3718 BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48(12), 3718—3722 (1975) [Vol. 48, No. 12

Charge-transfer Intermediate in The Reaction of Thioketone with Nucleophiles

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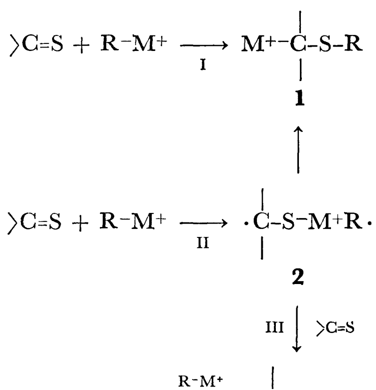
(Received August 14, 1975)

Thiobenzophenone reacts with butyllithium, phenyllithium, and sodium ethoxide in ethanol giving benzhydryl butyl sulfide, benzhydryl phenyl sulfide, and dibenzhydryl disulfide, respectively. On the other hand di-*t*-butyl thioketone affords 2,2,4,4-tetramethylpentane-3-thiol, 2,2,4,4-tetramethyl-3-phenylpentane-3-thiol, and 2,2,4,4-tetramethylpentane-3-thiol by the reaction with butyllithium, phenyllithium, and sodium ethoxide in ethanol, respectively. Product analyses and tracer experiments with deuteriums have revealed that these reactions proceed through a charge-transfer mechanism.

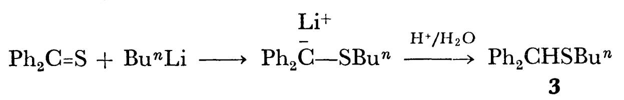
Thiophilic addition of nucleophiles to thiocarbonyl compounds has been reported by several groups.[1-4] Namely, Beak and Worley proposed three possible mechanisms for thiophilic reaction of thiocarbonyl groups (thiobenzophenone and phenyl trithiocarbonate) with phenyllithium.[1b] One of those is based on the concept that the bonding electrons of the thiocarbonyl group are intrinsically polarized with carbon negative relative to sulfur. Dipole moment[5] and SCF-LCAO-MO calculation[6] support the intrinsic polarity of the thiocarbonyl group proposed. Second mechanism involves the formation of a charge-transfer (CT) complex between a thiocarbonyl compound and a nucleophile followed by an in-cage radical combination giving an ion-pair, **1**. The presence of the thioketyl radicals in the reacting solution has been confirmed by ESR spectroscopy.[1b,7] This mechanism, however, cannot explain why the free-radical R· in **2** attacks on the sulfur instead of attacking on the carbon, on which locates an unshared electron. The third mechanism consists of free-radical chain reactions. That the thiocarbonyl-sulfur is a good acceptor of a carbon free-radical has been proved.[8,9]



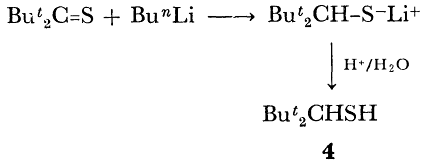
In this paper, we wish to report unequivocal evidence to support the CT-intermediate—radical-combination mechanism (Process II) for the reaction of thioketones with nucleophiles.

Results

Thiobenzophenone reacts with butyllithium affording benzhydryl butyl sulfide (**3**) in 70% yield as previously reported.[1,10] On the other hand, di-*t*-butyl thioketone[11] is reduced quantitatively by this reagent to the corresponding thiol, **4**, under the same condition.[10]



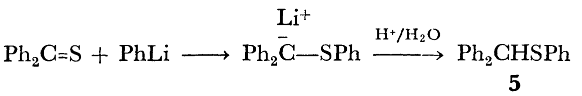
$$Ph_2C{=}S + Bu^nLi \longrightarrow Ph_2\overset{Li^+}{\bar{C}}\text{—}SBu^n \xrightarrow{H^+/H_2O} \underset{\mathbf{3}}{Ph_2CHSBu^n} \quad (1)$$



