A NEW ROUTE TO 1,2-DITHIOLE-3-THIONES (TRITHIONES) BY THE REACTION OF ENAMINONES WITH CARBON DISULFIDE

Yoshinori Tominaga,* Hajime Norisue, Chizuko Kamio, Toshiyuki Masunari, Yuji Miyashiro, and Akira Hosomi*

Faculty of Pharmaceutical Sciences, Nagasaki University, 1-14, Bunkyo-machi, Nagasaki, 852, Japan

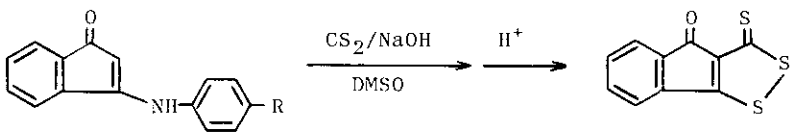
Abstract——Enaminones reacted with carbon disulfide in the presence of sodium hydroxide to give the corresponding 1,2-dithiole-3-thiones (trithiones) in 30-82% yields.

1,2-Dithiole-3-thiones (trithiones) are important and interesting substances for the synthesis of heterocycles, and much attention has been attracted as the basic key structural unit for the synthesis of pharmacologically active compounds in sulfur-containing heterocyclic chemistry.[1-7]

One of the most useful and versatile methods for the synthesis of 1,2-dithiole-3-thiones is the reaction of ketones with carbon disulfide in the presence of a base followed by treatment with phosphorus pentasulfide.[8-10] The sulfurization of β-keto esters with phosphorus pentasulfide or their mixture with elemental sulfur is also a general method for the synthesis of 1,2-dithiole-3-thiones.[11] However, it is difficult to prepare 4-acyl-1,2-dithiole-3-thiones by the sulfurization with phosphorus pentasulfide as shown above because of the lack of selectivity in the sulfurization of carbonyl groups. We now wish to report a new synthesis of fused 1,2-dithiole-3-thione derivatives by the reaction of enaminones, which are readily obtained by the condensation of 1,3-diketones with aromatic amines, with carbon disulfide in the presence of a base.

When enaminone, 3-anilinoinden-1-one (**1a**) was allowed to react with carbon disulfide in the presence of sodium hydroxide in dimethyl sulfoxide followed by treatment with 10% hydrochloric acid, a trithione, 4-oxoindeno[1,2-c][1,2]dithiole-3-thione (**2**)[12] was obtained in 78% yield (Scheme 1), though expected enamino dithiocarboxylate was not given.[13] Similarly, the reaction of **1b** with carbon disulfide gave the same trithione (**2**) in 82% yield. When the reaction

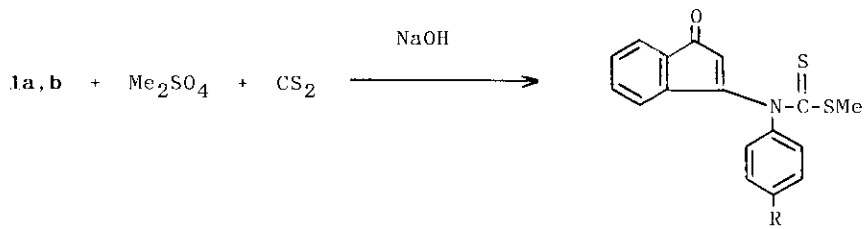
was carried out in the presence of dimethyl sulfate, methyl N-phenyl dithiocarbamate derivatives (**3a,b**) were obtained in 54 and 62% yields, respectively. Therefore the reaction was assumed to proceed by the addition of the amino group to carbon disulfide followed by the nucleophilic attack of the thiolate anion. Decomposition of the 3-azathiethane ring produced the corresponding β-oxothione derivative which works as a key intermediate for the formation of the trithione. The 3-oxo-1-thione, thus formed, reacted again with carbon disulfide and by air oxidation of the resultant dithiocarboxylate gave the desired trithione (**2**). The present reaction can be applied to the synthesis of 1,2-dithiolo[3,4-d]-pyrimidine (**5**). Namely, the reaction of **4** with carbon disulfide afforded the desired trithione (**5**)[14] in 40% yield, along with a tricyclic compound (**6**). However, the reaction of 3-anilino-2-cyclohexen-1-one derived from dimedone with carbon disulfide did not give the corresponding trithione derivatives. When a



