vapor phase inhibitors to military packaging.

The high pressure catalytic hydrogenation of aniline, as described below, was used to prepare the radioactive corrosion inhibitor. This process was used, since it resulted in the highest percent yield of finished product, required the minimum of personal handling and exposure to radioactivity, and the initial material was readily available as aniline-1-$C^{14}$.

### SYNTHESIS OF DICYCLOHEXYLAMINE-1-1'-$C^{14}$ (Reference 1)

The hydrogenation of aniline-1-$C^{14}$ was performed in a high-pressure autoclave. The catalyst used in this synthesis was prepared by taking 100 g. of nitric acid-washed kieselguhr and mixing it with 100 g. of nickel nitrate $[Ni(NO_3)_2 \cdot 6H_2O]$ in 150 ml. of water. This mixture then was ground in a ball-mill until a creamy consistency was obtained. The paste was carefully heated to 70–80° with stirring, and a solution of 60 g. of ammonium bicarbonate ($NH_4HCO_3 \cdot 5H_2O$) in 400 ml. of water was added gradually with continued stirring. The resulting mixture was filtered and washed twice with 75-ml. portions of distilled water. The moist cake was broken up and dried at 100–110°. A 3-g. portion of this dried, impregnated kieselguhr was reduced in a stream of hydrogen at 425–475° for about 70 minutes. The active catalyst thus prepared was immediately used in the hydrogenation.

Freshly distilled aniline (4 g.) (b.p. 184–185°), 51.0 mg. of aniline-1-$C^{14}$ hydrochloride (200 $\mu$c of activity), 50 ml. of dioxane, and the active catalyst were placed into the bomb and the whole was assembled. Hydrogen was added to a pressure of 2000 p.s.i. The temperature was raised to 250°, which caused an increase in pressure to 2300 p.s.i. The pressure was maintained at 2300 p.s.i. by the addition of hydrogen periodically, and the whole was heated at 250° for three hours, with stirring. The bomb then was cooled, disassembled, and the reaction mixture was removed with the aid of diethyl ether. The reaction mixture was filtered to re-

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(1) U. S. Patent 2,092,525, September 7, 1937, H. Adkins and H. Cramer.

move the catalyst and the filtrate was poured into 50 ml. of a 10% HCl solution, with stirring. The precipitated hydrochloride of dicyclohexylamine was filtered onto a Büchner funnel and washed several times with 25-ml. portions of distilled water. The material from the Büchner funnel was removed and placed into 100 ml. of a 15% solution of NaOH, with stirring. This mixture was cooled and extracted with four 50-ml. portions of ethyl ether. After flash-distilling the ethyl ether, the fraction boiling from 256–257° at atmospheric pressure was collected. Infrared spectrograms of the radioactive material compared to that of a freshly distilled sample of dicyclohexylamine (b.p. 256–257°) at atmospheric pressure) established the identity of the synthesized material and also that it was of a high degree of purity.

### SYNTHESIS OF DICYCLOHEXYLAMMONIUM-1-1′-$C^{14}$ NITRITE (Reference 2)

The dicyclohexylamine-1-1′-$C^{14}$ (1.00 g.) was added to 8 ml. of distilled water containing 0.2 ml. of 85% phosphoric acid, and 0.40 g. of sodium nitrite was added at 0°, with stirring. The dicyclohexylammonium-1-1′-$C^{14}$ nitrite precipitated and was filtered onto a Büchner funnel, washed with a 2-ml. portion of cold water, and dried. The material was placed into twice its weight of cold water, and the mixture was stirred. The purified dicyclohexylammonium-1-1′-$C^{14}$ nitrite then was filtered onto a Büchner funnel, washed with a 2-ml. portion of cold water, and dried.

The synthesized material had an activity of 62 microcuries. Thus the radiochemical yield of dicyclohexylammonium-1-1′-$C^{14}$ nitrite was 31%. The material had a melting point of 153.0–154.5° with decomposition. (Literature[3] m.p. 154.5°.)

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The opinions or assertions contained herein are the private ones of the writer, and are not to be construed as official or reflecting the views of the Navy Department, or the Naval service at large.

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(2) U. S. Patent 2,544,245 assigned to Shell Development Company (Preparation of dicyclohexylammonium nitrite).