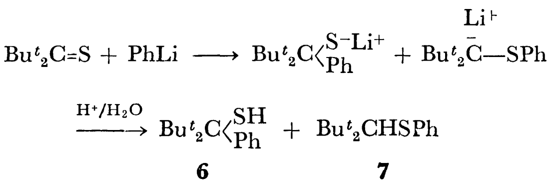
$$\begin{array}{l} Bu^t{}_2C{=}S + Bu^nLi \longrightarrow Bu^t{}_2CH\text{-}S^-Li^+ + C_2H_5CH{=}CH_2 \\ \qquad\qquad\qquad\qquad \downarrow H^+/H_2O \\ \qquad\qquad\qquad \underset{\mathbf{4}}{Bu^t{}_2CHSH} \end{array} \quad (2)$$

That butyllithium-β,β-d_2 transfers the deuterium onto the thiocarbonyl-carbon and that the reaction with butyllithium gives **4**-*S-d* after the treatment of the reaction mixture with deuterium oxide prove the reaction scheme shown in Eq. 2. It is noteworthy that, in general, organolithium compounds are less susceptible to the reduction of carbonyl compounds than Grignard reagents.[12]

The reaction of thiobenzophenone with phenyllithium affords benzhydryl phenyl sulfide (**5**),[1] whereas the same reaction with di-*t*-butyl thioketone results in the formation of **6** and **7** in 25 and 35% yields, respectively.[10]



$$Ph_2C{=}S + PhLi \longrightarrow Ph_2\overset{Li^+}{\bar{C}}\text{—}SPh \xrightarrow{H^+/H_2O} \underset{\mathbf{5}}{Ph_2CHSPh} \quad (3)$$



$$\begin{array}{l} Bu^t{}_2C{=}S + PhLi \longrightarrow Bu^t{}_2C\langle^{S^-Li^+}_{Ph} + Bu^t{}_2\overset{Li^+}{\bar{C}}\text{—}SPh \\ \xrightarrow{H^+/H_2O} \underset{\mathbf{6}}{Bu^t{}_2C\langle^{SH}_{Ph}} + \underset{\mathbf{7}}{Bu^t{}_2CHSPh} \end{array} \quad (4)$$

Essentially the same result was obtained when the organolithium compound was substituted by the corresponding Grignard reagent.

The reaction of thiobenzophenone with ethanol in the presence of sodium ethoxide at room temperature *in vacuo* (~10^{-6} Torr) in the dark resulted in the quantitative formation of dibenzhydryl disulfide (**8**)[13] immediately. A similar reaction with di-*t*-butyl thioketone gave **4** in quantitative yield after a day at 60 °C. The

TABLE 1. REACTIONS OF THIOKETONES IN DEUTERATED ALCOHOLS

Starting material	Product	Alcohol (D-Content, %)	D-Content in product, %	D-Transfered, %
$Ph_2C=S$	**8**-α,α'-d_2	Ethanol-*O*-*d* (99.9)	85±5	89±3
		1-Butanol-α,α-d_2 (91.8)	4	4
$Bu^t_2C=S$	**4**-α-*d*	Ethanol-*O*-*d* (99.9)	14.3	14.3
		1-Bntanol-α,α-d_2 (91.8)	65.4	71.2
4[a]	**4**-α-*d*	Ethanol-*O*-*d* (99.9)	0	0
8[a]	**8**-α,α'-d_2	Ethanol-*O*-*d* (99.9)	0	0

a) A controlled experiment to confirm the absence of isotope-exchange in products.

