[19] *F. W. Semmler & B. Zaar*, Ber. deutsch. chem. Ges. *43*, 1890 (1910).
[20] *F. W. Semmler & K. Bode*, Ber. deutsch. chem. Ges. *40*, 1124 (1907).
[21] *T. Reichstein*, Helv. *13*, 349 (1930).
[22] *M. Stoll, M. Winter, F. Gautschi, I. Flament & B. Willhalm*, Helv. *50*, 628 (1967).
[23] *A. Girard & G. Sandulesco*, Helv. *19*, 1095 (1936); *Y. R. Naves & A. V. Grampoloff*, ibid. *25*, 1500 (1942).
[24] *F. W. Semmler*, Ber. deutsch. chem. Ges. *43*, 1722 (1910).
[25] *G. Büchi & H. Wüest*, J. org. Chemistry *34*, 1122 (1969).
[26] *L. Horner, H. Hoffmann & H. G. Wippel*, Chem. Ber. *91*, 61 (1958); *L. Horner, H. Hoffmann, W. Klink, H. Ertel & V. G. Toscano*, ibid. *95*, 581 (1962).
[27] *A. F. Thomas*, Chem. Commun. *1968*, 1657; *A. F. Thomas & M. Ozainne*, J. chem. Soc. [C] *1970*, 220.
[28] *R. J. Lewis, D. H. Gustafson & W. F. Erman*, Tetrahedron Letters *1967*, 401.
[29] *A. F. Thomas & M. Ozainne*, Chem. Commun. *1969*, 46.
[30] *P. Chapoteaut*, Bull. Soc. chim. France *37* [2], 303 (1882).
[31] *F. Bohlmann & C. Zdero*, Tetrahedron Letters *1968*, 1533.
[32] *H. C. Kretschmar & W. F. Erman*, Tetrahedron Letters *1970*, 41.
[33] See ref. [1], p. 572.
[34] See ref. [9], p. 120.
[35] *S. Beckmann & A. Dürkop*, Liebigs Ann. Chem. *594*, 205 (1955).
[36] *R. H. Wiley, E. Imoto, R. P. Houghton & P. Veeravagu*, J. Amer. chem. Soc. *82*, 1413 (1960).
[37] *O. Diels & K. Alder*, Liebigs Ann. Chem. *486*, 202 (1931); *K. Alder & H.-J. Ache*, Chem. Ber. *95*, 503 (1962).
[38] *E. Klein & W. Rojahn*, Chem. Ber. *98*, 3045 (1965).
[39] *A. N. Pudovik & N. M. Lebedeva*, Dokl. Akad. Nauk SSSR *101*, 889 (1955); Chem. Abstr. *50*, 3219e (1956).
[40] *W. S. Wadsworth*, jr., & *W. D. Emmons*, J. Amer. chem. Soc. *83*, 1733 (1961); *G. Sturtz*, Bull. Soc. chim. France *1967*, 2477.
[41] *F. W. Semmler*, Ber. deutsch. chem. Ges. *43*, 1893 (1910).

---

77. Synthesis and Some Reactions of 2,4,6-Cycloheptatrienethione[1])

by **Harry A. Dugger**[2]) and **André S. Dreiding**

Organisch-Chemisches Institut der Universität Zürich, Rämistrasse 76, 8001 Zürich

(12. XII. 75)

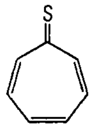
Summary. The synthesis of 2,4,6-cycloheptatrienethione (**1**) was accomplished by reaction of tropone and phosphorus pentasulfide. Although **1** proved to be extremely unstable in concentrated solution, its UV. spectrum was measured, the ε-values being determined indirectly by hydrolysis to tropone. The proof of structure rests on analytical data, conversion to tropone oxime on reaction with hydroxylamine and reaction with the sodium salt of malonitrile to give 2-amino-3-cyano-3a*H*-cyclohepta[*b*]thiophene (**4**) which rearranged on chromatography to give what is probably the corresponding 8*H*-compound (**5**). On dissolving **1** in 95% sulfuric acid, a large hypsochromic shift in the UV. spectrum was observed, which may be due to the mercaptotropylium ion.

