Synthesis and Reduction of Thiocarboxylic *O*-Esters

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Brian Jones was born in Salt Lake City, UT. He received his B.A. degree from Brigham Young University in 1979, where he continued study in pursuit of a Ph.D. degree in the field of macrocyclic chemistry under Professor Bradshaw. His dissertation concerned the preparation of chiral macrocyclic ligands and their use in enantiomeric recognition of chiral alkylammonium salts. Since completing the requirements for this degree in 1983, he has been working with Professor Milton L. Lee and Professor Bradshaw at BYU on the synthesis of speciality siloxane phases for chromatographic separations.

Jerald S. Bradshaw was born in Cedar City, UT, and received a B.A. degree in Chemistry at the University of Utah in 1955. After 4 years as an officer in the U.S. Navy, he enrolled in a Ph.D. program at UCLA. He received the Ph.D. in 1963 with Professor Donald J. Cram on electrophilic substitution at saturated carbon. He received an NSF postdoctoral fellowship for the 1962–1963 academic year to work with Professor George S. Hammond at Cal Tech. After 3 years as a research chemist at Chevron Research in Richmond, California, he joined the faculty at the Brigham Young University at Provo, Utah in 1966. He was named Professor of the Year at BYU in 1975. He was a U.S. National Academy of Science Exchange Professor for the academic year of 1972–1973 and the Summer of 1982 working with Professor Miha Tisler at the University of Ljubljana, Yugoslavia. He also was a visiting professor with Dr. J. F. Stoddart at the University of Sheffield, England in 1978. He is a member of the Advisory Board for the International Society of Heterocyclic Chemistry and a member of the American Chemical Society. His research interests are the synthesis and cation complexation properties of macrocyclic multidentate compounds, the photochemical reactions of heterocyclic compounds and the preparation of new polysiloxanes for chromatography uses.

I. Introduction

Thiocarboxylic *O*-esters are a class of compounds that have received relatively little attention in the chemical literature. Recent efforts, however, have led to an increasing variety of synthetic methods for preparing these compounds as well as new applications for their use, both as synthetic intermediates and final products.

A recent review by Scheithauer and Meyer[1] thoroughly describes the advances in this field through 1976. This review will follow a similar format but will be much more narrow in scope. It will concern itself only with compounds bearing the functionality –C(S)–OC– that are either new or that were prepared by a new synthetic method. The time period covered is January 1977 to July 1982.

Each section in the first portion discusses a synthetic method in some detail. The discussion is followed by a tabular listing of compounds prepared by that route, including yields, physical data, and references. The final portion is a section dealing with reduction reactions on thiocarboxylic *O*-esters. A brief discussion of each method is followed by a tabular listing of specific compounds reduced.

II. Preparation of Thiocarboxylic O-Esters

A. Sulfhydrolysis of Imino Esters

Imino esters are easily prepared from many nitriles through the Pinner synthesis.[2] These compounds can be treated with hydrogen sulfide in pyridine to give thiocarboxylic *O*-esters as shown below. Due to the

$$RC(=NR'')OR' \xrightarrow[H^+]{H_2S} RC(=S)OR' + R''NH_3^+$$

†Contribution No. 316 from the Institute for Thermochemical Studies.

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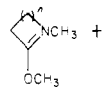
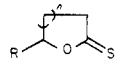
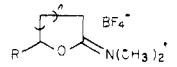
TABLE I. Thiocarboxylic *O*-Esters ($R^1C(=S)(OR^2)$) by Sulfhydrolysis of Imino Compounds