TABLE 2. CHARGE AND SPIN DENSITY DISTRIBUTIONS IN RADICAL ANIONS OF THIOACETONE AND THIOBENZALDEHYDE[a, b]

	Thioacetone		Thiobenzaldehyde	
	on C	on S	on C	on S
Charge density	+0.2192 (+0.2115)	−0.9490 (−0.9896)	−0.0154 (−0.0407)	−0.7594 (−0.7843)
Spin density	+0.8264 (+0.7692)	+0.1547 (+0.2073)	+0.6041 (+0.5409)	+0.1987 (+0.2683)

a) Numbers out of and in parentheses are results of calculations excluding and including d orbitals on sulfur, respectively. b) Geometries of molecules are shown in Table 3 and Fig. 1.

$$Ph_2C{=}S + C_2H_5OH/C_2H_5O^-Na^+ \longrightarrow \underset{\mathbf{8}}{Ph_2CHSSCHPh_2} \qquad (5)$$

$$Bu^t_2C{=}S + C_2H_5OH/C_2H_5O^-Na^+ \longrightarrow Bu^t_2CHS^-Na^+ \xrightarrow{H^+/H_2O} \mathbf{4} \qquad (6)$$

results listed in Table 1 were obtained from the reactions with deuterated alcohols, which indicate that thiobenzophenone abstracts a proton from the solvent whereas di-*t*-butyl thioketone abstracts a hydrogen atom.

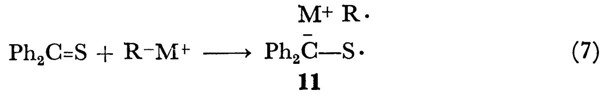
All reactions in Eqs. (1)—(6) were not affected by the presence of equimolar (to the thioketone) amount of hydroquinone, or the presence of air except for the reaction in Eq. (6), which afforded the corresponding disulfide under an aerobic condition. In other words, the formation of **8** cannot be accounted for by the oxidation of benzhydryl mercaptan. Instead, it might be formed by the combination of benzhydryl mercapto radicals.

Discussion

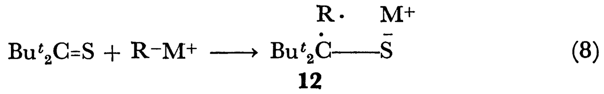
Since the phenyl group, or even the *t*-butyl group,[14] is bound to the carbonyl-carbon in di-*t*-butyl ketone, the difference of the reaction mode cannot be attributed to the steric effect in the reactants. The present result is best interpreted by assuming CT-intermediates for each reactions. Preliminary INDO-type molecular orbital calculations on anion radicals of thioacetone and thiobenzaldehyde, models for di-*t*-butyl thioketone and thiobenzophenone, respectively, indicate that a phenyl group attached to the thiocarbonyl group increases intrinsic negative charge on carbon and spin density on sulfur, respectively, in comparison to an aliphatic substituent (Table 2). That is, structures (or the most important canonical forms, i. not exclusive) for the radical anions of thiobenzophenone and di-*t*-butyl thioketone may be represented by **9** and **10**, respectively.

$$\underset{\mathbf{9}}{Ph_2\bar{C}\text{-}S\cdot} \qquad \underset{\mathbf{10}}{Bu^t_2\dot{C}\text{-}S^-}$$

Consequently, thiobenzophenone and di-*t*-butyl thioketone are expected to form CT-intermediates, **11** and **12**, respectively, in reactions with nucleophiles.

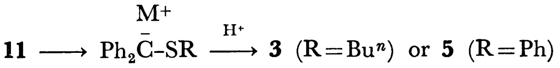


$$Ph_2C{=}S + R^-M^+ \longrightarrow \underset{\mathbf{11}}{\overset{M^+\ R\cdot}{Ph_2\bar{C}\text{—}S\cdot}} \qquad (7)$$

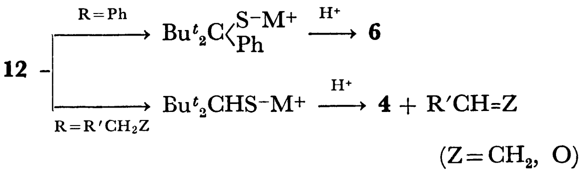


$$Bu^t_2C{=}S + R^-M^+ \longrightarrow \underset{\mathbf{12}}{\overset{R\cdot\quad M^+}{Bu^t_2\dot{C}\text{——}\bar{S}}} \qquad (8)$$