1a, b **2**

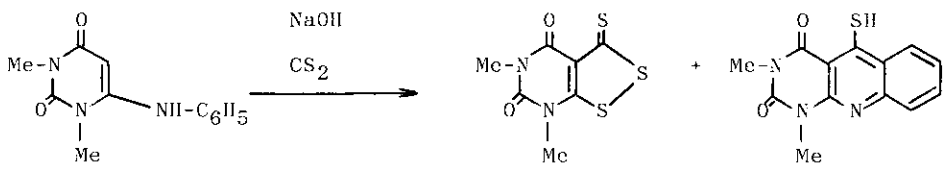
a: R=H
b: R=Me

2: mp 298°C
Yield (78% from R=H, 82% from R=Me)



3a, b

3a: R=H, mp 214°C, Yield 54%
b: R=Me, mp 248°C, Yield 62%

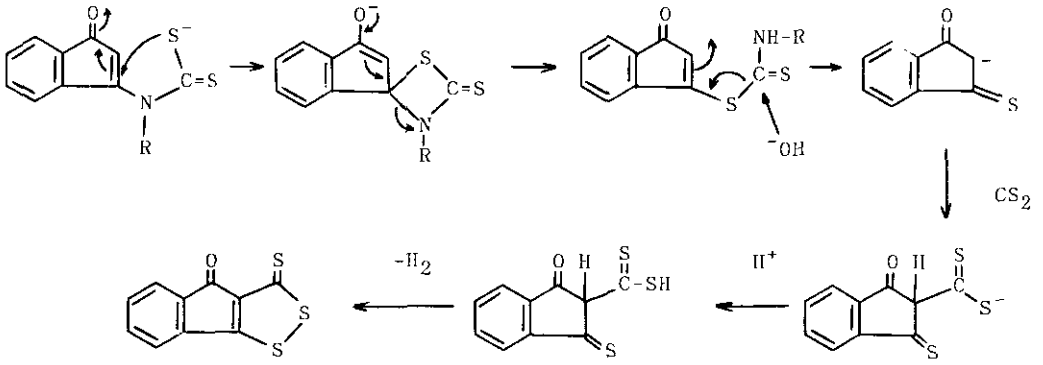


4 **5** **6**

mp 233°C
Yield: 40%

Scheme 1

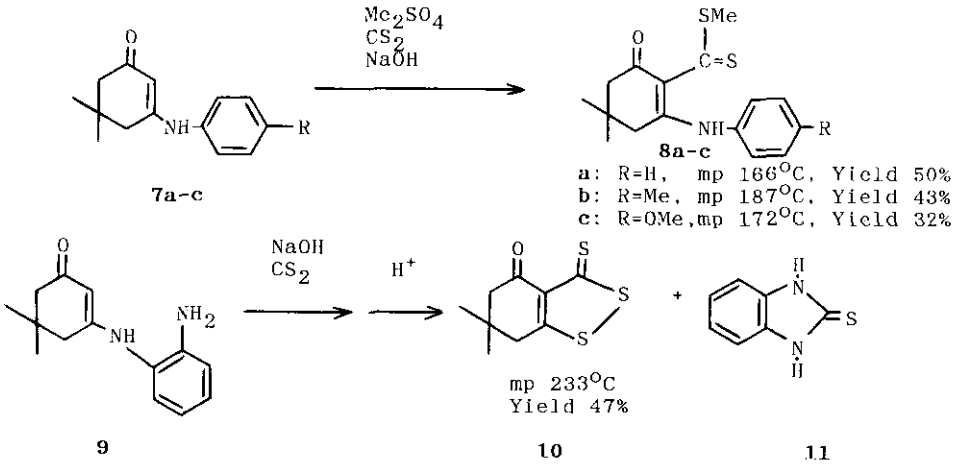
An outline of the reaction mechanism for the formation of **2** is shown in Scheme 2.