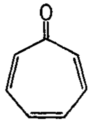
---

[1]) These results were presented at the 155th American Chemical Society Meeting.

[2]) National Institutes of Health Postdoctoral Fellow 1962–1964. Present address is Drug Metabolism Section, Sandoz Pharmaceuticals, Sandoz, Inc., East Hanover, New Jersey 07936 USA.

Recent publications on the cycloaddition of cycloheptatrienethione (**1**) (tropothione) with dienophiles [1], its reaction with dichloroketene and with tetracyanoethylene [2], its reaction with diazomethane [3] and a study of the electronic structure of **1** [4] have prompted this report on work carried out some time ago on the synthesis and some reactions of **1**.


1


2

Prior to the start of this study, only one other attempt to synthesize **1** had been reported wherein *Nozoe et al.* [5] on heating tropone (**2**) with phosphorus pentasulfide, obtained a brown oil which solidified on standing. Subsequently, *Kitahara et al.* [6] reported the synthesis of **1** by reaction of chlorotropylium chloride with hydrogen sulfide. The product was a red oil with UV. absorption maxima at $\lambda = 220$, 252 and 380 nm (no solvent mentioned). They also noted that **1** could be prepared by reaction of **2** with hydrogen sulfide in the presence of hydrochloric acid. The only other seven-membered ring thiones that were known prior to this study were 2-aminotropothione [7] and 2-hydroxytropothione [8] which as analogues of tropolone, are considerably more stable than **1**.

We first attempted[3] the synthesis of **1** by the disproportionation of ditropyl sulfide catalysed by tropylium ion in a reaction analogous to that reported to give tropone and cycloheptatriene from ditropyl ether [9]. The failure of this reaction prompted the synthesis of **1** by an alternative pathway and the study of its properties to see if product instability could account for the failure to isolate **1**. Several general methods reported for the preparation of aromatic and aliphatic thiones were tried but the one method which proved successful was a modification of the reaction of **2** with phosphorus pentasulfide reported by *Nozoe et al.* [5]. Although most ketones require high temperatures and solvents such as pyridine for conversion to the thione, an immediate coloration was observed on mixing tropone and phosphorus pentasulfide at room temperature using toluene as a moderating solvent. This high reactivity of tropone toward phosphorus pentasulfide is undoubtedly due to its dipolar character. After standing several hours at room temperature, the color darkened and measurement of the UV. spectrum of the liquid phase showed that the maximum at 310 nm due to the tropone had been replaced by a new maximum at 378 nm. When the intensity at 378 nm reached a maximum, the reaction was halted. Washing the toluene solution with water followed by chromatography over silica to remove unreacted P_2S_5 and any polymeric material gave a toluene solution which by TLC. analysis contained only one substance, **1**. (Alternatively, carbon tetrachloride could be used to elute the product). This substance proved to be extremely reactive, giving a reddish brown solid on concentration of its solutions. The products of the decomposition are unknown; they are at least partly insoluble in common solvents and those that do dissolve do not show a characteristic UV. spectrum. Attempts to isolate **1**

---

[3] Work carried out by *W. Renold.*

either by distillation at high vacuum in the cold or by crystallization of tetrafluoroborate or perchlorate salts failed. However, elemental analysis of the brown solid resulting on removal of the solvent showed that C, H and S were present but no phosphorus. A UV. spectrum of the residue indicated that it contained no more than 12% of **1**. This analysis, coupled with the conversion to tropone oxime (with evolution of hydrogen sulfide) by treatment with hydroxylamine in pyridine/ethanol, supported the assignment of structure **1** to the substance in solution. The clean reaction of **1** to tropone oxime contrasts with that of tropone which on reaction with hydroxylamine gives, in addition to the oxime, 2-amino-tropone [5].