Under an aprotic condition, **11** is stabilized by radical-combination, whereas **12** is stabilized by either radical-combination or hydrogen-transfer, when possible.



$$\mathbf{11} \longrightarrow \overset{M^+}{Ph_2\bar{C}\text{-}SR} \xrightarrow{H^+} \mathbf{3}\ (R{=}Bu^n) \text{ or } \mathbf{5}\ (R{=}Ph) \qquad (9)$$

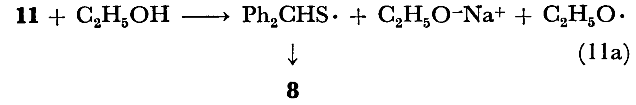


$$\mathbf{12} \begin{cases} \xrightarrow{R=Ph} Bu^t_2C\langle{}^{S^-M^+}_{Ph} \xrightarrow{H^+} \mathbf{6} \\ \xrightarrow[R=R'CH_2Z]{} Bu^t_2CHS^-M^+ \xrightarrow{H^+} \mathbf{4} + R'CH{=}Z \end{cases} \qquad (10)$$

$$(Z{=}CH_2,\ O)$$

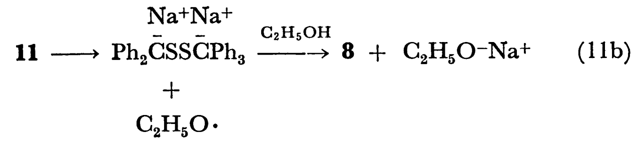
Note that a thiyl radical has less ability than a carbon radical to abstract a hydrogen atom.[15]

Under a protic condition, on the other hand, **11** abstracts a proton from the solvent to form a stable thiyl radical rather than to form relatively unstable carbanion. The fate



$$\mathbf{11} + C_2H_5OH \longrightarrow \underset{\substack{\downarrow\\ \mathbf{8}}}{Ph_2CHS\cdot} + C_2H_5O^-Na^+ + C_2H_5O\cdot \qquad (11a)$$

and/or



$$\mathbf{11} \longrightarrow \underset{\substack{+\\ C_2H_5O\cdot}}{\overset{Na^+Na^+}{Ph_2\bar{C}SS\bar{C}Ph_3}} \xrightarrow{C_2H_5OH} \mathbf{8} + C_2H_5O^-Na^+ \qquad (11b)$$

$$C_2H_5O\cdot + C_2H_5OH \longrightarrow C_2H_5OH + CH_3\dot{C}HOH \qquad (12)$$

$$CH_3\dot{C}HOH \xrightarrow{-H\cdot} CH_3CH{=}O \qquad (13)$$

$$(R^-M^+ = C_2H_5O^-Na^+)$$

of ethoxy radical is well known.[16] The reaction in Eq. (12) explains the scrambling of deuterium.

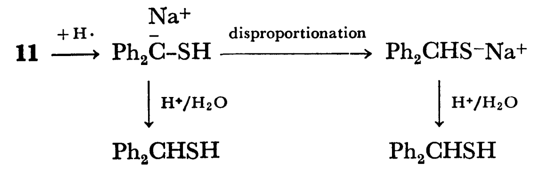
Similarly, **12** affords a stable thiolate anion by hydrogen-abstraction instead of forming an unstable carbon radical.

$$\mathbf{12} \longrightarrow Bu^t{}_2CHS^-Na^+ + CH_3CH{=}O \qquad (14)$$

$$(R^-M^+ = C_2H_5O^-Na^+)$$

About 20% of scrambling in the last reaction indicates that not all of the radical-ion pairs, **12**, undergo the spontaneous reaction shown in Eq. (14). Instead some of them dissociate and the ethoxy radical abstracts a hydrogen from ethanol (Eq. (12)). Note that the reaction with di-*t*-butyl thioketone is much slower than that of thiobenzophenone, which may describe larger scrambling in the reaction of di-*t*-butyl thioketon than in the reaction of thiobenzophenone.