R^1	R^2	method	yield, %	bp, °C (mm)	ref
CH_3	$(CH_2)_2C_6H_5$	imino ester-HCl + H_2S		98 (1.8)	3
$CH_3CH=CH$	C_2H_5	imidinium BF_4 + H_2S	90	61 (12)	4
$CH_3CONCH_3(CH_2)_n$	CH_3	 + BF_4^- + NaHS			
$n = 2$			66, 90	oil	5, 6
$n = 3$			70	oil	5, 6
C_6H_5CHOH	C_2H_5	imino ester-HCl + H_2S	75	93 (0.08)[a]	7
C_6H_5CHOH	$CH(CH_3)_2$	imino ester-HCl + H_2S	69	97 (0.06)	7
$2,3\text{-}(CH_3)_2C_6H_3OCH_2$	C_2H_5	imino ester-HCl + H_2S	27		8
$C_6H_5CH=CH$	C_2H_5	imidinium BF_4 + H_2S	87	80 (0.2)	4
C_6H_5	C_2H_5	imidinium BF_4 + (1) NaCN, (2) H_2S			9
C_6H_5	C_5H_{11}	imino ester-HCl + H_2S		128 (3.4)	3
C_6H_5	$(CH_2)_2CH(CH_3)_2$	imino ester-HCl + H_2S		129-130 (3.4)	3
C_6H_5	$(CH_2)_2SO_2C_6H_4CH_3\text{-}4$	imino ester-HCl + H_2S	92	mp 96-97	10
$3\text{-}BrC_6H_4$	C_2H_5	imino ester-HCl + H_2S		98-99.5 (3)	11
$4\text{-}ClC_6H_4$	C_2H_5	imidinium BF_4 + (1) NaCN, (2) H_2S			9
$2\text{-}HOC_6H_4$	CH_3	imino ester-HCl + H_2S	77	75-77 (0.2)	7
$3\text{-}CH_3C_6H_4$	C_2H_5	imidinium BF_4 + (1) NaCN, (2) H_2S			9
$4\text{-}CH_3C_6H_4$	C_2H_5	imidinium BF_4 + (1) NaCN, (2) H_2S			9
$3\text{-}NO_2C_6H_4$	C_2H_5	imidinium BF_4 + (1) NaCN, (2) H_2S			9
$4\text{-}NO_2C_6H_4$	C_2H_5	imidinium BF_4 + (1) NaCN, (2) H_2S			9
$4\text{-}(CH_3O_2C)C_6H_4$	CH_3	imino ester + H_2S			12
$3\text{-}(C_2H_5O_2C)C_6H_4$	C_2H_5	imino ester + H_2S			12
$3\text{-}(C_2H_5O_2C)\text{-}5\text{-}((CH_3)_3C)C_6H_3$	C_2H_5	imino ester + H_2S			12
$C_2H_5OC(S)(CH_2)_n$	C_2H_5				
$n = 1$		bis(imino ester-HCl) + H_2S	81	71 (0.2)	13
$n = 2$		bis(imidinium BF_4) + H_2S	81	73 (0.04)	14
$n = 3$		bis(imidinium BF_4) + H_2S	89	84 (0.04)	14
$n = 4$		bis(imidinium BF_4) + H_2S	75	75 (0.04)	14
$C_2H_5OC(S)(CH_2)_5$	C_2H_5	bis(imidinium BF_4) + H_2S	67	108 (0.04)	14
$C_2H_5OC(S)CH=CH$	C_2H_5	bis(imidinium BF_4) + H_2S	98	mp 61-62	4
$3\text{-}(C_2H_5OC(S))C_6H_4$	C_2H_5	bis(imino ester) + H_2S			12
$3\text{-}(C_2H_5OC(S))\text{-}5\text{-}(C(CH_3)_3)C_6H_3$	C_2H_5	bis(imino ester) + H_2S			12, 15
	CH_3	bis(imino ester-HCl) + H_2S	70	mp 110-110.5	16
$S(CHCH_3CH_2CSOC_2H_5)_2$		$CH_3CH=CHC(OC_2H_5)=N(CH_3)_2^+$ BF_4^- + H_2S	73	124 (0.05)	4
$S(CH(CSOC_2H_5)CH_2\text{-}CSOC_2H_5)_2$		$=(CHC(OC_2H_5)=N(CH_3)_2)_2^+$ + H_2S	80		4
		 + NaHS (CH_3COCl)			
$n = 1$; R = H			78		6, 17
$n = 2$; R = H			43		17
$n = 3$; R = H			84		17
$n = 1$; R = CH_3			93		17

[a] mp 34 °C.

availability of nitriles, this synthetic route is one of the more commonly employed methods for preparing the thiocarboxylic *O*-esters. Thioamides are often major side products, but their production can be minimized by including an equivalent amount of acid in the reaction medium to protonate the evolved amine. Imidimium ester salts also have been used in this reaction.

