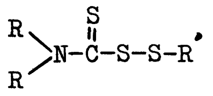
CHEMISTRY LETTERS, pp. 441-444, 1976. Published by the Chemical Society of Japan

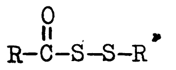
THE PREPARATION AND REACTIONS OF UNSYMMETRICAL THIOCARBONYL DISULFIDES

Tomonori KATADA, Sadaaki TSUJI, Tatsushi SUGIYAMA,
Shinzi KATO, and Masateru MIZUTA
Department of Chemistry, Faculty of Engineering,
Gifu University, Kagamihara, Gifu 504

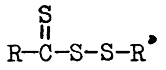
Unsymmetrical thiocarbonyl disulfides (3) have been easily synthesized in good yields by the reaction of piperidinium dithiocarboxylates with sulfenyl chlorides. In the reaction of these disulfides with nucleophiles (amine and metal alkoxide), both thiocarbonyl carbon and sulfenyl sulfur atom seem to be attacked by nucleophiles. By desulfurization with triphenylphosphine thiocarbonyl disulfides converted into corresponding dithioesters in high yields.

Although a number of compounds such as thiocarbamoyl disulfides (1)1) and carbonyl disulfides (2)2) have been reported, the corresponding thiocarbonyl disulfides (3) have been unknown so far, which would be expected to possess interesting properties. Moreover, desulfurization of organic disulfides by triphenylphosphine in boiling benzene has been reported,3) but desulfurization of unsymmetrical disulfides such as (3) are not known.


1


$\mathrm{R{-}\overset{O}{\overset{\|}{C}}{-}S{-}S{-}R'}$

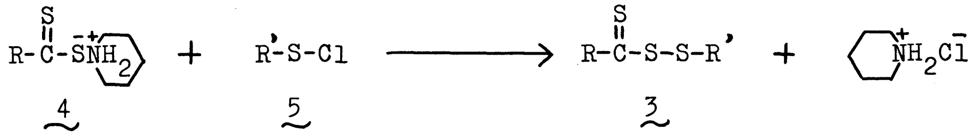
2


$\mathrm{R{-}\overset{S}{\overset{\|}{C}}{-}S{-}S{-}R'}$

3

In this communication, we wish to report the preparation and some reactions of thiocarbonyl disulfides (3).

When an equimolar amount of piperidinium salt of dithiocarboxylic acid (4) was treated with sulfenyl chloride (5),4) corresponding thiocarbonyl disulfide (3) was obtained in good yield as shown in Table 1.


(1)

A general procedure is shown as follows: equimolar amounts of piperidinium p-dithiotoluate 4b (2.50 g, 10 mmol) and benzenesulfenyl chloride 5 (1.45 g, 10 mmol) in dry ether (50 ml) were stirred under argon atmospher for 1 hr at room temperature. After removal of the precipitate by filtration, evapolation of the filtrate and purification of the resulting residue by sillica gel column chromatography with cyclohexane as an eluent gave reddish pink oil of p-methylthiobenzoyl phenyl disulfide 3b (2.54 g, 92 %). The structure of (3b) was established on the basis of the following spectral data as well as elemental analyses. Calcd for $C_{14}H_{12}S_3$: C, 60.87; H, 4.35; S, 34.78 %. Found: C, 60.71; H, 4.34; S, 34.95 %. UV(cyclohexane) λmax(εmax) 310 nm(13,400), 534 nm(97). NMR($CDCl_3$) δ(ppm) 2.34(s,3H,CH_3-), 7.10-7.70(m,7H,aromatic), 7.95(ca.d, 2H,aromatic). IR(neat) νc=s 1245, νc-s 850, νs-s 475 cm.$^{-1}$

Table 1. Yields and Some Physical Properties of Thiocarbonyl Disulfides (3)

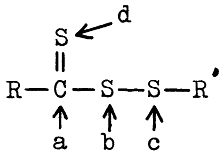
No	Compound (3) R	R'	Yield* (%)	IR(neat) cm^{-1} νc=s	νc-s	νs-s	UV(cyclohexane) nm λmax(ε max)	
a	Ph	Ph	90	1240	835	475	293(13,000)	537(72)
b	p-$CH_3C_6H_4$	Ph	92	1245	850	475	310(13,400)	534(97)
c	p-ClC_6H_4	Ph	88	1240	820	470	306(13,400)	537(90)
d	Ph	Et	79	1248	838	475	295(9,000)	527(70)
e	Ph	t-Bu	80	1240	838	470	298(9,200)	537(75)
f	i-Pr	Ph	85	1215	905	475	291(4,900)	484(30)
g	i-Pr	Et	70	1245	940	505	312(2,400)	468(10)

* Isolated yield

Thiocarbonyl disulfides (3) obtained were fairly stable at room temperature in the dark.

It is known that unsymmetrical disulfide (R-S-S-R') disproportionates into symmetrical disulfides (R-S-S-R and R'-S-S-R'), but (3b) did not change even in boiling benzene under argon atmospher for 6 hrs; only starting material was recovered.

