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Convenient Preparation of S-Alkyl Thiol Ester

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〈**Abstract**〉

The use of tri-*n* butyl phosphine in place of triphenylphosphine for conversion of carboxylic acid into S-alkyl thiol esters and the scope and the limitation of the reaction have been studied.

Reaction of carboxylic acid with tri-*n*-butylphosphine and primary dialkyl disulfide and secondary dialkyl disulfide in methylene chloride at room temperature affords corresponding thiol esters in high yields. But the reaction does not occur with tertiary dialkyl disulfide.

편리한 알킬 티올 에스테르의 제조

양 성 봉 · 홍 창 용*
화 학 과
(1986. 9. 30 접수)

〈**요 약**〉

카르복실산과 디알킬디설파이드 트리노르말부틸포스핀과 반응시켜서 알킬티올에스테르를 얻을 수 있는 방법을 연구했다.

카르복시산과 1차 또는 2차 디알킬디설파이드를 디클로로메탄을 용매로 하여 실온에서 트리부틸포스핀과 반응을 시켜주었더니 빛시간 내로 상당히 좋은 수득률로 알킬티올에스테르가 얻어졌다. 그러나 3차 디알킬 설파이드의 경우에는 티올에스테르를 얻을 수 없었다.

I. Introduction

In general, thiol esters show higher reactivity and selectivity towards nucleophile than the corresponding oxygen analogues, which makes them the universal acylating agents in biochemical process. Recently, thiol esters have attracted a great deal of attention as active acylating agents in the synthesis of ketones[1], esters[2], peptides[3], β-lactams[4] and especially naturally occuring macrocyclic lactones[5]. Therefore, considerable attentions had been focused on the preparation of thiol esters, and a number of new methods have been developed[6].

Among these reported synthetic methods for the preparation of thiol esters which proceed under extremely mild conditions, the reaction of carboxylic acids and diphenyl disulfide with triphenylphosphine is the most frequently used and

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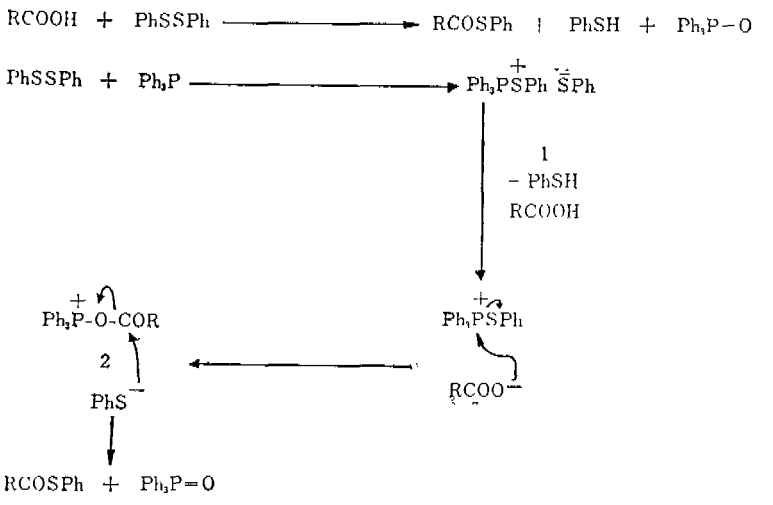


(1)

most effective[7]. The reaction pathway suggested by T. Mukaiyama et al., formulated by assuming the initial formation of the phosphonium salt 1 by nucleophilic attack of triphenylphosphine to diphenyl disulfide, which in turn is transformed by attack of the carboxylic acid to give 2. This then undergoes decomposition to give thiol ester.

A major drawback associated with this method is the inability of preparation of alkyl thiol esters due to the inertness of triphenylphosphine toward dialkyl disulfides.

$R'SSR' + Ph_3P \not\longrightarrow Ph_3\overset{+}{P}SR'\ \overset{-}{S}R' \cdots \rightarrow RCOSR'$

They suggested that the reactivity of the disulfide in this reaction is dependent on its oxidizing power which in turn decrease with the decreasing stability of the thiolate anion.

However, there is a report on the nucleophilicity of various organic phosphines which can solve this problem[8].