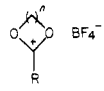
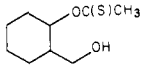
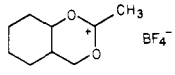
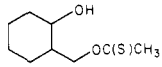
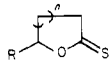
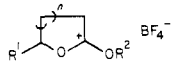
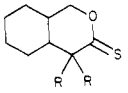
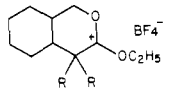
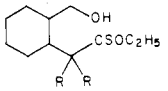
Thiocarboxylic *O*-esters prepared from the imino esters and the imidimium ester salts are listed in Table I.

B. Sulfhydrolysis of Dialkoxycarbonium Ions

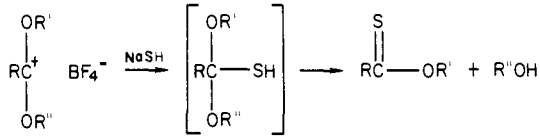
This synthetic method has only recently been utilized for the preparation of thiocarboxylic *O*-esters and lactones. Kaloustian and Khourin report that the sulfhydrolysis of dialkoxycarbonium ions is a convenient synthetic route to thiono lactones as well as various open-chain thiono ester derivatives.[18-21] These reactions were studied as part of a continuing investigation by those authors on the chemistry of tetrahedral intermediates.

The procedure involves treatment of the dialkoxycarbonium tetrafluoborate compound with anhydrous sodium sulfide or sodium hydrosulfide in acetonitrile at low temperatures. Acetone was used as the solvent in a few cases. The thiono lactone or ester is isolated

TABLE II. Thiocarboxylic O-Esters by Sulfhydrolysis of Dialkoxycarbonium Ions

product	starting compound	method	yield, %	ref
C_6H_5CSOR	$C_6H_5C(OR)_2^+ BF_4^-$	Na_2S		
$R = CH_3$			46	19
$R = C_2H_5$			40	19
$RCSO(CH_2)_nOH$		Na_2S		
$n = 2; R = CH_3$			85	18, 19
$n = 3; R = CH_3$			77	18, 19
$n = 2; R = C_6H_5$			78	18, 19
$n = 3; R = C_6H_5$			60	18, 19
		Na_2S	30	21
		Na_2S	20	21
		NaS		
$n = 1; R^1 = H; R^2 = CH_3$			90	20
$n = 2; R^1 = H; R^2 = CH_3$			54	20
$n = 3; R^1 = H; R^2 = C_2H_5$			44	20, 21
$n = 1; R^1 = CH_3; R^2 = C_2H_5$			78	20, 21
$n = 2; R^1 = C_2H_5; R^2 = C_2H_5$			43	20, 21
$R^1CHOHCH_2(CH_2)_nCSOR^2$		NaSH		
$n = 2; R^1 = H; R^2 = CH_3$			40	20
$n = 1; R^1 = CH_3; R^2 = C_2H_5$			10	20, 21
$n = 2; R^1 = C_2H_5; R^2 = C_2H_5$			49	20, 21
		Na_2S (acetone)		
$R = H$			trace	21
$R = CH_3$			trace	21
				
$R = H$			major product	21
$R = CH_3$			major product	21

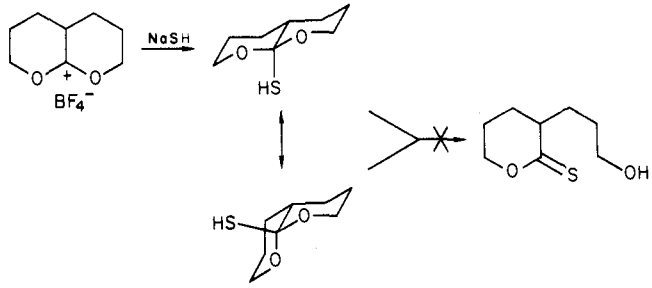
directly (or by treatment with tetrafluoboric acid). One equivalent of a hydroxyl-containing compound is produced as a side product as shown below.