On the other hand, treatment of (3b) with an equimolar amount of triphenylphosphine in benzene at 80°C for 2 hrs afforded phenyl p-dithiotoluate (6) and triphenylphosphine sulfide (7) in 85 and 90 % yields, respectively (eq. 2).



$$R-\overset{\overset{S}{\|}}{C}-S-S-R'$$

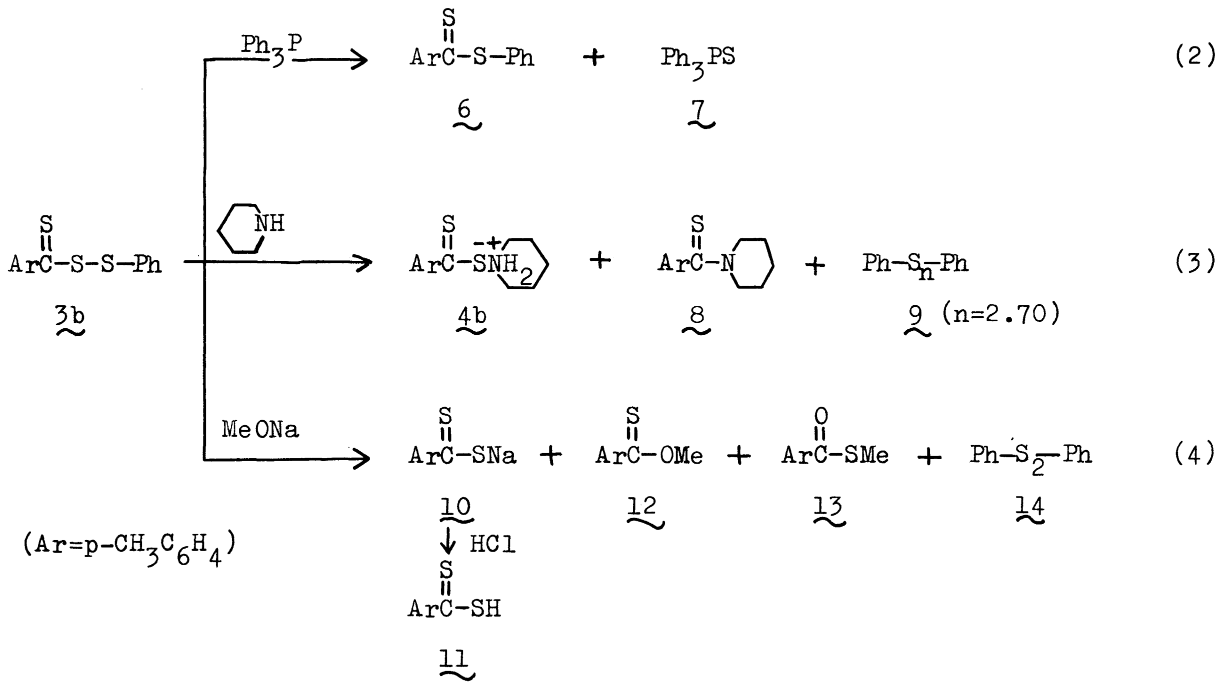
Fig. 1 (3)

One of the interesting points for thiocarbonyl disulfides (3) are their reactions with nucleophiles because they have multi-reaction centers, shown with the arrows a, b, c, and d in Figure 1.

When p-methylthiobenzoyl phenyl disulfide (3b) was treated with two-molar amount of piperidine in dry ether at room temperature, piperidinium p-dithiotoluate (4b), p-methylthiobenzpiperidide (8), and diphenyl polysulfides (9) ($Ph-S_n-Ph$, n=2.70; mixture of diphenyl disulfide, trisulfide, and tetrasulfide) were obtained in 50, 46, and 86 % yields, respectively (eq. 3).

Moreover, the reaction of (3b) with 2.2 molar equivalent of sodium methoxide in ether containing small amount of methanol at room temperature gave sodium p-dithiotoluate (10) (isolated as p-dithiotoluic acid (11)), O-methyl p-thiotoluate (12), S-methyl p-thiotoluate (13), and diphenyl disulfide (14) in 35, 43, 13, and 87 % yields, respectively (eq. 4).

These reaction products were identified by comparison of their spectral data with those of the authentic samples.



The mechanism of the reaction mentioned above is now under investigation. The fact that the piperidinium and sodium p-dithiotoluate (4b and 10) are isolated from the reaction mixture (see, eq. 3 and 4) suggests that the cleavage of sulfur-sulfur bond of the thiocarbonyl disulfide (3b) occured by attacking of nucleophiles.

However, the direct attack of the nucleophiles on the thiocarbonyl carbon of (3b) is proved by the formation of thioamide (8) with no evolution of hydrogen sulfide and isolation of thionester (12) and thiolester (13).

References

1) a. A.A.Watson, J. Chem. Soc., 2100 (1964).
   b. F.Fischer and R.Gottfied, J. Prakt. Chem., 30, 230 (1965).
   c. L.Field and J.D.Buckman, J. Org. Chem., 33, 3865 (1968).
2) a. L.Field and J.D.Buckman, J. Org. Chem., 32, 3467 (1967).
   b. L.Field, W.S.Hanley, I.McVeigh and Z.Evans, J. Med. Chem., 14, 202 (1971).
3) a. A.Schonberg and M.Z.Barakat, J. Chem. Soc., 892 (1949).
   b. S.Kawamura, A.Sato, T.Nakabayashi and M.Hamada, Chem. Lett., 1231 (1975).
4) E.Kuhle, Synthesis, 561 (1970).

(Received March 5, 1976)