Once it became apparent that the isolation of **1** was not probable, an attempt was made to obtain the pertinent UV. spectra and the ^{1}H-NMR. spectrum. The UV. spectrum of **1** was measured in a number of solvents; the results are in the Table. There is a small bathochromic shift on increasing the polarity of the solvent which is characteristic of π–π transitions. These results are in good agreement with the UV. spectrum first reported by *Kitahara* [6] (noted above) but does not agree with the spectrum published recently by *Machiguihi* [4]. The latter spectrum in methanol contains an additional maximum at $\lambda = 316$ nm which may in fact be due to the presence of some tropone in the sample. The absorption maximum for tropone in ethanol is 310 nm. The large hypsochromic shift of 20 nm on changing the solvent to 95% sulfuric acid could be explained by postulating the appearance of a mercaptotropylium ion. This assignment appears reasonable from a comparison of the long wavelength UV. bands of the four ions summarized in *Scheme 1*. The overall shift due to substituting sulfur for oxygen or ethyl for hydrogen in every case was of the same order of magnitude and in the same direction. The differences may be due in part to a difference in the solvents used.

Table. *UV. Spectrum of 2,4,6-Cycloheptatrienethione* (**1**)

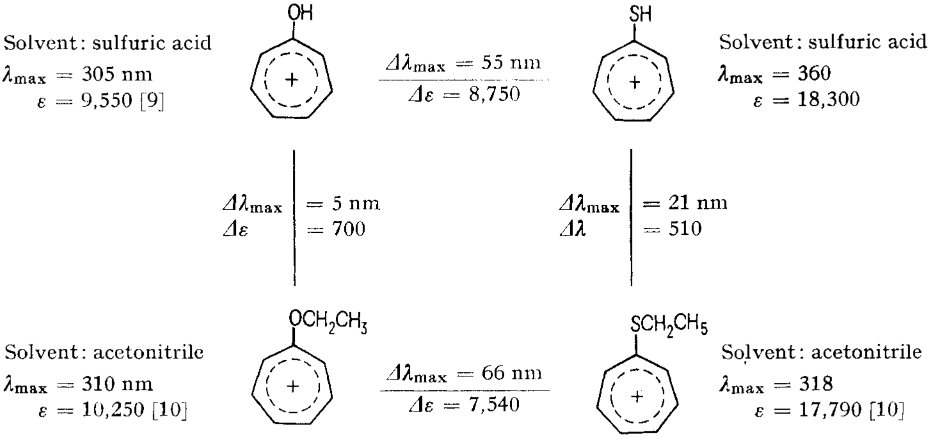
Solvent[a]	First Maximum λ_{max} (nm)	ε[b]	Second Maximum λ_{max} (nm)	ε
Ethanol	380	16,900	sh 250–260	
Toluene	378	15,400	–	
Carbon Tetrachloride	376	16,100	sh 258	
95% Sulfuric Acid	360	18,300	256	17,900

[a] Solutions in various solvents were prepared by diluting 0.8 ml of a CCl_4 stock solution with the indicated solvents.

[b] Values are determined by conversion of tropothione to tropone and comparison of the values before and after: 100% conversion is assumed.

The ε-values for the UV. maxima of tropothione (**1**) were determined indirectly by hydrolysis to tropone (**2**), a common reaction of thiones which can be catalysed by base or acid [11]. In this case both acid and base catalysis were tried but the data from acid catalysis are considered more reliable as tropone is less stable in base than in acid. The ε-values calculated assuming 100% conversion to tropone are given in the Table. If the conversion of **1** into **2** were not 100%, the ε-values given would be too