Mixtures of products are often obtained as either alkoxy group may be eliminated on breakdown of the hemiorthothiol ester intermediate. In some cases thiono lactones are favored products over the open chain hydroxy compounds, giving up to 90% yields with some systems.[20] In other cases, the bond to the endocyclic C–O group is cleaved giving nearly exclusively open-chain products.[21] Stereoelectronic, kinetic, and thermodynamic effects influence the breakdown of the tetrahedral intermediates. A combination of these factors account for the distribution of products.[21]

Not all dialkoxonium tetrafluoborates undergo the reaction. Below is an example of such a system.[21]

Compounds prepared by the sulfhydrolysis of dialkoxycarbonium ions are listed in Table II.



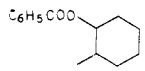
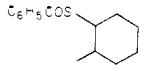
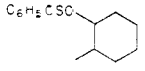
C. Alcoholysis of Thioacyl Halides

Thioacyl chlorides are generally very unstable compounds. Aliphatic thioacyl chlorides decompose rapidly even below −70 °C.[1] Only a few thiobenzoyl chlorides continue to find use in synthesis.[22,23]

A novel synthesis of thioacyl chloride precursors that gives moderate to good yields of thiocarboxylic *O*-esters has been recently described. Certain methyl ketones which contain no α-hydrogens on the opposite side of the carbonyl group react with thionyl chloride in pyridine to form the mixture of products shown below.

$$RC(=O)CH_3 \xrightarrow[\text{pyridine}]{SOCl_2} RC(=O)CH(SCl)Cl + RC(=O)CCl_2S_3CCl_2C(=O)R$$

TABLE III. Thiocarboxylic *O*-Esters ($R^1C(=S)OR^2$) by Alcoholysis of Thioacyl Halides and Their Precursors