(3) *Dicyclohexylammonium Nitrite*, A. Wachter, T. Skei, and N. Stillman, Shell Development Company, presented at the symposium on Industrial Use of Corrosion Inhibitors, March 1951, Conference, New York National Association of Corrosion Engineers.

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## 2-N-Alkylaminopyrimidine

I. C. KOGON[1]

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It has been previously reported that 2-aminopyrimidine methiodide warmed with an ethanolic or aqueous solution of sodium hydroxide yields 2-N-methylaminopyrimidine.[2,3] Treatment of the methiodide with a cold aqueous solution of sodium hydroxide has been reported to give 1-methyl-2-iminopyrimidine.[3] Prior to this recent disclosure, it was desirable to determine the alkylation products when 2-aminopyrimidine was treated with ethyl or *n*-butyl iodide. Our results indicate that the major product in both cases is the 2-N-alkylaminopyrimidine and that the 1-N-alkyl products, if formed, are very unstable in dilute sodium hydroxide in the cold. These compounds were synthesized by (A) reaction of 2-chloropyrimidine with ethyl or *n*-butylamine for comparison purposes and (B) reaction of 2-aminopyrimidine with ethyl or *n*-butyl iodide followed by neutralization with cold aqueous sodium hydroxide.

### EXPERIMENTAL[4]

*2-Chloropyrimidine.* The compound was prepared from 2-aminopyrimidine[5] as described by Overberger, Kogon, and Minin,[6] m.p. 64–65°.

*Preparation of 2-N-ethylaminopyrimidine. Method A. From 2-chloropyrimidine and ethylamine.* A solution of 11.4 g. (0.1 mole) of 2-chloropyrimidine, 9.5 g. (0.21 mole) of ethylamine, and 50 ml. of absolute alcohol was refluxed for 4 hours. The solution was cooled in an ice-bath for one hour. The ethylamine hydrochloride that precipitated was filtered and washed with ether, 7.33 g. (95.5%), m.p. 107–108°. The filtrate was evaporated on a steam-bath and the residue was recrystallized from petroleum ether (b.p. 30–60°), yield 11.0 g. (89.6%), m.p. 50–51°.

*Anal.* Calc'd for $C_6H_9N_3$: C, 58.5; H, 7.3; N, 34.1. Found: C, 58.7; H, 7.6; N, 34.5.

The *picrate* was prepared by adding an excess of a saturated solution of ethereal picric acid to an ethereal solution of the free base. A yellow crystalline solid precipitated which was recrystallized from ethyl alcohol, m.p. 160–161°.

*Anal.* Calc'd for $C_{12}H_{12}N_6O_6$: N, 23.8. Found: N, 23.6.

*Method B. From 2-aminopyrimidine and ethyl iodide.* A mixture of 9.4 g. (0.1 mole) of 2-aminopyrimidine, 31.2 g. (0.2 mole) of ethyl iodide, and 75 ml. of absolute alcohol was refluxed for 24 hours. The resulting solution was concentrated to half the volume and was chilled in an ice-bath for one hour. The iodide (I) that precipitated was filtered and washed thoroughly with ether, 21.5 g. (86.0%). Compound I was recrystallized from ethyl alcohol yielding 21.0 g. (84.0%) of a white crystalline solid, m.p. 154–155°.

*Anal.* Calc'd for $C_6H_{10}IN_3$: C, 28.7; H, 4.0; N, 16.8. Found: C, 28.4; H, 3.9; N, 16.8.

The free base was obtained by the addition of sufficient cold (10°) aqueous sodium hydroxide solution to neutralize a cold (10°) aqueous solution of compound I. The aqueous solution was extracted with three 25-ml. portions of ether, and the ether then was dried over sodium sulfate for 24 hours. After the removal of the drying agent, the solvent was removed on a steam-bath and the residue was recrystallized from petroleum ether (b.p. 30–60°). The product, 8.5 g.

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(1) Present address: Jackson Laboratory, Organic Chemicals Department, E. I. du Pont de Nemours & Co., Deepwater, New Jersey.

(2) Overberger and Kogon, *J. Am. Chem. Soc.*, **76**, 1065 (1954).

(3) Brown, Hoerger, and Mason, *J. Chem. Soc.*, 4035 (1955).

(4) All melting points are uncorrected.

(5) A sample of 2-aminopyrimidine was generously contributed by the American Cyanamid Company.

(6) Overberger, Kogon, and Minin, *Org. Syntheses*, **35**, 35 (1955).