In that paper, Handerson, Jr. and Buckler reported thas tri-*n*-butylphosphine has much more powerful nucleophilicity than triphenylphosphine on the basis of kinetic data. They explained the effect of substituents on the nucleophilicity of the phosphine in terms of inductive, steric and bond hybridization.

$$R_3P + C_2H_5I \xrightarrow{k} R_3PC_2H_5^{+} + I^-$$

	k
$(n\text{-Bu})_3P$	$1.54\pm0.05, 10^{-3}$
$(Ph)_3P$	$3.78\pm0.02\times10^{-5}$

Lately, there are some reports on the reaction of the dialkyl disulfide by tri-*n*-butylphosphine. Humphrey and Potter observed the reduction of the alkyl and aromatic disulfides by tri-*n*-butylphosphine for the first time[9].

$$RSSR + (n\text{-Bu})_3P + H_2O \longrightarrow 2RSH + (n\text{-Bu})_3PO \qquad (2)$$

Tazaki and Takagi recently reported thioacetalization of epoxides and carbonyl compounds by the thiolate anion generated from the cleavage of dialkyl disulfide by tri-*n*-butylphosphine[10].

$$RCHO + R'SSR' + (n\text{-Bu})_3P \longrightarrow \begin{matrix} R & SR \\ & \times \\ R & SR \end{matrix} + (n\text{-Bu})_3P{=}O \qquad (3)$$

However, there are no reports in the literature on the preparation of thiol esters by reaction of tri-*n*-butylphosphine and disulfide with carboxylic acids. Therefore, we have expected that the use of tri-*n*-butylphosphine in place of triphenylphosphine as a nucleophile in the reaction of carboxylic acids and dialkyl disulfide

would lead to the formation of the corresponding alkyl thiol esters, alkyl thiols and tri-*n*-butylphosphine oxide.

$$RCOOH + RSSR + (n\text{-}Bu)_3P \longrightarrow RCOSR + RSH + (n\text{-}Bu)_3P\ O \quad (4)$$

Ⅱ. Results and Discussion

The reaction is normally carried out with equimolar amounts of carboxylic acids, dialkyl disulfide and tri-*n*-butylphosphine in methylene chloried under the dry nitrogen atmosphere. The reaction may be performed in acetonitrile, but it requires longer reaction time to complete the reaction than in methylene chloride.

Both aliphatic and aromatic, simple and sterically hindered carboxylic acids are used to determine the scope and the limitation of this method. Primary and secondary and tertiary disulfides are also used in this reaction.

1. Alkyl thiol esters from primary and secondary dialkyl disulfides

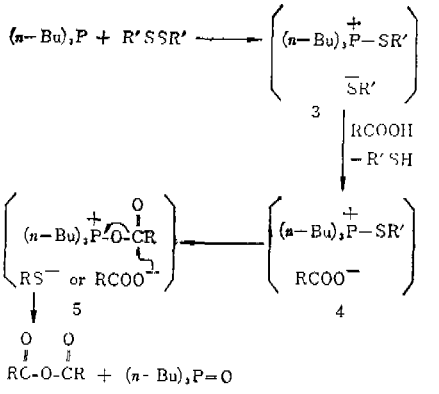
In the case of employment of primary dialkyl disulfides such as dimethyl disulfide, di-*n*-butyl disulfide and dibenzyl disulfide, the reaction is normally complete within 1 hour and can be best performed on aliphatic and simple aromatic carboxylic acids. In the case of secondary dialkyl disulfides, the reaction is complete within 3 hours with simple carboxylic acids. As shown in Table Ⅰ, yield of pure isolated thiol esters are generally high.

The IR spectrum of these thiol esters showed a carbonyl absorption at near 1,670cm^{-1} for thiol esters from aromatic carboxylic acids and at near 1,695cm^{-1} for thiol esters from aliphatic carboxylic acids, and their NMR spectra were in good agreement with the structure assigned.

However, as in Table Ⅱ, with sterically hindered acids like 1-adamantanecarboxylic acid, the reaction is slower and the yields are lower than simple carboxylic acids. But when the reaction is carried out without the solvent, the reaction is faster and complete within 1 hour.

The highly hindered 2,4,6-trimethylbenzoic acid(mesitoic acid) provides after workup a 72, 80% yield of mesitoic anhydride individually with dimethyl disulfide and di-*n*-butyl disulfide. Respectively, in addition to mesitoic anhydride, trace amounts of corresponding thiol esters are indicated by TLC. But, in the case of employment of dibenzyl disulfide, approximately equal amounts of mesitoic anhydride and benzyl thiomesitoate are obtained.

The formation of mesitoic anhydride can be explained by following mechanism. When the carboxylate anion instead of thiolate anion attacks phosphonium salt 5, corresponding anhydride can be produced.