2 Scheme 2

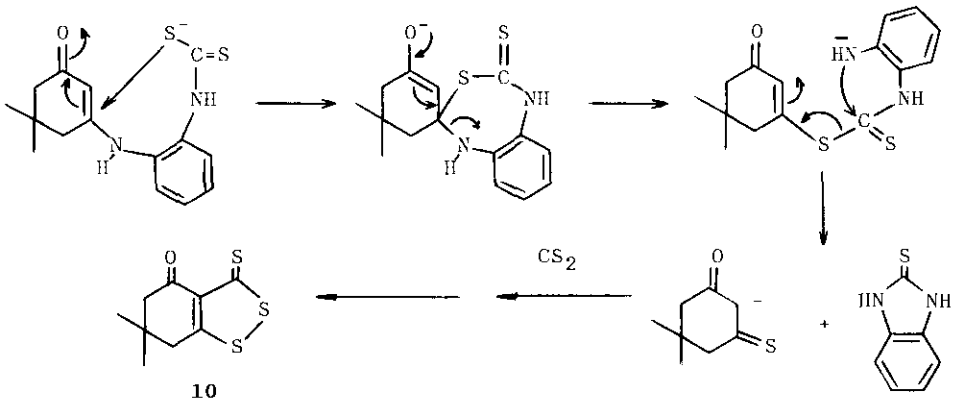
solution of sodium hydroxide was added to a solution of **7a-c**, carbon disulfide, and dimethyl sulfate in dimethyl sulfoxide, the enamino dithiocarboxylate compounds (**8a-c**) were obtained in 32-50% yields. Thione derivatives as a key intermediate did not form in this reaction because the 2-position of **7a-c** reveals higher nucleophilicity than the nitrogen atom of the amino group. In order to prompt the reaction with the amino group in preference to the 2-position, we chose the o-aminoanilinocyclohexen-1-one (**9**) derived from dimedone and o-phenylenediamine. The reaction of **9** with carbon disulfide gave an expected trithione derivative, benzo[1,2]dithiolo-3-thione (**10**)[15] in 47% yield (Scheme 3).

The advantages of the present method are the ready availability of the starting materials and easy manipulation for the preparation of trithione derivatives. This procedure apparently displays considerably promising preparative method of fused 1,2-dithiole-3-thione derivatives and these products can be used as key intermediates for further conversion to various heterocyclic compounds.



Scheme 3

An outline of the reaction mechanism for the formation of **10** is shown in Scheme 4.



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Scheme 4

ACKOWLEDGMENT

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12. **2**: mp 298°C, dark violet needles; ir ν(max, KBr) cm^{-1}: 1700(CO); uv λ(EtOH, insufficient solubility): max nm 227, 290, 329, 490: min nm: 258, 305, 425; ms(m/z): 236(M^+, 100), 192(28), 160(35), 144(63), 70(23), 57(27).
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14. **5**: mp 233°C, yellow needles; ir ν(max, KBr) cm^{-1}: 1708, 1665(CO); uvλ(max, EtOH)nm(log ε): 235(4.10, 291(4.32), 398(3.75); ^{1}H-nmr(TFAc) δ: 3.54(3H, s, N-Mc), 3.85(3H, s, N-Me); ms(m/z): 247(M^++1, 11), 246(M^+, 100), 189(23), 105(46), 97(41), 57(13), 43(29).
15. **10**: red leaflets; ir ν(max, KBr) cm^{-1}: 1667(CO); uv λ(max, EtOH)nm(log ε): 227(4.17), 262(3.92), 312(3.86), 335(3.76), 420(3.82); ^{1}H-nmr($CDCl_3$)δ: 1.22(6H, s, Me), 2.59(2H, s, $-CH_2-$), 2.97(2H, s, $-CH_2-$); ms(m/z): 231(M^++1, 11), 230(M^+, 100), 187(10), 174(40), 82(45), 55(25), 43(25).
16. The structure of all products (**3a, b, 6, 8a-c**) in the reactions described above was determined by ir, uv, ^{1}H-nmr, mass spectra, and elemental analysis.

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