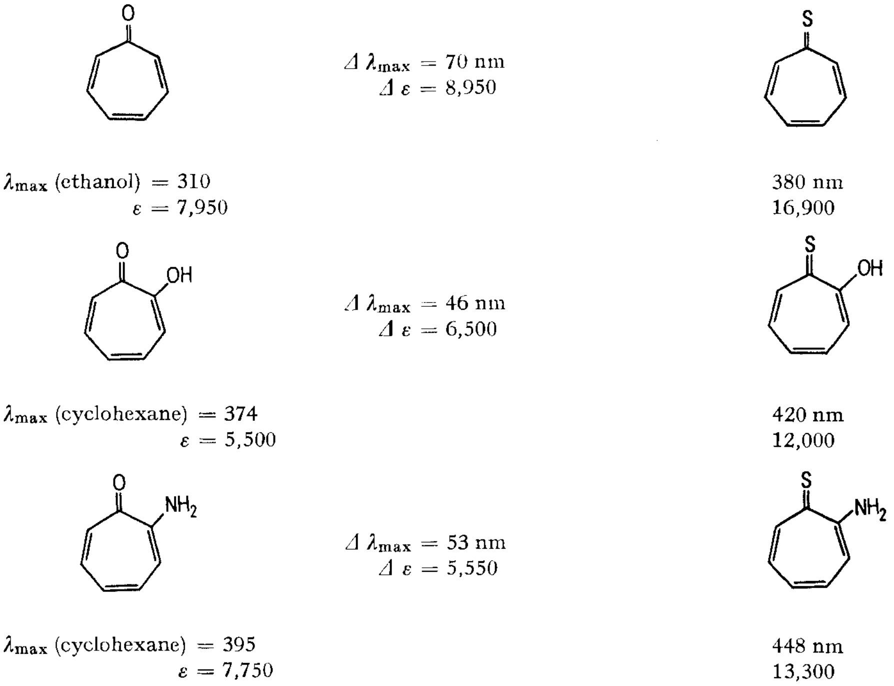
Scheme 1. *Comparison of the longest wavelength maximum of hydroxy, mercapto, ethoxy and ethylmercapto tropylium ions*



large but the yields of **1** calculated using these ε-values, which in these preparations was 26–45%, would be larger.

The shift in the UV. maximum and the increase in ε-value on going from tropone to tropothione, $\Delta\lambda_{max} = 70$ nm, $\Delta\varepsilon = 8{,}950$ (ethanol) (see *Scheme 2*), is of the same

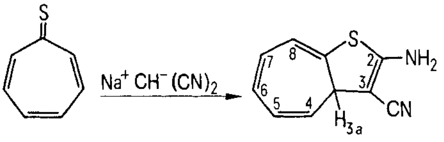
Scheme 2. *UV. absorptions*



order as going from 2-aminotropone to 2-aminotropothione, $\Delta\lambda_{max} = 53$ nm, $\Delta\varepsilon = 5{,}500$ (cyclohexane) [7], or in going from tropolone to 2-hydroxytropothione, $\Delta\lambda_{max} = 46$ nm, $\Delta\varepsilon = 6{,}600$ (cyclohexane) [8]. One would not expect the correlation to be exact since there is undoubtedly a change in the internal hydrogen bonding in the above structures on replacing an oxygen with sulfur. Again in all three cases the shift is in the same direction and of approximately the same order of magnitude.

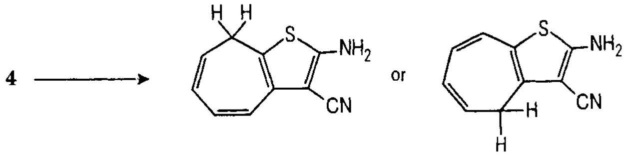
Attempts to measure the ^{1}H-NMR. spectrum of distilled tropothione failed due to decomposition. However, dilute solutions gave a satisfactory spectrum at 100 MHz; the more concentrated solutions required for a 60 MHz spectrum showed several additional multiplets probably due to polymers. The low field doublet at 7.71 ppm ($J = 10.7$) was assigned to those protons on carbon atoms adjacent to the thione group. The other two multiplets at 6.4–6.6 and at 6.6–6.8 ppm were assigned to the remaining four ring protons. Although these values must be regarded with caution since the substance was never isolated, they support the conclusion of *Machiguchi et al.* [4] based on a molecular orbital calculation that tropothione shows polyolefinic character and that dipolar contributions to the overall resonance structure similar to those proposed for tropone [12] are small. Under similar conditions tropone gives a single broad signal in the ^{1}H-NMR. spectrum at 7.20 ppm.