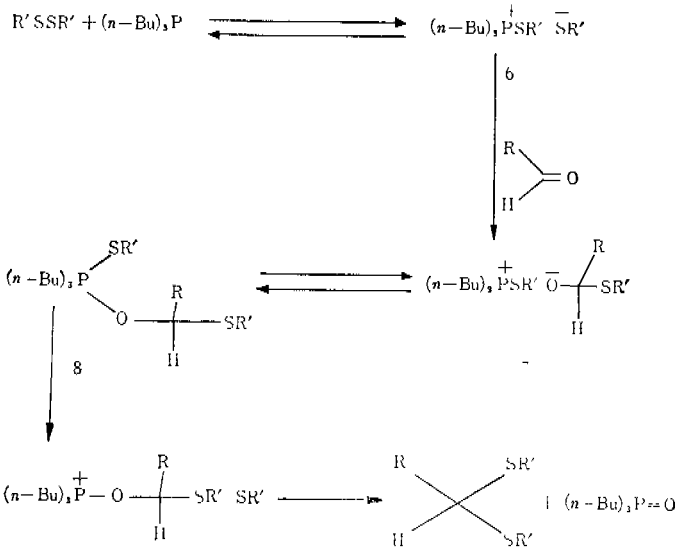


2. Thiolesterification of carboxylic acid in the presence of other functional groups.

Selective thiolesterification of carboxylic acid in the presence of other functional groups such as ketone or aldehyde has also been tested under the same conditions.

3-Benzoylpropionic acid which has aromatic ketone group gives corresponding thiol ester in high yield with its ketone group totally unaffected.

$$PhCOCH_2CH_2COOH + CH_3SSCH_3 \xrightarrow{(n\text{-}Bu)_3P} PhCOCH_2CH_2COSCH_3$$



But competitive reaction of phenylacetic acid and benzaldehyde with di-*n*-butyl disulfide and tri *n* butylphosphine gives not only *n*-butyl thiophenylacetate in 52% yield, but also benzaldehyde *n* butylthioacetal in 36% yield after separation by silica gel column chromatography using petroleum ether-ethyl ether(20 : 1) as an eluant.

$$PhCH_2COOH \xrightarrow[(n\text{-}Bu)_3P]{(n\text{-}Bu)_2S_2} PhCH_2COSCH_2CH_2CH_2CH_3 \quad 52\%$$

$$PhCHO \xrightarrow[(n\text{-}Bu)_3P]{} PhCH(SCH_2CH_2CH_2CH_3)_2 \quad 36\%$$

Tazaki and Takagi suggested the following reaction mechanism for this thioacetal formation of aldehyde.

The thiolate anion of the thiophosphonium thiolate 6 attacks carbon to produce 7. Then phosphonium cation in 7 undergoes a ligand exchange reaction with the external anion via pentacoordinated phosphonium 8 to form oxyphosphonium thiolate 9, which further degrades into phosphine oxide and thioacetal via Arbuzov-type reaction.

In the case of trans-cinnamic acid, not only methyl thiocinnamate 10 but also methyl(3-methylthio) thiocinnamate 11 is obtained as a ratio of 53 : 47, which is determined by the integration ratio of SCH_3 group in NMR spectrum. The adduct 11 resulted from the 1,4-addition of methyl thiol to 10 initially formed by the reaction of equation(5).

$$PhCH{=}CHCSCH_3 + CH_3SH \longrightarrow PhCHCH_2CSCH_3 \quad (5)$$

(10 → 11)

3. Phenyl thiol esters from phenyl disulfide and tri-*n*-butylphosphine

The tentative reaction of several carboxylic acids with diphenyl disulfide and tri-*n*-butylphosphine instead of triphenylphosphine has also been performed to compare with the results of Mukaiyama group's experiment.

As shown in Table Ⅲ, the reactions are very fast and complete within 10 minutes at room temperature, and corresponding phenyl thiol esters are obtained in high yield after column separation. Even sterically hindered mesitoic acid gives its phenyl thiol ester in 90% yield without anhydride formation.

