

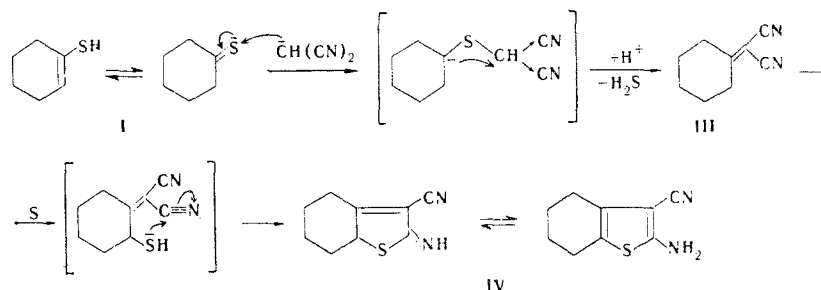
# LETTERS TO THE EDITOR

## NEW SYNTHESIS OF 2-AMINO-3-CYANO-4,5-TETRAMETHYLENETHIOPHENE

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We have shown that 2-amino-3-cyano-4,5-tetramethylenethiophene (IV) is formed in the reaction of cyclohexanethione (I) with malononitrile (II) and sulfur in the presence of triethylamine. The reaction proceeds through a step involving the formation of cyclohexylidenemalononitrile (III) and occurs via attack by the malononitrile anion on the sulfur atom of the thiocarbonyl group of I.  $\Delta^2, \alpha$ -Bornanylmalononitrile (V) was similarly obtained from thiocamphor and II; the latter reaction cannot be realized with camphor because of the steric hindrance of the carbonyl carbon atom.



### EXPERIMENTAL

**2-Amino-3-cyano-4,5-tetramethylenethiophene (IV).** A mixture of 2.3 g (0.02 mole) of cyclohexanethione, 0.64 g of powdered sulfur, 1.32 g (0.02 mole) of malononitrile, and 1 ml of triethylamine was stirred in 15 ml of dimethylformamide for 2 weeks with protection from light and access to oxygen. The precipitate that formed on dilution of the reaction mixture with water was recrystallized from alcohol to give 2.1 g (60%) of IV with mp 145-146° [1]. IR spectrum (in  $\text{CHCl}_3$ ): 3493, 3397, 1618 ( $\text{NH}_2$ ), and 2220 ( $\text{CN}$ )  $\text{cm}^{-1}$ . PMR spectrum (in  $\text{CDCl}_3$  with tetramethylsilane as the internal standard): 4.85 ( $\text{NH}_2$ ), 1.8 (multiplet of the 5,6- $\text{CH}_2$  groups), 2.5 (multiplet of the 4,7- $\text{CH}_2$  groups) ppm. Molecular weight 178 (by mass spectrometry).

**Cyclohexylidenemalononitrile (III).** A mixture of 2.3 g (0.02 mole) of cyclohexanethione, 1.32 g (0.02 mole) of malononitrile, 0.5 ml of triethylamine, and 15 ml of alcohol was allowed to stand for 3 days, after which it was worked up to give 1.8 g (62%) of III with bp 90-95° (1 mm) and  $n_D^{25}$  1.5100 [2]. IR spectrum (liquid film): 2220 ( $\text{CN}$ ), 1602 ( $\text{C}=\text{C}$ )  $\text{cm}^{-1}$ .

**$\Delta^2, \alpha$ -Bornanylmalononitrile (V).** A 0.4-g sample of powdered potassium hydroxide was added to a solution of 1.68 g (0.01 mole) of thiocamphor and 0.66 g (0.01 mole) of malononitrile in 10 ml of alcohol, and the mixture was stirred for 30 min. The resulting precipitate was recrystallized successively from alcohol and light petroleum ether to give 1 g (50%) of colorless crystals with mp 116-117°. IR spectrum (in  $\text{CHCl}_3$ ): 2270 ( $\text{CN}$ ) and 1608 ( $\text{C}=\text{C}$ )  $\text{cm}^{-1}$ . Molecular weight 200 (mass spectrometrically).

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