The proposed mechanism is supported by the fact that the reaction of thiobenzophenone with sodium ethoxide in an aprotic solvent such as tetrahydrofuran or diglyme affords benzhydryl mercaptan in 79% yield together with small amount (10% yield) of the disulfide, **8**. Since there is no proton in the system and the sulfenate, expected to be formed by radical combination, is an unstable compound, **11** has to be stabilized by hydrogen-atom-transfer.



$$\begin{tikzcd} \mathbf{11} \arrow[r, "+H\cdot"] & \overset{Na^+}{Ph_2\bar{C}\text{-}SH} \arrow[r, "\text{disproportionation}"] \arrow[d, "H^+/H_2O"] & Ph_2CHS^-Na^+ \arrow[d, "H^+/H_2O"] \\ & Ph_2CHSH & Ph_2CHSH \end{tikzcd}$$

Experimental

Materials. Di-*t*-butyl thioketone,[11] thiobenzophenone,[17] hexyllithium,[18] and phenyllithium[19] were prepared according to literatures. Butyllithium was purchased from Merck & Co., Inc. Solvents were dried and purified by distillation prior to use. 1-Butanol-α,α-d_2 was obtained by reduction of methyl butyrate with lithium aluminium deuteride. Ethanol-*O*-*d* was purchased from Merck & Co., Inc. Butyllithium-β,β-d_2 was prepared according to the following scheme:

$$CH_3CH_2CO_2CH_3 \xrightarrow[2)\ H^+/H_2O]{1)\ LiAlD_4} CH_3CH_2CD_2OH \xrightarrow[H_2SO_4]{NaBr}$$

$$CH_3CH_2CD_2Br \xrightarrow[2)\ HCHO]{1)\ Mg} CH_3CH_2CD_2CH_2OH \xrightarrow[H_2SO_4]{NaBr}$$

$$CH_3CH_2CD_2CH_2Br \xrightarrow{Li} CH_3CH_2CD_2CH_2Li$$

General Procedure. All reactions were run both under nitrogen atmosphere with stirring and under high vacuum of about 10^{-6} Torr. For the latter reactions a solution of thioketone, a solution of organometallic reagent, and water were respectively vacuum-sealed in ampoules, which were connected with break-seals. The thioketone and organometallic reagent were mixed through a break-seal and, at the end of the reaction, water was added to the reaction mixture through the other break-seal. The apparatus was wrapped by aluminium foil to avoid unnecessary photoreactions.

*Reaction of Di-*t*-butyl Thioketone with Butyllithium.* Into 1.2 g of 20% hexane solution of butyllithium (4 mmol), was added 316 mg (2 mmol) of di-*t*-butyl thioketone at room temperature. The color of the thioketone disappeared immediately. Water (5 ml) was added to the reaction mixture and the organic materials were extracted with ether. The ether layer was dried over Drierite and the solvent was evaporated *in vacuo*. The residue was subjected to column chromatography over silica gel with benzene eluent, yielding 2,2,4,4-tetramethylpentane-3-thiol (**4**)[10] quantitatively.

*Reaction of Di-*t*-butyl Thioketone with Phenyllithium.* Into 7 ml of ether solution containing 420 mg (5 mmol) of phenyllithium was added 574 mg (3 mmol) of di-*t*-butyl thioketone at 0 °C. Usual work-up and column chromatography over silica gel with hexane eluent gave 210 mg (25% yield) of 2,2,4,4-tetramethyl-3-phenylpentane-3-thiol (**6**)[10] and 280 mg (35% yield) of di-*t*-butylmethyl phenyl sulfide (**7**).[10]