R^1	R^2	method	yield, %	bp, °C (mm)	ref
$(CF_3)_2CH$	C_2H_5	$R^1CSF + R^2OH$			26
$(CH_3)_3CCO$	CH_3	(1) $(CH_3)_3COCH_3 + SOCl_2$, (2) R^2OH + pyridine	79	68–69 (9)	24
C_6H_5CO	CH_3	(1) $C_6H_5COCH_3 + SOCl_2$, (2) R^2OH + pyridine	56	86.5 (0.2)	24
4-$((CH_3)_3C)C_6H_4CO$	CH_3	(1) 4-$((CH_3)_3C)C_6H_4COCH_3$ + $SOCl_2$, (2) R^2OH + pyridine	40	114 (0.2)	24
3,5-$((CH_3)_3C)_2C_6H_3CO$	CH_3	(1) 3,5-$((CH_3)_3C)_2C_6H_3COCH_3$ + $SOCl_2$, (2) R^2OH + pyridine	51	mp 37.5–39	24
4,3-$(CH_3O)(NO_2)C_6H_3CO$	C_2H_5	(1) 4,3-$(CH_3O)(NO_2)C_6H_4COCH_3$ + $SOCl_2$, (2) R^2OH + pyridine			25
C_6H_5	$CH_2CH_2O_2CC_6H_5$	$R^1CSCl + R^2OH$			23
C_6H_5	$CH_2CH_2SC(O)C_6H_5$	$R^1CSCl + R^2OH$			23
C_6H_5	$CH_2CH_2OC(S)C_6H$	$R^1CSCl + R^2OH$			23
C_6H_5	$(CH_2)_3O_2CC_6H_5$	$R^1CSCl + R^2OH$			23
C_6H_5	$(CH_2)_3OC(S)C_6H_5$	$R^1CSCl + R^2OH$			23
C_6H_5	$(CH_2)_3S_2CC_6H_5$	$R^1CSCl + R^2OH$			23
C_6H_5	$CHCH_3CH_2SC(O)C_6H_5$	$R^1CSCl + R^2OH$			23
C_6H_5	$CHCH_3CH_2OC(S)C_6H_5$	$R^1CSCl + R^2OH$			23
C_6H_5	$CH(CH_2O_2CC_6H_5)CH_2OC(S)C_6H_5$	$R^1CSCl + R^2OH$			23
C_6H_5	$CH(CH_2OC(S)C_6H_5)_2$	$R^1CSCl + R^2OH$			23
C_6H_5	$CH(CH_2SC(O)C_6H_5)CH_2CH_3$	$R^1CSCl + R^2OH$			23
C_6H_5	$CH(CH_2OC(S)C_6H_5)CH_2CH_3$	$R^1CSCl + R^2OH$			23
C_6H_5	$CHCH_3CH_2CH_2SC(O)C_6H_5$	$R^1CSCl + R^2OH$			23
C_6H_5	$CHCH_3CH_2CH_2OC(S)C_6H_5$	$R^1CSCl + R^2OH$			23
C_6H_5	$CHCH_3CHCH_3SC(O)C_6H_5$	$R^1CSCl + R^2OH$			23
C_6H_5	$CHCH_3CHCH_3OC(S)C_6H_5$	$R^1CSCl + R^2OH$			23
C_6H_5	$CH_2CH_2CH(OC(S)C_6H_5)CH_2$-$SC(O)C_6H_5$	$R^1CSCl + R^2OH$			23
C_6H_5	$CH_2C(CH_3)_2CH_2SC(O)C_6H_5$	$R^1CSCl + R^2OH$			23
C_6H_5	$CH_2C(CH_3)_2CH_2OC(S)C_6H_5$	$R^1CSCl + R^2OH$			23
C_6H_5		$R^1CSCl + R^2OH$			23
C_6H_5		$R^1CSCl + R^2OH$			23
C_6H_5		$R^1CSCl + R^2OH$			23
C_6H_5	$CH(C_6H_{13})CH(SO_2C_6H_5)C_7H_{15}$	$R^1CSCl + R^2OH$			23

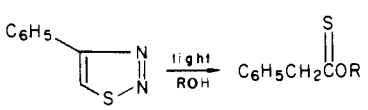
The resulting mixture reacts with alcohols in the presence of pyridine to give α-oxo thiocarboxylic *O*-esters in overall yields of 40–79%.[24,25]

Thioacyl fluorides are the most stable of the thioacyl halides and are used as precursors to thiocarboxylic *O*-esters.[26] See Table III for a list of thiocarboxylic *O*-esters prepared by the alcholysis of thioacyl halides.

D. Addition of Alcohols to Thioketenes

Thioketenes are generally very unstable and can only be isolated at very low temperatures except in a few cases.[1] They also tend to dimerize readily. When these compounds are used as precursors to the thiocarboxylic *O*-esters, they are usually generated in the presence of the appropriate alcohol with which they immediately react to form the desired product. The presence of a triphenylphosphine group in the α-position stabilizes the thioketene.[27]

Thioketenes have been formed from silylated thioalkynes[28,29] and the flash photolysis or thermolysis of 1,2,3-thiadiazoles, thioketene dimers, and some dithietane derivatives.[30–34] Carbon-13 labeling has been used

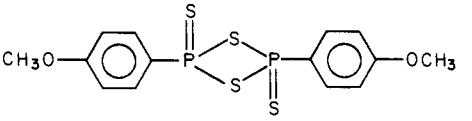


to probe the mechanism of thioketene formation in the photolysis and thermolysis experiments.[32–34] Thioketenes have been postulated as short-lived intermediates in the formation of thionolactones by an intramolecular reaction with hydroxyl groups.[35,36]

Thiocarboxylic *O*-esters prepared from the thioketenes are listed in Table IV.