An experiment was tried to synthesize a known derivative, 8,8-dicyanoheptafulvene, and at the same time to demonstrate again the elimination of sulfide which was already observed in the reactions of **1** with acid or base to give **2** and with hydroxylamine to give tropone oxime. This reaction is conceptually similar to the reaction of ethoxytropylium fluoroborate with the sodium salt of malonitrile to give dicyanoheptafulvene [13]. In fact, the initial attack of the malonitrile anion on **1** was at the 2-position followed by cyclization to give 2-amino-3-cyano-3a*H*-cyclohepta[*b*]-thiophene in 73% yield based on the calculated amount of **1** present. The structure of **4** is supported by elemental analysis for $C_{10}H_8N_2S$, molecular weight, its IR.



1 **4**

($\lambda = 4.60\,\mu$, CN; $\lambda = 2.96$, 3.04, 3.13 μ, NH_2) and its ^{1}H-NMR. spectrum (a 1 proton double triplet at $\delta = 3.45$ with $J = 4.5$ and 2.2 for H–C(3a), a 1 proton doublet of doublet at $\delta = 5.07$ with $J = 4.5$ and 9.0 for H–C(4), two 2-proton multiplets in the 5.9–6.6 region for H–C(5) to H–C(8), and a broad signal near $\delta = 6.5$, which is removed on adding acid, for NH_2. **4** rearranged by slow chromatography on silica gel



5 **6**

to a single compound which is **5** or **6**. The 8*H*-isomer (**5**) was considered the more probable structure since it is the product of a single 1,5-hydrogen shift from **4** and since no driving force for a second 1,5-shift to give **6** is evident, the aromatization of the thiophene ring already having occurred in the first shift to give **5**.

The assignment of structure **5** or **6** was based on analysis for $C_{10}H_8N_2S$, molecular weight and the spectral data as follows: Characteristic IR. bands ($\lambda = 4.55\,\mu$, CN; 2.90, 2.98 and 3.15 μ NH_2) are in good agreement with those reported [14] for 2-amino-3-cyano-4-phenyl-thiophene. The UV. spectrum exhibits a single broad absorption at 338 nm, $\varepsilon = 10{,}400$, which represents a bathochromic shift of about 70 nm when compared with strongest bands of **4**. The ^{1}H-NMR. spectrum lends itself to a first order analysis (interpreted on structure **5**): Aside from the $\delta = 6.4$–6.8 broad signal for NH_2 and the $\delta = 2.95$ doublet ($J = 6.8$) for the H–C(8)'s, four signals in the vinyl-proton region are seen; $\delta = 6.66$ as $d \times d$ ($J = 11.3$ and ~ 1) is attributed to H–C(4), $\delta = 6.30$ as $d \times d \times d$ ($J = 11.3$, 5.8 and ~ 1) to H–C(5), $\delta = 6.03$ as $d \times d$ ($J = 10.0$ and 5.8) to H–C(6) and $\delta = 5.41$ as $d \times t \times t$ ($J = 10.0$, 6.8 and ~ 1) to H–C(7).

The reaction of tropone with malonitrile in the presence of base has been reported to give 2-amino-1,3-dicyanoazulene, obviously a very complex reaction involving cyclization and dehydrogenation [15]. The reaction pathway is not clear, but it is possible that the oxaazulene corresponding to **4** is an intermediate which after oxidation reacts with additional malonitrile to give the observed product, inasmuch that at least one oxa-azulene, 2-amino-3-aminocarbonyl-1-oxa-azulene has been found to undergo such a reaction with excess cyanoacetamide to give 2-amino-1,3-bis(aminocarbonyl)-azulene [16].

Experimental Part

1. General. – Melting points were taken using a heated oil apparatus and were not corrected. The IR. spectra were measured on a *Perkin-Elmer* 21 spectrometer. They are recorded as follows: IR. (support): frequency in μ, intensity as w = weak, m = medium and s = strong. The electronic spectra were measured on a *Beckman* D.U. spectrometer. They are recorded as follows: UV. (solvent): maxima and inflections in nm (extinction ε). The proton resonance spectra were measured on a *Varian* A-60 or HA-100 instrument. They are recorded as follows: ^{1}H-NMR. (frequency and solvent): chemical shifts in ppm on the δ-scale (TMS internal = 0)/multiplicity with s = singlet, d = doublet, t = triplet and m = multiplet, splitting J in Hz, relative integration (interpretation). *Abreviations*: RV. = Rotatory evaporator.

