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Synthesis of New Classes of Thiocarbonyl Ylides and Imines[1]

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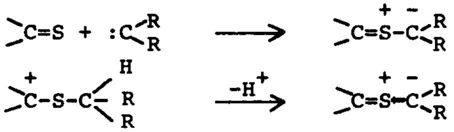
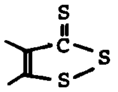
Recently thiocarbonyl ylides have been reported to be unstable and unisolable intermediates formed in the addition reaction of carbene toward thiocarbonyl compounds (>C=S) or by base-catalyzed deprotonation of sulfonium compounds[2,3].



However, the thiocarbonyl ylides so formed have never been isolated and are so reactive that their physical properties have never been explicitly characterized.

We have attempted synthesis of stable thiocarbonyl ylides and their nitrogen-analogs, thiocarbonyl imines.

In this communication, we wish to report reactions of cyclic thiocarbonyl compounds, trithiones (I), with carbene or nitrene.

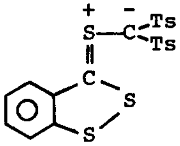


(I)

Trithiones are chosen since they are relatively stable due to their aromaticity, while the exocyclic sulfur atom accumulates a substantial negative charge to become a good nucleophilic center toward alkyl halides. When trithione is actually reacted with methyl iodide, methyl dithiolylium iodide is obtained in a good yield only by refluxing in benzene[4].

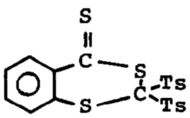
Accordingly, we have attempted the reaction of trithiones with carbene or nitrene bearing strongly electronegative substituents, i.e., bis(toluenesulfonyl) carbene or sulfonylnitrene, respectively.

1,2-Benzodithiole-3-thione (benzotrithione) was refluxed in benzene with bis(toluenesulfonyl) diazomethane in the presence of a catalytic amount of copper acetylacetonate. After 5 minutes, the reaction was found to be complete as the trithione disappeared completely according to the thin-layer chromatography test. After removing the solvent, red-colored crystals formed quantitatively were recrystallized from benzene-hexane (mp. 163-164°C). Based on the elemental analysis, NMR, UV, and IR. (Anal: Calcd. for $C_{22}H_{19}O_4S_5$: C,52.10; H,3.56%. Found: C,51.88; H,3.53%. NMR:τ7.46 (6,d,CH_3),τ 2-3 (12,m,phenyl H) in $CDCl_3$. UV: λmax 450nm (ε: 4,700) in EtOH. IR(KBr): 1490,1390,1320-1290,1140,1070,840,800,755,700 cm^{-1}), the structure of this material was assigned to have the following formula (II):

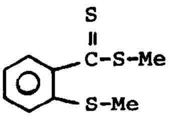


(II)

A question if the red-colored crystals would be the insertion product (III) to S-S bond can be ruled out from the IR and UV data, since if it would be an insertion product, its IR spectrum would show and characteristic band due to the thiocarbonyl group at 1200 and 800-900 cm^{-1}; moreover, the UV spectrum would indicate a similar absorption band to that of the model compound (IV). However, this was not the case.

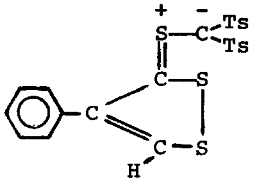


(III)



(IV)

In a similar way, we have prepared an ylide derivative (V) of another trithione, 4-phenyl-1,2-dithiole-3-thione, by refluxing the mixture of the trithione with bis(toluenesulfonyl) diazomethane in the presence of copper salt for one hour in benzene. The structure of this compound thus obtained (mp. 115-116°) was also comfirmed by the elemental analysis, NMR, UV, and IR (Anal: Calcd. for $C_{24}H_{20}O_4S_5$: C,54.10; H,3.75. Found: C,54.25; H,3.95%. NMR:τ7.46 (6,d,CH_3),τ2-3 (14,m,phenyl H and C-H) in $CDCl_3$. IR(KBr):1490, 1370,1320-1290,1035,840-800,760,700 cm^{-1}.

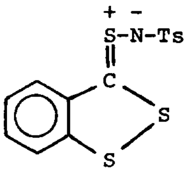


(V)

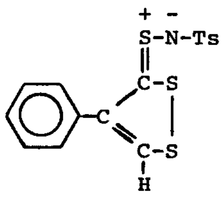
Obviously the presence of benzo group is not necessary for this reaction. The fact that the 6π-electrons system is retained also in the products would be another important factor for the remarkable stability of the crystalline ylide.

We have attempted synthesis of the nitrogen-analogs of ylides, i.e., imines. Both trithiones were found to react readily with chloramine-T in methanol to give the following red-colored compounds in good yields; (VI):mp 135-136°C and (VII): mp 165-166°C, which structures were assigned rather unequivocally by the elemental analysis and the spectroscopic methods: (VI): elemental analysis: Found: C,47.57; H,3.22%; N,4.17. Calcd for $C_{14}H_{11}O_2NS_4$: C,47.59; H,3.11; N,3.97% UV:λmax 492 nm (ε:14,700) in CH_3CN. IR(KBr): 1590, 1455,1305-1280,1140,1090,970,910 cm^{-1}.

(VII): elemental analysis: Found C,50.25; H,3.43; N,3.69%: Calcd. for $C_{16}H_{13}NO_2S_4$: C,50.65; H,3.43; N,3.65%. IR(KBr): 1470,1355,1280,1140,1080, 925,850 cm^{-1}.



(VI)

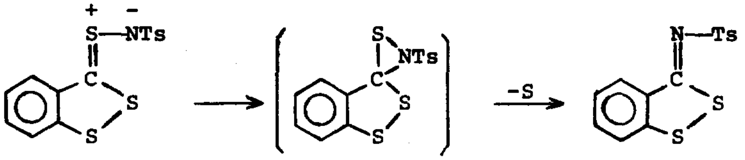


(VII)

To our knowledge both these stable types of ylides and imines have never been prepared. The corresponding oxygen-isoelectronomer is the stable sulfine in which the following basic resonance forms contribute to its stabilization and its physical and chemical properties have been studied substantially.5)

$$>C=\overset{+}{S}-\overset{-}{O} \longleftrightarrow >\overset{+}{C}-S-\overset{-}{O} \longleftrightarrow >C=S=O$$

Like sulfines, the former imine (VI) was also found to be desulfurized at its decomposition temperature or by addition of a catalytic amount of acid to the compound (VIII) (mp. 153-154°) as shown below :



(VIII)

(VIII): Anal. Calcd. for $C_{14}H_{11}O_2NS_3$: C,52.33; H,3.43; N,4.36. Found: C,51.91; H,3.38; N,4.43%. NMR:τ7.46 (3,s,CH_3),τ1.5-8.6 (8,m,phenyl H). IR(KBr): 1470 (C=N,very strong), 1280 (SO_2), 1140 (SO_2), 1080,1068,930, 840 cm^{-1}. UV:λmax 398 nm (ε:9,500) in CH_3CN.

Since the ylides and imines we obtained should also display interesting chemical behaviors, studies on their physical properties and chemical behaviors are now in progress.

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