Previously, Mukaiyama et al. obsered that thiol ester formation of several acids with

Table I

RCOOH	RSSR	Time	Product	Yield(%)
$CH_3(CH_2)_6COOH$	$(CH_3)_2S_2$	0.5h	$CH_3(CH_2)_6COSCH_3$	90
$CH_3(CH_2)_6COOH$	$(n\text{-}Bu)_2S_2$	1h	$CH_3(CH_2)_6COS(CH_2)_3CH_3$	89
$CH_3(CH_2)_6COOH$	$(PhCH_2)_2S_2$	0.5h	$CH_3(CH_2)_6COSCH_2Ph$	90
PhCOOH	$(CH_3)_2S_2$	0.5h	$PhCOSCH_3$	81
PhCOOH	$(n\text{-}Bu)_2S_2$	1h	$PhCOS(CH_2)_3CH_3$	87
PhCOOH	$(PhCH_2)_2S_2$	0.5h	$PhCOSCH_2Ph$	89
$Ph_2CHCOOH$	$(CH_3)_2S_2$	0.5h	$Ph_2CHCOSCH_3$	91
$Ph_2CHCOOH$	$(n\text{-}Bu)_2S_2$	1h	$Ph_2CHCOS(CH_2)_3CH_3$	88
$Ph_2CHCOOH$	$(PhCH_2)_2S_2$	0.5h	$Ph_2CHCOSCH_2Ph$	90
$(CH_3)_2CHCOOH$	$(n\text{-}Bu_2)S_2$	1h	$(CH_3)_2CHCOS(CH_2)_3CH_3$	81
$CH_3(CH_2)_6COOH$	$(sec\text{-}Bu)_2S_2$	3h	$CH_3(CH_2)_6COS(sec\text{-}Bu)$	88
PhCOOH	$(sec\text{-}Bu)_2S_2$	3h	$PhCOS(sec\text{-}Bu)$	86
$PhCH_2COOH$	$(sec\text{-}Bu)_2S_2$	3h	$PhCH_2COS(sec\text{-}Bu)$	90
$Ph_2CHCOOH$	$(sec\text{-}Bu)_2S_2$	3h	$Ph_2CHCOS(sec\text{-}Bu)$	81

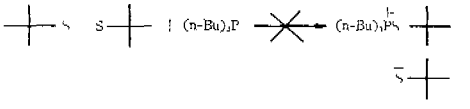
diphenyl disulfide and triphenylphosphine required cosiderably strong reaction condition, i. e. refluxing in acetonitrile for 3—5 hours[6]. Therefore, our experimental result directly suggests that tri-*n*-butylphosphine is much more effective than triphenylphosphine for the cleavage of disulfide bond and thus much more effective for the preparation of thiol esters.

4. Alkyl thiol esters from tertiary dialkyl disulfide-ineffective

However, in the case of employment of di-tert-butyl disulfide, the reaction did not occured at all even after prolonged stirring at 40°C for 24 hours. But these are not unexpected results according to the report of Harpp and Gleason. They have found that tris(diethylamino) phosphine 12 is a very effective reagent for desulfurization of disulfides by examining the reaction with a wide variety of disulfides which usually resist desulfurization by ordinary trivalent phosphines[11].

$$R'SSR' + \underset{12}{(Et_2N)_3P} \longrightarrow (Et_2N)_3\overset{+}{P}SR'\ \overset{-}{S}R' \longrightarrow \underset{+}{R'SR'} \quad (Et_2N)_3P{=}S \qquad (6)$$

In their report, primary dialkyl disulfides are easily desulfurized, but tertiary dialkyl disulfide no reaction has occured after 48 hours at 80°C. Therefore, it seems to us that tri-*n*-butylphosphine is less effective toward thiolesterification of carboxylic acids with hindered dialkyl disulfide such as tertiary disulfides, because tri-*n*-butylphosphine has a less powerful nucleophilicity than tris(diethylamino) phosphine.

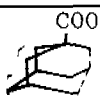
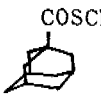
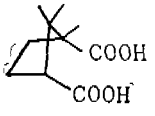
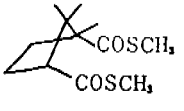
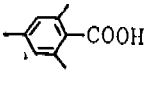
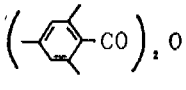
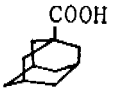
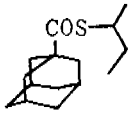


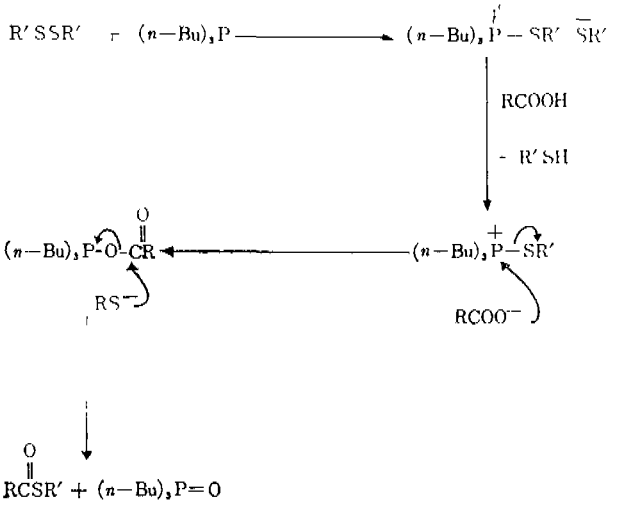
In conclusion, the reaction mechanism for the preparation of alkyl thiol esters by the reaction of carboxylic acids and dialkyl disulfide with tri-*n*-butylphosphine can be suggested as following pathway:

Finally; from all experimental results described here, the relative reactivities of various disulfides and trivalent phosphines can be suggested as follows:

$$PhSSPh > PHCh_2SSCH_2Ph > CH_3SSCH_3 > n\text{-}BuSS\text{-}n\text{-}Bu > sec\text{-}BuSSsec\text{-}Bu > tert\text{-}BuSStert\text{-}Bu$$
$$(Et_2N)_3P > (n\text{-}Bu)_3P > (Ph)_3P$$
(decreasing order)

Table II

RCOOH	R′ SSR′	Time	Product	Yield (%)
	$(CH_3)_2S_2$	0.5h (neat)		85
〃	〃	1h (CH_2Cl_2)	〃	76
〃	$(n\text{-Bu})_2S_2$	1h (neat)		57
〃	〃	6h (CH_2Cl_2)	〃	—
〃	$(PhCH_2)_2S_2$	0.5h		84
	$(CH_3)_2S_2$	0.5h (neat)		80
	$(CH_3)_2S_2$	0.5h		72
〃	$(n\text{-Bu})_2S_2$	1h	〃	80
〃	$(PhCH_2)_2S_2$	0.5h	〃	37
			Thiol ester	31
	$(sec\text{-Bu})_2S_2$	6h		76
$CH_3(CH_2)_6COOH$	$(tert\text{-Bu})_2S_2$	24h	No reaction	
PhCOOH	〃	24h	〃	



Ⅲ. Experimental Section

Proton nuclear magnetic resonance spectra were obtained on a Varian A-60 spectrometer, and chemical shifts are expressed as δ units relative tetramethylsilane.

Infrared spectra were recored on a Perkin-Elmer 267, and the frequences are given in reciprocal centimeters.

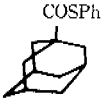
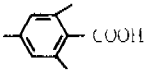
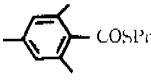
Analytical thin-layer chromatography was performed on precoated silica gel glass plates(0.25mm, 60F-254, E. Merck), and silica gel (activity Ⅲ, 04526, ICN) was used for column chromatography.

Methylene chloride was distilled over lithium aluminium hydride under the nitrogen atmosphere and most of the organic compounds utilized in this study were commercial products of highest purity.

All glassware was dried in a drying oven and cooled under the dry nitrogen atmosphere, and all experiments were carried out under the dry nitrogen atmosphere.

Since the reaction performed are all similar in many respects, typical reactions will be described as specific examples.

Table Ⅲ

RCOOH	RSSR	Time	Product	Yield
PhCH=CH(COOH)	$(CH_3)_2S_2$	30 min	$PhCH{=}CHCOSCH_3$ 53 $PhCH(SCH_3)CH_2COSCH_3$ 47	88
PhCH=CH(COOH)	$(CH_3)_2S_2$	30 min	$CH_3CH{=}CHCOSCH_3$ 5 $CH_3CH(SCH_3)CH_2COSCH_3$ 95	63
$PhCOCH_2CH_2$(COOH)	$(CH_3)_2S_2$	30 min	$PhCOCH_2CH_2COSCH_3$	90
$PhCH_2COOH$			$PhCH_2CO(CH_2)_3CH_3$	52
PhCHO	$(n\text{-}Bu)_2S_2$	30 min	$PhCH(SCH_2CH_2CH_2CH_3)_2$	36
PhCOOH	Ph_2S_2	10 min	PhCOSPh	90
$(CH_3)_3CCOOH$	Ph_2S_2	10 min	$(CH_3)_3CCOSPh$	84
	Ph_2S_2	10 min		86
	PH_2S_2	10 min		90

1. Preparation of S-methyl thiocaprylate

To 144.2mg(1mmol) of *n*-caprylic acid and 94.2mg(1mmol) of dimethyl disulfide dissolved in 4cc of methylene chloride was added 202.3 mg(1mmol) of tri-*n*-butylphosphine under the nitrogen atmosphere. The reaction mixture was stirred for 30 minutes and concentrated under reduced pressure. The residue was subjected to silica gel column chromatography with hexane-ethyl ether(10 : 1 V/V) as an eluant to give pure S-methyl thiocaprylate as colorless oil(156 mg, 90% yield):