2. Preparation of Tropothione. 0.588 g (5.55 mmol) of tropone (**2**) was added in one portion to a rapidly stirring suspension of 2.471 g (11.1 mmol) of phosphorus pentasulfide in 400 ml of dry toluene under a nitrogen atmosphere. After 6 h, water was added and the toluene layer was separated and dried over anhydrous sodium sulfate. TLC. showed that only one substance (**1**), which was capable of migration, was present. This red toluene solution was concentrated to about 20 ml in a RV. at reduced pressure and at a temperature never surpassing 40°. The tropothione contained in the solution was freed from impurities present and from the toluene by chromatography on a column of 30 g silica gel, using carbon tetrachloride as the eluting solvent. The spectroscopically determined yield[4]) of tropothione (**1**) in solution is 226 mg or 33%.

A solution containing 27.8 mg of tropothione, was concentrated to dryness in RV. and then kept for an additional hour under 10^{-2} Torr. The residue was analysed immediately, the weighing being done in the open air.

C_7H_6S Calc. C 68.9 H 5.0 P 0.0% S 26.3 Found C 66.2 H 5.8 P 0.0% S 20.9

---

[4]) The calculation of this weight is based on an ε-value for tropothione at 380 nm of 16,800. This value was derived in an indirect manner as will be described below.

A part of this analytical sample, weighing 0.500 mg, dissolved partially in 25 ml of methanol. The UV. spectrum of this sample showed that **1** had decomposed to the extent of at least 88%.

UV. Spectrum. Aliquot portions of the carbon tetrachloride solution described above were each diluted in the cold to a total volume of 25 ml with ethanol, toluene, carbon tetrachloride and concentrated sulfuric acid[5]), and their UV. absorption curves were measured immediately. The observed results are shown in the Table. The ε_{380} value was determined in the ethanolic solutions by conversion to tropone on a micro scale in the following way: to an ethanolic solution prepared by dilution of a carbon tetrachloride solution (obtained by chromatography) was added a catalytic amount of 60% $HClO_4$-solution and the conversion to tropone was followed spectroscopically until the maximum at 380 nm had disappeared and the new one at 310 nm did not increase any more. Authentic tropone, b.p. 120–121°/20 Torr, under identical conditions had $\varepsilon_{310} = 7{,}950$. Assuming a 100% conversion to tropone the ε-value for tropothione was calculated. Duplicate determinations gave an average ε-value for the absorption maximum of tropothione in ethanol at 380 nm of 16,800. The ε-values for the other solutions were calculated accordingly.

Attempts to Distill Tropothione. A concentrated CCl_4 solution containing 70 mg tropothione was evaporated to dryness in a *Kugelrohr* and the residue was distilled at 10^{-2} Torr. At 40–50° 6 mg of viscous red oil were collected and shown to contain tropothione by TLC. and its UV. spectrum (sample did not completely dissolve in ethanol $\lambda_{max} = 378$, $\varepsilon = 6{,}550$). The black residue from the distillation weighed 0.063 g. The possibility that **1** decomposed during the interval between removal of the last of the solvent and the beginning of the distillation was checked using a second solution containing 50 mg of **1**. After degassing, the solution was concentrated to about 0.2 ml on a distillation bridge using a liquid air trap and warming the arm containing **1** with a 15° water bath. After freezing in liquid air, closing the arm containing **1**, exchanging the trap for an NMR. tube, evacuating the system to 10^{-6} Torr for 1 h, and opening the arm containing **1** to the system again, an attempt was made to distill **1** along with the remaining CCl_4 into the NMR.-tube by freezing the tube in liquid air and warming the arm containing **1** to 40° on a water bath. Since after 1 h the intensity of the color of the CCl_4 solution in the NMR. tube indicated little **1** had distilled, the temperature was raised to 60° for 1 h and finally to 80° for 1 h. The UV. spectrum showed that only 0.04 mg of **1** had distilled.