E. Direct Sulfurization of Esters

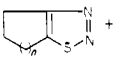
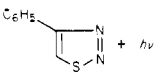
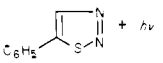
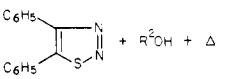
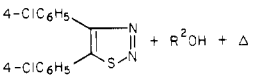
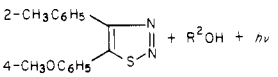
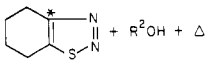
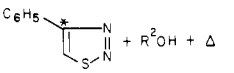
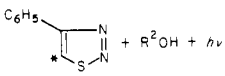
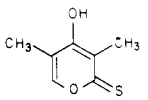
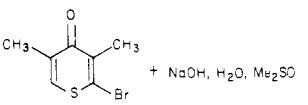
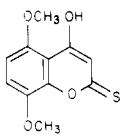
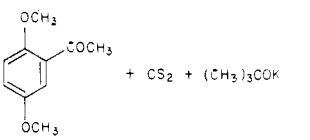
Several new reagents that directly convert esters to thiocarboxylic *O*-esters have been recently developed. Probably the most efficient is the dimer of (4-methoxyphenyl)thioxophosphine sulfide, or Lawesson's reagent,[37] shown below. This material thionates lac-



tones and esters generally in high yield. β-Lactones[38] and esters with conjugated electron-withdrawing groups[39] fail to give the reaction with Lawesson's reagent. Conditions are mild for this transformation (refluxing toluene or xylene).[37–41]

Pentaphosphorus decasulfide is used occasionally as

TABLE IV. Thiocarboxylic *O*-Esters ($R^1C(=S)OR^2$) by Addition of Alcohols to Thioketenes and Thioketene Precursors[a]

R^1	R^2	method	yield, %	bp, °C, (mm)	ref
$(CH_3)_3SiCH_2$	CH_3	$(CH_3)_3SiC{\equiv}CSSi(C_2H_5)_3 + R^2OH$			29
$(CH_3)_3SiCH_2$	CH_3	$(CH_3)_3SiC{\equiv}CSSi(CH_3)_3 + R^2OH$			28
$(CH_3)_3SiCH_2$	C_2H_5	$(CH_3)_3SiC{\equiv}CSSi(CH_3)_3 + R^2OH$			28
$(CH_3)_3SiCH_2$	$CH(CH_3)_2$	$(CH_3)_3SiC{\equiv}CSSi(CH_3)_3 + R^2OH$			28
$(C_6H_5)_3P^+CH^-$	C_6H_5	$(C_6H_5)_3P^+C^-{=}C{=}S + R^2OH$	69	mp 109	27
	$(CH_2CH_2O)_2H$				
$n = 1$			52	81-82 (0.01)	30
$n = 2$			95	99-101 (0.01)	30
$n = 3$			59	99-100 (0.02)	30
$n = 4$			71	116-120 (0.05)	30
$C_6H_5CH_2$	$(CH_2CH_2O)_2H$		36	123-126 (0.03)	30
$C_6H_5CH_2$	$(CH_2CH_2O)_2H$		31	123-126 (0.03)	30
$(C_6H_5)_2CH$	C_2H_5				31
$(4\text{-}ClC_6H_5)_2CH$	C_2H_5		64	mp 37	31
$(2\text{-}CH_3C_6H_5)CH(4\text{-}CH_3OC_6H_5)$	$(CH_2CH_2O)_2H$		43	118 (0.03)	30
	$(CH_2CH_2O)_2H$				32
$C_6H_5{*}CH_2$	$(CH_2CH_2O)_2H$	 I	100, 59		33, 34
$C_6H_5{*}CH_2$	CH_3	I + R^2OH + $h\nu$	100, 15		33, 34
$C_6H_5{*}CH_2$	CH_3	 II	8		33
$C_6H_5{*}CH_2$	$(CH_2CH_2O)_2H$	II + R^2OH + $h\nu$	97		33
$C_6H_5CH_2{*}CSOCH_3$		II + CH_3OH + $h\nu$	92		33
$C_6H_5CH_2{*}CSO(CH_2CH_2O)_2H$		II + $O(CH_2CH_2)_2OH$ + Δ	3		33
				123-126 (impure)	35
			86	220-221	36