^{1}HNMR($CDCl_3$); δ 0.88(br *t*, 3H, CH_3)
1.35(br *s*, 8H, CH_2)
1.40—2.00(*m*, 2H, CH_2)
2.34(*s*, 3H, SCH_3)
2.58(*t*, *J*=7 Hz, 2H, CH_2)

IR(CCl_4); 1692cm^{-1}(C=O)

2. Reaction of mesitoic acid with dimethyl disulfide and tri-*n*-butyl-phosphine.

To 164.2mg(1 mmol) of mesitoic acid and 94.2mg (1 mmol) of dimethyl disulfide dissolved in 4cc of methylene chloride was added 202.3 mg(1 mmol) of tri-*n*-butylphosphine under the nitrogen atmosphere. After 30 minutes, the reaction mixture was concentrated in vacuo and subjected to silica gel column chromatography with hexane-ethyl ether(20 : 1) as an eluant to give mesitoic anhydride as white solid(262mg, 72% yield).:

^{1}HNMR($CDCl_3$); δ 2.42 and 2.56(*s*, 9H, CH_3)
6.90(*s*, 2H, aromatic protones)

IR(CCl_4); 1730 and 1790cm^{-1}(aromatic anhydride)

Ⅳ. Spectral Data of Products

1. $CH_3(CH_2)_6COSCH_3$
^{1}HNMR($CDCl_3$); δ 0.88(br *t*, J=5Hz, 3H, CH_3)
1.35(br *s*, 8H, CH_2)
1.40—2.00(*m*, 2H, CH_2)
2.35(*s*, 3H, SCH_3)
2.58(*t*, *J*=7 Hz, 2H, CH_2-CO)
IR(CCl_4); 1,692cm^{-1}(C=O)

2. $CH_3(CH_2)_6COS(CH_2)_3CH_3$
^{1}HNMR($CDCl_3$); δ 0.90(*m*, 6H, CH_3)
1.35(br *s*, 10H, CH_2)
1.40—2.00(*m*, 4H, CH_2)
2.55(*t*, *J*=7 Hz, 2H, SCH_2)
2.82(*t*, *J*=7 Hz, 2H, $COCH_2$)
IR(CCl_4); 1,690cm^{-1}(C=O)

3. $CH_3(CH_2)_6COSCH_2Ph$
^{1}HNMR($CDCl_3$); δ 0.90(br *t*, *J* 5 Hz, 3H, CH_3)
1.34(br *s*, 6H, CH_2)
1.51(*m*, 4H, CH_2)
2.45(*t*, *J* 7 Hz, 2H, CH_2-CO)
2.98(*s*, 2H, CH_2Ph)
7.20(*s*, 5H, aromatic protons)
IR(CCl_4); 1,690cm^{-1}(C=O)

4. $PhCOSCH_3$
^{1}HNMR($CDCl_3$); δ 2.47(*s*, 3H, SCH_3)
7.20- 8.10(*m*, 5H, aromatic H)
IR(CCl_4); 1,660cm^{-1}(C=O)

5. $PhCOS(CH_2)_3CH_3$
^{1}HNMR($CDCl_3$); δ 1.00(br *t*, *J*=5 Hz, 3H, CH_3)
1.20—2.00(*m*, 4H, CH_2)
3.10(*t*, *J*=7, Hz, 2H, SCH_2)
7.20—8.10(*m*, 5H, aromatic H)
IR(CCl_4); 1,670cm^{-1}(C=O)

6. $PhCOSCH_2Ph$
^{1}HNMR($CDCl_3$); δ 4.30(*s*, 2H, SCH_2)
7.20—8.10(*m*, 10H, aromatic H)

IR(CCl_4); 1,670cm^{-1}(C=O)

7. $Ph_2CHCOSCH_3$

^{1}HNMR($CDCl_3$); δ 2.35(*s*, 3H, CH_3)
5.22(*s*, 1H, CHCO)
7.28(*s*, 10H, aromatic H)

IR(CCl_4); 1,698cm^{-1}(C=O)

8. $Ph_2CHCOS(CH_2)_3CH_3$

^{1}HNMR($CDCl_3$); δ 0.90 (*m*, 3H, CH_3)
1.10—1.90(*m*, 4H, CH_2)
2.92(*t*, *J*=7 Hz, 2H, SCH_2)
5.20(*s*, 1H, CHCO)
7.30(*s*, 10H, aromatic protones)