The sulfide, **7**, was oxidized with 30% hydrogen peroxide in acetic acid by keeping the solution in a refrigerator for 2 days. The solution was neutralized with sodium bicarbonate and the product was extracted with ether. The ether layer was dried over Drierite and the solvent was evaporated *in vacuo*. The white crystals thus obtained were recrystallized from hexane giving the corresponding sulfone: mp 138 °C. NMR $\delta_{CCl_4}^{TMS}$ 1.33 (s, 18H), 3.20 (s, 1H), and 7.33—7.90 (m, 5H). ν_{SO_2} 1130 and 1290 cm^{-1}. Found: C, 66.86; H, 9.22; S, 12.11%. Calcd for $C_{15}H_{24}O_2S$: C, 67.17; H, 8.92; S, 11.94%.

*Reaction of Di-*t*-butyl Thioketone with Sodium Ethoxide in Ethanol.* Into 5 ml of ethanol, 50 mg of metallic sodium was added. This ethanol solution was mixed with a solution of di-*t*-butyl thioketone (500 mg, 3.4 mmol) in 5 ml of ethanol. The whole mixture was kept at 60 °C for a day.

The reaction under nitrogen atmosphere, after work-up and column chromatography on silica gel with an eluent of a mixture of hexane–benzene (1 : 1), gave 250 mg (50% yield) of di(di-*t*-butyl)methyl disulfide: mp 74 °C. NMR $\delta_{CDCl_4}^{TMS}$ 1.15 (s, 18H) and 2.54 (s, 1H). IR 1215, 1362, 1387, 1475, and 2950 cm^{-1}. Found: C, 67.67; H, 12.13; S, 20.02%. Calcd for $C_{18}H_{38}S_2$: C, 67.85; H, 12.02; S, 20.13%. Mass spectrum M$^+$: *m/e* 318.

The reaction under high vacuum yielded, after work-up and column chromatography, 490 mg (98% yield) of **4**.

Reaction of Thiobenzophenone with Sodium Ethoxide in Ethanol. Into 1 ml of ethanol was dissolved 50 mg of metallic sodium and the solution was mixed with 2 ml of ethanol solution of thiobenzophenone (480 mg, 2.4 mmol) at room temperature. The reaction took place immediately. After addition of 2 ml of water, the precipitate was filtered off and recrystallized from a mixture of benzene and ethanol giving 480 mg (99% yield) of dibenzhydryl disulfide: mp 151—152 °C (lit,[20] 151—152 °C).

Reaction of Thiobenzophenone with Sodium Ethoxide in Tetrahydrofuran. Into 10 ml of tetrahydrofuran were dissolved 198 mg (1 mmol) of thiobenzophenone and 500 mg (7.35 mmol) of sodium ethoxide at room temperature. The reaction took place immediately. After addition of 10 ml of water, the organic materials were extracted with ether. The ether layer was dried over sodium sulfate and the solvent was removed *in vacuo.* The residue was chromatographed on a column of silicic acid and eluted with a hexane–benzene (8 : 2) mixture affording 157 mg of benzhydryl mercaptan[13] and 20 mg of dibenzhydryl disulfide.

*Reaction of Di-*t*-butyl Thioketone with Sodium Ethoxide in Tetrahydrofuran.* The reaction with di-*t*-butyl thioketone was similarly run as menthioned above and **4** was isolated in quantitative yield.

2,2,4,4-Tetramethylpentane-3-thiol. Into 10 ml of solution containing 40 mg of lithium aluminium hydride was added dropwise a solution of di-*t*-butyl thioketone (158 mg, 1 mmol) in 5 ml of ether under nitrogen atmosphere at 0 °C. After usual work-up, **4** was obtained in 72% yield (115 mg).[10]

Identification of Oxidized Products. An ether solution obtained from the reaction of di-*t*-butyl thioketone with hexyllithium was subjected to vpc analysis on Yanagimoto G-1800 (5% SD-200, 2 m, 27 °C, N_2 0.4 kg/cm^2, FID). Quantitative formation of hexene was thus confirmed. Another ether solution obtained form the reaction of di-*t*-butyl thioketone or thiobenzophenone with sodium isopropoxide in 2-propanol was quantitatively analyzed on vpc (Yanagimoto G-1800: 15% PEG, 1 m, 76 °C, N_2 0.4 kg/cm^2, FID). The formation of acetone was thus confirmed.

