at 135–140° for two hours produced 17.3 g. (80.8%) of (VI), a yellow liquid, at 183–185° (8 mm.).

(2) Twenty-nine grams of N,N′-dibutyl-ethylenediamine dithiocarbamate heated at 130–135° for about two hours gave 21.5 g. (85%) of (VI) at 183–184° (8 mm.).

1,3-Dibutyl-trimethylenethiourea (VII).[11]—(1) Starting with 21.4 g. (0.1 mole) of N-formyl-(III) and 4.0 g. of sulfur and heating at 145–150° for two hours and at 175° for one-half hour, 9.2 g. of unconverted N-formyl-(III) was recovered, and 5.8 g. (25%) of (VII) was obtained as a yellow liquid, b. p. 177–178° (3 mm.).

(2) A stirred solution of 37.2 g. (0.2 mole) of (III) in 50 cc. of methanol was treated with a solution of 15.2 g. (0.2 mole) of carbon disulfide in 40 cc. of methanol in the course of fifteen minutes. The solvent was evaporated from the resulting solution and the remaining thick liquid, the dithiocarbamate, was heated at 150–155° until the evolution of gas ceased (about two hours). The reaction mixture then was distilled, yielding 12.4 g. of recovered (III), b. p. 107° (7 mm.), and 14.6 g. (31%) of (VII), b. p. 177–178° (3 mm.).

1,3-Diphenyl-ethylenethiourea.—This product was prepared in 71% yield by heating N-formyl-(V) with sulfur, but in this case little reaction was observed below 195°. (V) did not form a dithiocarbamate on treatment with carbon disulfide and water under reflux at atmospheric pressure for twenty hours.

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[11] N-Monosubstituted-trimethylenethioureas have been made by pyrolysis of the dithiocarbamates of the corresponding N-substituted-trimethylenediamines; Goldenring, *Ber.*, **23**, 1171 (1890); Fränkel, *ibid.*, **30**, 2501 (1897).

COMMUNICATIONS TO THE EDITOR

CRYSTALLINE VITAMIN A METHYL ETHER

Sir:

In recent years much interest has been shown in the synthesis of vitamin A ethers. However, since no data are available concerning the biological activity of these ethers, we have undertaken the preparation of vitamin A methyl ether from the natural vitamin.

The methyl ether was prepared by the action of dimethyl sulfate on the lithium derivative of the vitamin, which was formed by the reaction of *n*-butyl lithium[1] and crystalline vitamin A alcohol.[2] It was purified by chromatography on activated alumina[3] and was obtained as an orange oil, which crystallized from methanol after several months at −70°, m. p. 31–33°. After three recrystallizations from methanol and two from a 65–70° hydrocarbon fraction [Purified Skelly Solve B],[4] vitamin A methyl ether was obtained as light yellow crystals melting at 33–34°. *Anal.* Calcd. for $C_{21}H_{32}O$: C, 83.95; H, 10.74; OCH_3, 10.34. Found: C, 83.76; H, 11.07; OCH_3, 9.94.

The spectrophotometric curve for crystalline vitamin A methyl ether is identical in all respects with that of vitamin A alcohol, both having absorption maxima at 326 mμ on the Beckman spectrophotometer. The extinction coefficient ($E^{1\%}_{1\,\text{cm.}}$) in isopropanol at 326 mμ is 1660. This corresponds to an equivalent extinction coefficient of 1742 for vitamin A alcohol.

Vitamin A methyl ether possesses a biological potency greater than 3,000,000 U. S. P. XII units per gram and is of the same order of activity as crystalline vitamin A alcohol.

The experimental details and complete biological data will appear in a forthcoming paper.

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[1] Gilman, Langham and Moore, THIS JOURNAL, **62**, 2327 (1940).

[2] Distillation Products, Inc., Rochester, N. Y.

[3] Aluminum Ore Co., East St. Louis, Illinois.

[4] Purified by treatment with concentrated sulfuric acid and distillation.

AMINOMETHYLATION OF THIOPHENE

Sir:

During the course of formylation studies with thiophene it was noted that in the presence of ammonium chloride and formaldehyde thiophene appeared to undergo a reaction to give water-soluble amine hydrochlorides. From the reaction mixture was isolated 2-thenylamine (2-aminomethylthiophene) (I), b. 58° (5 mm.), $n^{20}\text{D}$ 1.5589; secondary di-(2-thenyl)-amine, b. p. 150–152° (10 mm.), $n^{22}\text{D}$ 1.5914; and a third amine (III). Amine III is polymeric in nature and is believed to contain methylol groups. The hydroxyl number of III produced by the reaction of one mole of thiophene with four moles of 37% formaldehyde and one mole of ammonium chloride at the reflux was 475, indicating that methylol groups may be substituted around the thiophene in all remaining positions. Other analysis obtained on the product were as follows: 20.6% sulfur and 7.3% nitrogen. With the use of aqueous 37% formaldehyde in excess III is obtained exclusively and molecular weights of 600–750 are the usual order. The use of trioxymethylene with a few per cent. by weight acetic acid (to promote depolymerization at lower temperatures) gave