IR(CCl_4); 1,697cm^{-1}(C=O)

9. $Ph_2CHCOSCH_2Ph$

^{1}HNMR($CDCl_3$); δ 4.10(*s*, 2H, SCH_2Ph)
5.18(*s*, 1H, CHCO)
7.22(*s*, 10H, aromatic protones)

IR(CCl_4); 1,697cm^{-1}(C=O)

10. $(CH_3)_2CHCOS(CH_2)_3CH_3$

^{1}HNMR($CDCl_3$); δ 1.00(*t*, *J*= 5 Hz, 3H, CH_3)
1.35 (*d*, *J*=7 Hz, 6H, $(CH_3)_2C$)
1.40—2.00(*m*, 4H, CH_2)
2.50—3.10(*m*, 1H, CH)
3.00(*t*, *J*=7 Hz, 2H, SCH_2)

IR(CCl_4); 1,695cm^{-1}(C=O)

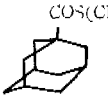
11. Methyl thioadamantanecarboxylate

^{1}HNMR($CDCl_3$); δ 1.60—2.20(*m*, 15H, aliphatic H)
2.25(*s*, 3H, SCH_3)

IR(CCl_4); 1,675cm^{-1}(C=O)

12. *n*-Butyl thioadamantanecarboxylate

^{1}HNMR($CDCl_3$); δ 0.90(*t*, *J*=5 Hz, 3H, CH_3)
1.20—2.00(*m*, 4H, CH_2)
1.60—2.30(*m*, 15H, aliphatic H)
2.80(*d*, *J*=7 Hz, 2H, SCH_2)



IR(CCl_4); 1,680cm ^{1}(C=O)

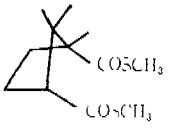
13. Benzyl thioadamantanecarboxylate

^{1}HNMR($CDCl_3$); δ 1.60—2.30(*m*, 15H, aliphatic H)
4.20(*s*, 2H, SCH_2)
7.38(*m*, 5H, aromatic H)

IR(CCl_4); 1,680cm^{-1}(C=O)

14. Dimethyl *d*-camphorate

^{1}HNMR($CDCl_3$); δ 0.80(*s*, 3H, CH_3)
1.30 and 1.40(*s*, 6H, CH_3)
2.36 and 2.40(*s*, 6H, SCH_3)
2.70—3.22(*m*, 1H, CH)



IR(CCl_4); 1,680 and 1,690cm^{-1}(C=O)

15. Mesitoic anhydride

^{1}HNMR($CDCl_3$); δ 2.42 and 2.56(s, 9H, CH_3)
6.90(*s*, 2H, aromatic H)

IR(CCl_4); 1,730 and 1,790 (CO—O—CO) cm^{-1}

16. Benzyl thiomesitoate

^{1}HNMR($CDCl_3$); δ 2.42 and 2.56(*s*, 9H, CH_3)
4.22(*s*, 2H, SCH_2)
6.90(*s*, 2H, aromatic H)
7.22(*s*, 5H, aromatic H)

IR(CCl_4); 1,670cm^{-1}(C=O)

17. $PhCH{=}CHCOSCH_3$ 53
$PhCH(SCH_3)CH_2COSCH_3$ 47

^{1}HNMR($CDCl_3$); δ 1,90(*s*, 3H, SCH_3)
2.23(*s*, 3H, $COSCH_3$)
2.42(*s*, 3H, $COSCH_3$)
3.07(*d*, *J*=8 Hz, 2H, CH_2)
4.12(*t*, *J*=8 Hz, 1H, CH)
6.62(*d*, *J*=16 Hz, 1H, C=CH)
7.57(*d*, *J*=16 Hz, 1H, C=CH)
7.25(*m*, 10H, aromatic H)

IR(CCl_4); 1,695cm^{-1} and 1,665cm^{-1}(C=O)

18. $CH_3CH{=}CHCOSCH_3$ 5
$CH_3CH(SCH_3)CH_2COSCH_3$ 95

^{1}HNMR($CDCl_3$); δ 1.40(*d*, *J*=6 Hz, 3H, CH_3)
2.21(*s*, 3H, SCH_3)
2.43(*s*, 3H, $COSCH_3$)
2.70—3.00(*m*, 2H, CH_2)
3.00—3.60(*m*, 1H, CH)

IR(CCl_4); 1,695cm^{-1}(C=O)

