On 2-Aminotropothione Derivatives

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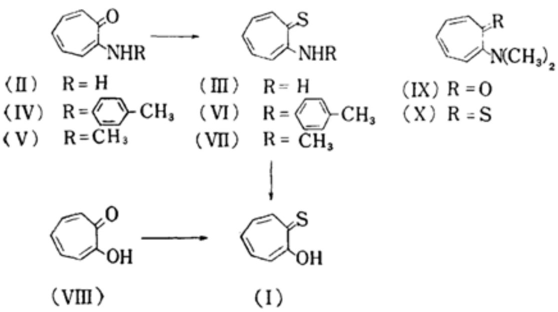
2-Mercaptotropone (I) with two possible tautomeric structures, A and B, was synthesized in 1953 in our laboratory[1,2]. Although the structure of 2-mercaptotropone (B) was assigned at that time from its chemical behaviors, further examinations on its physicochemical properties as well as those of its homologs suggested that I should take the structure A of 2-hydroxytropothione rather than B, in a static state[3].

(A) (B)

As another type of tropothione derivatives, 2-aminotropothiones (1-amino-7-thioxo-1, 3, 5-cycloheptatrienes) were recently synthesized by Brasen et al.[4] from 2-aminotroponeimines (1-amino-7-imino-1, 3, 5-cycloheptatrienes) by the action of hydrogen sulfide. This report deals with another synthesis of 2-aminotropothiones, probably identical with Brasen's compounds and reactions thereof.

Heating 2-aminotropone (II) with excess of phosphorus pentasulfide in pyridine for 2 hr. on a water bath yields 2-aminotropothione (III) as orange red prisms, m. p. 135~136°C, in 60% yield. III is neutral substance and stable in air, and gives benzoate, m. p. 136~137°C. Hydrolysis of III with excess of potassium hydroxide in ethanol affords I.



(II) R = H
(IV) R = $-C_6H_4-CH_3$
(V) R = CH_3
(III) R = H
(VI) R = $-C_6H_4-CH_3$
(VII) R = CH_3
(IX) R = O
(X) R = S
(VIII) (I)

Similarly, 2-*p*-toluidinotropothione (VI), orange red plates of m. p. 98~99°C, and 2-methylaminotropothione (VII), orange needles of m. p. 67~68°C, are obtained respectively from 2-*p*-toluidinotropone (IV) and 2-methylaminotropone (V). Both VI and VII are stable substances and benzene layer colors dark red with cupric acetate by the formation of chelate compound.

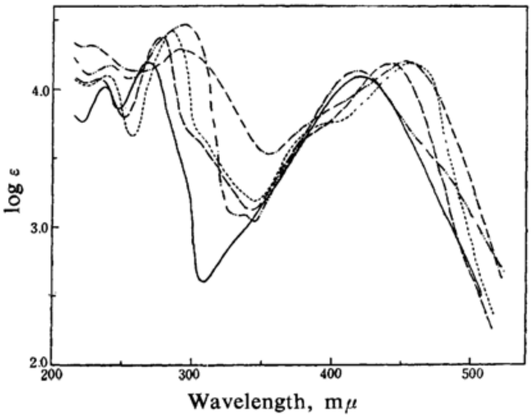


Fig. 1. Ultraviolet absorption spectra of I (——), III (——), VI (-·-·), VII (----) and benzoate of III (-·····) in methanol.

Reaction of tropolone (VIII) with phosphorus pentasulfide gives I even in a lower yield. But 2-dimethylaminotropone (IX) failed to give any objective 2-dimethylaminotropothione (X) except resinous materials by the same method.

These facts imply that hydrogen bond formation between C=S and NH or OH group considerably affects the stability of tropothione derivatives.

As electrophilic substitution, bromination of III in acetic acid was carried out, but only a yellow complex was obtained and heating of it with water ended in decomposition with the recovery of the original substance (III).

There can be two tautomeric structures, C and D, for each III, VI and VII. But their ultraviolet spectra fairly resemble that of 2-hydroxytropothione (I) (structure A) (Fig. 1). This fact suggests, that all these should exist as 2-aminotropothiones (structure C).

(C) (D)

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[1] T. Nozoe, M. Sato and K. Matsui, *Proc. Japan Acad.*, **29**, 22 (1953).

[2] Idem., *Sci. Repts. Tohoku Univ., Ser. I*, **37**, 211 (1953).

[3] T. Nozoe and K. Matsui, This Bulletin, **34**, 616 (1961).

[4] W. R. Brasen, H. E. Holquist and R. E. Benson, *J. Am. Chem. Soc.*, **82**, 995 (1960).

Infrared spectrum of III is shown in Fig. 2. Absorption assignable to SH group usually seen at 2600∼2550 cm^{-1} is absent, and according to Mecke's law,[5] strong absorption at 1045 cm^{-1} must correspond to $\nu_{C=S}$. Thus, the infrared spectrum also supports the structure C for III. This result is in agreement with that obtained by Brasen from nuclear magnetic resonance studies[4].

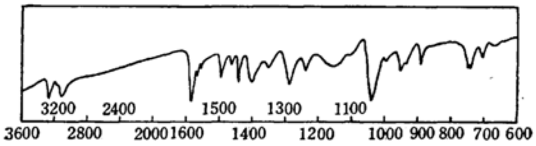

Fig. 2. Infrared absorption spectum of III (KBr disk).

It is known that although I takes structure A in the static state, it behaves like 2-mercaptotropone (structure B) during various reactions, affording only *S*-substituted derivatives[1,2]. However, the possibility of the structure of 2-mercaptotroponeimine (D) for III is excluded even during chemical reactions from its inertness toward diazomethane and the formation of *N*-benzoate as described below.