^{1}H-NMR. (100 MHz, CCl_4): 7.71/*d*, $J = 10.7$, 2H (H—C(2), H—C(7)); 6.8–6.6 and 6.6–6.4/2*m*, 4H (H—C(3)), H—C(6)), H—C(4), H—C(5)). This spectrum was measured after concentration of a carbon tetrachloride solution which was obtained by chromatography as described above. In addition to the above signals, there was an additional signal at 6.43 ppm due to an impurity in the carbon tetrachloride which is most probably tetrachloroethylene. If a toluene solution, also purified by chromatography, was concentrated almost to dryness and the residue quickly taken up in carbon tetrachloride, the same spectrum was obtained at 60 MHz except that the signal at 6.43 ppm had been replaced by the two signals characteristic of toluene at 2.32 and 7.17 ppm. In addition, there were other low intensity multiplets at higher fields which are probably due to polymeric decomposition products.

3. Reaction of Tropothione. *With Hydroxylamine Hydrochloride.* A solution of 1.5 mmol of tropothione, 26% yield determined spectroscopically, was prepared as described above using 0.611 g (5.76 mmol) of tropone and 1.684 g (7.6 mmol) of phosphorus pentasulfide. The volume of the carbon tetrachloride solution obtained after chromatography was reduced in a RV. at reduced pressure to a volume of about 20 ml. This was added to a boiling solution of 0.153 g (2.2 mmol) of hydroxylamine hydrochloride in 10 ml of ethanol/pyridine 1:1. The solution was maintained at the boiling point for 2 h during which hydrogen sulfide was evolved as shown by a positive test using moist lead acetate paper. Addition of water, extraction with ether, drying the ether layer and, after removal of the solvent, chromatography of the residue on silica gel using ether as the eluting solvent gave pure tropone oxime which was precipitated from a concentrated ether solution as its hydrochloride, m.p. 146–147°, reported 146–147°, weight 111 mg., 48% yield. Mixed m.p. showed it to be identical with an authentic sample. No 2-aminotropone or 2-aminotropothione was isolated.

---

[5]) The tropothione dissolved in the sulfuric acid and the carbon tetrachloride separated as a layer on the top.

*2-Amino-3-cyano-3a*H*-cyclohepta*[b]*thiophene* (**4**). A solution of 2.96 mmol of tropothione, 42% yield, were prepared as described above from 0.746 g (7.05 mmol) of tropone and 2.982 g (13.4 mmol) of phosphorus pentasulfide. The carbon tetrachloride solution from chromatography, 3.455 l, was evaporated on a RV. at reduced pressure to a volume of about 20 ml. This was added quickly to 5 ml of an ethanolic solution of the sodium salt of malonitrile prepared from 0.122 g (5.3 mmol) of sodium and 0.38 g (5.7 mmol) of malonitrile. The reddish color of tropothione disappeared immediately on addition. There was a transient light green color and then the solution slowly became orange. After 24 h, pouring the mixture into water, extracting with ether and purifying by chromatography on silica gel using ether as the eluting solvent gave **4** slightly contaminated by **5** (or **6**), weight 0.405 g (2.15 mmol), 73% yield. Compound **4**, m.p. 142.5–144° with decomposition, was obtained pure on crystallization from ether. UV. (ethanol): max 215 3.8–4.0. – ^{1}H-NMR. (100 MHz, CCl_4): 6.6–6.3/*m*, 2H and 6.3–5.9/*m*, 2H (H–C(5), H–C(6), H–C(7), H–C(8)); 6.5/br. covered, 2H (2H–N); 5.07/*d*×*d*, $J_{3a,4} = 4.5$, $J_{4,5} = 9.0$, 1H (H–C(4)); 3.45/*d*×*t*, $J_{3a,4} = 4.5$, $J_{3a,5} = J_{3a,8} = 2.2$, 1H (H–C(3a)).