[a] * = ^{13}C labeled.

a thionating agent for esters.[12,42-44] The yields are usually low with this reagent. *O,O'*-Diethyl dithiophosphate was used to prepare one thiono ester from the ester.[45] Boron sulfides are poor thionating agents unless generated in the presence of the ester by reaction of a trialkyltin sulfide with boron trichloride. The tin may play a mechanistic role in the reaction.[46]

In each of the above cases, the reaction seems to involve electrophilic attack of the phosphorus or boron atom on the carbonyl oxygen. The formation of the very strong phosphorus(boron)–oxygen bond helps drive the oxygen–sulfur exchange reaction to completion.

Some very reactive esters, i.e., selenocarboxylic *O*-esters can be thionated directly with elemental sulfur.[47,48] Due to the unavailability of selenocarboxylic *O*-esters, this method has only been used for isotope labeling.

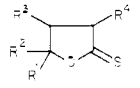
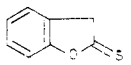
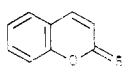
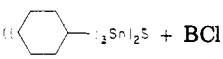
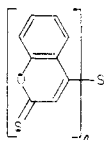
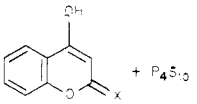
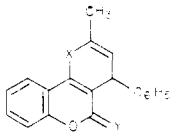
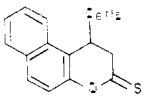
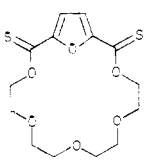
Table V lists the thiocarboxylic *O*-esters prepared by direct sulfurization of esters.

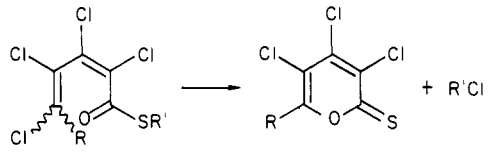
F. Thiolo–Thiono Rearrangements

There are many examples of the rearrangement of thiocarboxylic *O*-esters to the *S*-esters under the influence of chemical reagents, heat, and electron impact,[1] but only recently was the reverse reaction demonstrated. Dealkylation of certain thiocarboxylic *S*-esters takes place on the sulfur to give a 2*H*-pyran-2-thione[49,50] as shown below. The only other system on which this rearrangement occurs is the *S*-(4-aryl-5-thioxo-3-iso-

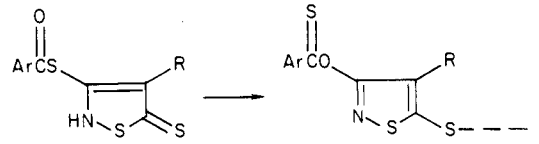
TABLE V. Thiocarboxylic *O*-Esters ($R^1C(=S)OR^2$) by Direct Sulfurization of Esters