Table 3. Cartesian coordinates of thiocarbonyl compounds[a)]

Atom	*x*	*y*	*z*
	Thioacetone		
S	1.600000	0.000000	0.000000
Cl	0.000000	0.000000	0.000000
C2	−0.775000	1.342339	0.000000
C3	−0.775000	−1.342339	0.000000
H1	−0.956707	1.657066	−1.027633
H2	−0.185983	2.102044	0.513816
H3	−1.727432	1.212088	0.513816
H4	−0.956707	−1.657066	1.027633
H5	−0.185983	−2.102044	−0.513816
H6	−1.727432	−1.212088	−0.513816
	Thiobenzaldehyde		
S	0.000000	1.610000	0.000000
Cl	0.000000	0.000000	0.000000
C2	1.316359	−0.760000	0.000000
C3	1.316359	−2.150000	0.000000
C4	2.520134	−2.845000	0.000000
C5	3.723909	−2.150000	0.000000
C6	3.723909	−0.760000	0.000000
C7	2.520134	−0.065000	0.000000
H1	0.381052	−2.690000	0.000000
H2	2.520134	−3.925000	0.000000
H3	4.659216	−2.690000	0.000000
H4	4.659216	−0.220000	0.000000
H5	2.520134	1.015000	0.000000
H6	−0.540000	−0.935307	0.000000

a) Atom-numbers are shown in Fig. 1.

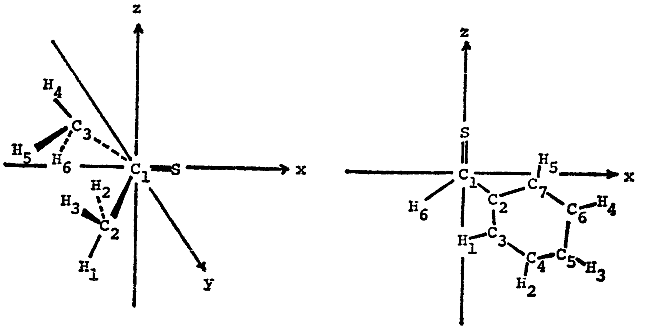


Fig. 1. Cartesian coordinates of thiocarbonyl compounds.

Into this ether solution was added ethanol solution of 2,4-dinitrophenylhydrazine. The isolated 2,4-dinitrophenylhydrazone (98% yield) melted at 128 °C (lit,[21] mp 128 °C).

Analyses of Deuterium Contents. Deuterium contents were analyzed on Varian T-60 NMR Spectrometer and Shimadzu LKB-9000S GC-MS Spectrometer attached by a MID-PM peak matcher.

Method of Calculation. Semi-empirical MO calculations were carried out with the usual unrestricted Hartree-Fock (UHF) method[22] using the INDO-type approximation. To evaluate the core resonance integrals, the Wolfsberg-Helmholz equation,[23] $H_{rs} = -KS(I_r + I_s)/2$, was used, where the value of the parameter K was taken to be 0.85. The two-center Coulomb repulsion integrals were calculated according to the Ohno's approximation.[24] The exponent of sulfur 3d orbitals and one-center Coulomb integrals between d orbitals were adopted to be 1.0 and 7.19, respectively, as reported by Nanda and Narasimhan.[25]

Other parameters including one-center exchange repulsion integrals were the same as those employed by Yonezawa and co-workers.[26] Furthermore, we discussed on the calculated results after a single annihilation proposed by Amos and Snyder.[27] The expectation values of the spin angular momentum operator S^2 from UHF method, $\langle S^2 \rangle_{UHF}$, were near 0.75, which is the eigenvalue of the pure doublet state.

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