$C_{10}H_8N_2S$	Calc.	C 63.9	H 4.3	N 14.9	S 17.1%
(188)	Found	,, 63.8	,, 4.4	,, 14.7	,, 17.0%

*2-Amino-3-cyano-8*H*(or 4*H*)-cyclohepta*[b]*thiophene* (**5** *or* **6**). **5** (or **6**) was prepared by slow chromatography of **4** on silica gel using 5% ether in 30–60° petroleum ether as the eluting solvent. Decolorization with a minimum amount of activated charcoal[6]) and crystallization from hexane/ether gave pure **5** (or **6**), m.p. 176–177.5° (dec.). – UV. (ethanol): min 266 (2,000) max 338 (10,400). – IR. (KBr): 2.90*s*; 2.98*s*; 3.15*s*; 4.55. – ^{1}H-NMR. (100 MHz, CCl_4; Numbering according to structure **5**): 6.8–6.4/broad, 2H (2H–N); 6.66/*d*×*d*, $J = 11.3$ and ∼1, 1H (H–C(4)); 6.30/*d*×*d*×*d*, $J = 11.3$, 5.8 and ∼1, 1H (H–C(5)); 6.03/*d*×*d*, $J = 10.0$ and 5.8, 1H (H–C(6)); 5.41/*d*×*t*×*t*, $J = 10.0$, 6.8 and ∼1, 1H (H–C(7)); 2.95/*d*, $J = 6.8$, 2H (2H–C(8)).

$C_{10}H_8N_2S$	Calc.	C 63.9	H 4.3	N 14.9	S 17.1%
(188)	Found	,, 63.7	,, 4.5	,, 15.0	,, 16.9%

Mol. wt. (osmometric in 2-propanol): 183.

REFERENCES

[1] *T. Machiguchi, M. Hoshino, S. Ebine & Y. Kitahara*, Chem. Commun. *1973*, 196.

[2] *R. Cabrino, G. Biggi & F. Pietra*, Synthesis *1974*, 276; *T. Machiguchi, K. Okuma, M. Hoshino & Y. Kitahara*, Tetrahedron Letters *1973*, 2011.

[3] *T. Machiguchi, Y. Yamamoto, M. Hoshino & Y. Kitahara*, Tetrahedron Letters *1973*, 2627.

[4] *T. Machiguchi, T. Hoshi, J. Yoshino & Y. Kitahara*, Tetrahedron Letters *1973*, 3873.

[5] *T. Nozoe, T. Mukai & K. Takase*, Sci. Repts. Tohoku Univ. *39*, 164 (1956).

[6] *K. Kitahara, M. Funamizu & T. Asao*, Abstracts of the XVth Anniversary Meeting of the Chemical Society of Japan, p. 235 (1962).

[7] *T. Nozoe & K. Matsue*, Bull. chem. Soc. Japan *34*, 616 (1961).

[8] *W. R. Brasen & R. E. Benson*, J. Amer. chem. Soc. *83*, 3135 (1961).

[9] *H. Hosaya, J. Inaka & S. Nagakura*, Tetrahedron *1962*, 859.

[10] *B. Föhlisch & E. Haug*, Chem. Ber. *104*, 2324 (1971).

[11] *H. Klinger*, Ber. deutsch. chem. Ges. 10, 1877 (1877); *O. Wallach*, Liebigs Ann. *259*, 300 (1890); *L. Gattermann & H. Schulze*, Ber. deutsch. chem. Ges. *29*, 2944 (1896).

[12] *L. Kurita, S. Seto, T. Nozok & M. Kubo*, Bull. chem. Soc. Japan *26*, 272 (1953).

[13] *K. Hafner, H. W. Riedel & M. Danielisz*, Angew. Chem. *75*, 344 (1963).

[14] *K. Gerwald*, Chem. Ber. *98*, 3571 (1965).

[15] *Y. Kitahara & K. Doe*, Japan Pat. 3572 (1962) [C.A. *58*, 9004 (1963)].

[16] *S. Ito, J. Isungtsuga, T. Kanno, H. Sugiyama & H. Takeshito*, Tetrahedron Letters *41*, 3659 (1965).

---

[6]) There is some loss during this step which is increased if large amounts of charcoal are used.