Two possible structures are assumed for benzoate of III, i. e. *N*- and *S*-benzoate. Its ultraviolet spectrum, however, considerably resembles that of III itself (Fig. 1), and $\nu_{C=S}$ appears at 1065 cm^{-1} in its infrared spectrum. It has therefore been clarified, that this must be *N*-benzoate.

These experiments thus show an essential difference in the chemical properties between I and III.

Experimental[6]

2-Aminotropothione (III).—A mixture of 0.5 g. of 2-aminotropone (II), 1.5 g. of phosphorus pentasulfide and 5 ml. of pyridine was stirred on a water bath for 2 hr. After removal of pyridine under a reduced pressure, water was added to the residue and separated crystals were collected by filtration and dried. This was extracted with methanol for 1 hr. and left cooling. Precipitated crystals were filtered off and methanol was evaporated. The residue was extracted with hot benzene and the crystals obtained was recrystallized from benzene to give 0.3 g. of III as orange red prisms, m. p. 136∼137°C.

Found: C, 61.42; H, 4.83; N, 10.00. Calcd. for C_7H_7NS: C, 61.27, H, 5.15, N, 10.21%.

Benzoate: Prepared from III and benzoyl chloride in pyridine, and recrystallized from ethanol to red leaflets, m. p. 136∼137°C.

Found: C, 69.66; H, 4.45; N, 5.40. Calcd. for $C_{14}H_{11}ONS$: C, 69.68; H, 4.59; N, 5.81%.

Hydrolysis of III; Formation of 2-Mercaptotropone (I).—A mixture of 30 mg. of III, 1 ml. of 20% potassium hydroxide and 4 ml. of ethanol was refluxed for 6 hr., ethanol was evaporated under a reduced pressure, water was added to the residue and the solution was treated with activated carbon. The filtrate thereby obtained was acidified with 6 N sulfuric acid and the crystals that separated out were collected by filtration. Sublimation of this product under 3 mmHg pressure afforded I as orange red crystals m. p. 54∼55°C. Yield, 15 mg. This was identified by mixed fusion with authentic sample.

2-*p*-Toluidinotropothione (VI).—A mixture of 0.3 g. of 2-*p*-toluidinotropone (IV), 1 g. of phosphorus pentasulfide and 5 ml. of pyridine was stirred on a water bath for 2 hr. Pyridine was removed under a reduced pressure, water was added to the residue and extracted with chloroform. Extract was washed with 2 N hydrochloric acid and the solvent was evaporated in vacuo. The residue was extracted with hot ethanol, and the substance so obtained was recrystallized first from cyclohexane then from ethanol to give VI as orange red plates, m. p. 98∼99°C. Yield, 50 mg.

Found: C, 74.31; H, 5.49; N, 5.85. Calcd. for $C_{14}H_{13}NS$: C, 73.99; H, 5.76; N, 6.17%.

2-Methylaminotropothione (VII).—A mixture of 0.3 g. of 2-methylaminotropone (V), 1.5 g. of phosphorus pentasulfide and 5 ml. of pyridine was stirred on a water bath for 1.5 hr. Pyridine was removed under a reduced pressure, water was added to the residue and extracted with chloroform. After evaporation of chloroform, the residue was triturated with 5 ml. of methanol and insoluble materials were filtered off. Methanol was evaporated in vacuo and the residue was extracted with hot cyclohexane. Extracted material was recrystallized two times from cyclohexane to give 50 mg. of VII as orange needles, m. p. 67∼68°C.

Found: C, 63.92; H, 5.68; N, 9.27. Calcd. for C_8H_9NS: C, 63.53; H, 6.00; N, 9.27%.

Reaction of Tropolone (VIII) **and Phosphorus Pentasulfide; Formation of I.**—A mixture of 0.2 g. of VIII, 0.5 g. of phosphorus pentasulfide and 5 ml. of pyridine was stirred on a water bath for 30 min. Pyridine was evaporated under a reduced pressure, 10 ml. of 2 N potassium hydroxide was added to the residue, and the solution was treated with activated carbon. The filtrate thereby obtained was acidified with 6 N sulfuric acid and the crystals that separated were collected by filtration. Sublimation of this product under 3 mmHg pressure and recrystallization of the sublimate from petroleum ether afforded I as orange red prisms, m. p. 53∼55°C. Yield, 20 mg. This was identified by admixture.

Reaction of Dimethylaminotropone (IX) **and Phosphorus Pentasulfide.**—To a solution of 1 g. of IX dissolved in 5 ml. of pyridine, 1.5 g. of phosphorus pentasulfide was added under stirring. The solution colored red immediately and darkened after a short time. After stirring for 1.5 hr. at room temperature, pyridine was evaporated under a reduced pressure, water was added to the residue and separated dark

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[5] R. Mecke, R. Mecke and A. Lüttringhaus, *Chem. Ber.*, **90**, 975 (1957).

[6] All m. p. are uncorrected. The microanalyses were carried out by Miss A. Iwanaga and Miss M. Suzuki to whom the authors express their deep gratitude.

crystals were collected by filtration. This was extracted with methanol for 1 hr., but only small amounts of resinous materials were obtained.

Bromination of III.—A solution of 40 mg. of bromine in 0.5 ml. of acetic acid was added to 30 mg. of III dissolved in 3 ml. of acetic acid under stirring. Yellow crystals that separated were collected by filtration. This substance, m. p. over 280°C, is insoluble in benzene or ethanol. By heating it with water, followed by extraction with chloroform and sublimation of the extract under 3 mmHg pressure, 15 mg. of III, m. p. 130∼135°C, was recovered, identified by mixed fusion.

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