19. $PhCOCH_2CH_2COSCH_3$

^{1}HNMR($CDCl_3$); δ 2.28(*s*, 3H, SCH_3)
2.55—3.45(*m*, 4H, CH_2)
7.20—8.00(*m*, 5H, aromatic H)
IR(CCl_4); 1,685 and 1,690cm^{-1}(COS and CO)

20. *n*-Butyl thiophenylacetate
^{1}HNMR($CDCl_3$); δ 0.90(*t*, *J*=5 Hz, 3H, CH_3)
1.20—1.90(*m*, 4H, CH_2)
2.81(*t*, *J*=7 Hz, 2H, SCH_2)
3.71(*s*, 2H, CH_2CO)
7.22(*s*, 5H, aromatic H)
IR(CCl_4); 1,690cm^{-1}(C=O)

21. Benzaldehyde *n*-butylthioacetal
^{1}HNMR($CDCl_3$); δ 0.95(*m*, 6H, CH_3)
1.20—2.00(*m*, 8H, CH_2)
2.58(*t*, *J*=7 Hz, 4H, SCH_2)
4.83(*s*, 1H, CH)
7.10—7.60(m, 5H, aromatic H)

22. Phenyl thiobenzoate
IR(CCl_4); 1,688cm^{-1}(C=O)

23. $(CH_3)_3CCOSPh$
^{1}HNMR($CDCl_3$); δ 1.34(*s*, 9H, CH_3)
7.37(s, 5H, aromatic H)
IR(CCl_4); 1,692cm^{-1} (C=O)

24. Phenyl thioadamantanecarboxylate
^{1}HNMR($CDCl_3$); δ 1.50—2.20(*m*, 15H, aliphatic H)
7.12(*s*, 5H, aromatic H)
IR(CCl_4); 1,695cm^{-1}(C=O)

25. Phenyl thiomesitoate
^{1}HNMR($CDCl_3$); δ 2.25 and 2.37(*s*, 9H, CH_3)
6.75(*s*, 2H, aromatic H)
7.42(*s*, 5H, aromatic H)
IR(CCl_4); 1,685cm^{-1}(C=O)

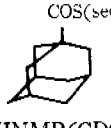
26. $CH_3(CH_2)_6COS$(sec-Bu)
^{1}HNMR($CDCl_3$); δ 0.88 and 0.99(br *t*, *J*=5 Hz, 6H, CH_3)
1.33(*d*, *J* 8 Hz, 3H, CH_3-CH)
1.35(br *s*, 8H, CH_2)
1.45—2.00(*m*, 4H, CH_2)
2.55(*t*, *J*=7 Hz, 2H, CH_2-CO)
3.52(*m*, 1H, SCH)
IR(CCl_4); 1,695cm^{-1}(C=O)

27. PhCOS(sec-Bu)
^{1}HNMR($CDCl_3$); δ 0.96(*t*, *J*=5 Hz, 3H, CH_3)
1.33(*d*, *J*=7 Hz, 3H, CH_3-CH)
1.50—2.00(*m*, 2H, CH_2)
3.75(*m*, 1H, SCH)
7.20—8.20(*m*, 5H, aromatic H)
IR(CCl_4); 1,670cm^{-1}(C=O)

28. $PhCH_2COS$(sec-Bu)
^{1}HNMR($CDCl_3$); δ 0.96(*t*, *J*=5 Hz, 3H, CH_3)
1.33(*d*, J=8 Hz, 3H, CH_3 CH)
1.45—2.00(*m*, 2H, CH_2)
3.51(*m*, 1H, SCH)
3.79(*s*, 2H, CH_2CO)
7.30(*s*, 5H, aromatic H)
IR(CCl_4); 1,690cm^{-1}(C=O)

29. PhCHCOS(sec-Bu)
^{1}HNMR($CDCl_3$); δ 0.98(*t*, *J*=5 Hz, 3H, CH_3)
1.33(*d*, *J*=8 Hz, 3H, CH_3 CH)
1.40—2.00(*m*, 1H, SCH)
5.20(*s*, 1H, CHCO)
7.30(*s*, 5H, aromatic H)
IR(CCl_4); 1,692cm^{-1}(C=O)

30.



^{1}HNMR($CDCl_3$); δ 0.99(*t*, *J*=5 Hz, 3H, CH_3)
1.33(*d*, *J*=8 Hz, 3H, CH_3 CH)
1.40—2.00(*m*, 2H, CH_2)
1.60—2.30(*m*, 15H, aliphatic H)
3.51(*m*, 1H, SCH)
IR(CCl_4); 1,680cm^{-1}(C=O)

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