R^1	R^2	method	yield, %	bp, °C (mm)	ref
$CH_3CH_2CH_2$	$CH_2C_6H_5$	Lawesson's reagent + ester	90	63-65 (0.4)	37
$(CH_3)_3C$	C_2H_5	Lawesson's reagent + ester			39
$CH_3(CH_2)_3$	C_2H_5	Lawesson's reagent + ester	91	80-85 (12)	37
$C_2H_5OC(S)CH_2OCH_2$	C_2H_5	Lawesson's reagent + ester			39
$(C_6H_5)_2P(S)CH_2$	C_2H_5	$(C_6H_5)_2P(O)CH_2CO_2C_2H_5 + P_4S_{10}$			42
C_6H_5	CH_3	Lawesson's reagent + ester	87	110-112 (10)	37, 39
C_6H_5	C_2H_5	$(C_2H_5O)_2P(S)SH$ + ester	98	112-116 (10)	46
C_6H_5	C_2H_5	Lawesson's reagent + ester			37, 39
C_6H_5	$CH(CH_3)_2$	Lawesson's reagent + ester	93	105-110 (15)	37, 39
C_6H_5	$CH_2C_6H_5$	Lawesson's reagent + ester	88	115-120 (1)	37
C_6H_5	$CH_2CH_2C_6H_5$	Lawesson's reagent + ester			40
C_6H_5	$CH=CHC_6H_5$	Lawesson's reagent + ester			40
C_6H_5	C_6H_5	Lawesson's reagent + ester			40
$4\text{-}(CH_3O)C_6H_6$	CH_3	Lawesson's reagent + ester			39
$4\text{-}(CH_3OSC)C_6H_4$	CH_3	P_4S_{10} + ester			12
$1\text{-}C_{10}H_7$	C_2H_5	Lawesson's reagent + ester	70	mp 41	37
$2\text{-}C_{10}H_7$	C_2H_5	Lawesson's reagent + ester	92	165 (10)	37
	CH_3	Lawesson's reagent + ester			39
	C_2H_5	Lawesson's reagent + ester			39

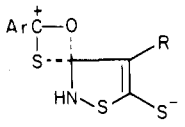
RC(=S)OR'	method	yield, %	bp, °C (mm)	ref
$4\text{-}((CH_3)_3C)C_6H_4C^{33}SOCD_3$	$4\text{-}((CH_3)_3C)C_6H_4CSeOCD_3 + {}^{33}S_8$	95		47, 48
	Lawesson's reagent + lactone			
$R^1 = H; R^2 = H; R^3 = H; R^4 = H$		98	96-97 (11)	41
$R^1 = H; R^2 = CH_3; R^3 = H; R^4 = H$		97	125-127 (30)	41
$R^1 = CH_3; R^2 = CH_3; R^3 = CH(CH_3)_2; R^4 = H$		66	mp 33	41
$R^1 = CH_3; R^2 = CH_3; R^3 = CN; R^4 = H$		90	mp 130	41
$R^1 = CH_3; R^2 = CH_3; R^3 = CH(CH_3)_2; R^4 = CO_2C_2H_5$		31	oil	41
$R^1 = CH_3; R^2 = CH_3; R^3 = CH_2C_6H_5; R^4 = CO_2C_2H_5$		27	103	41
	Lawesson's reagent + ester			40
 I	 + BCl_3 + coumarin	94	mp 99	46
I	Lawesson's reagent + coumarin	99		40, 41
				
	X = O	57	mp 206-209	43
	X = S			44
				
X, Y = S	warfarin + P_4S_{10}	10	mp 166-167	43
X, Y = S	X = O; Y = S + P_4S_{10}	19	mp 166-167	43
X, Y = S	X = S; Y = O + P_4S_{10}	59	mp 166-167	43
X, Y = S	cyclocumarol + P_4S_{10}	17	mp 166-167	43
X = O; Y = S	cyclocumarol + P_4S_{10}	17	mp 184-186	43
X = O; Y = S	warfarin + P_4S_{10}	12	mp 184-186	43
	Lawesson's reagent + lactone	87	mp 162	41
	Lawesson's reagent + diester	83	mp 125-126	39



thiazolin-3-yl) thio esters. Rearrangement in this case has been caused by treatment of the *S*-(thio ester) with diazomethane, alkyl iodides, triethyloxonium tetrafluoborate, acylation reagents, thallium(I) alkoxides, peracid, *N*-bromosuccinimide (NBS), and aluminum chloride.[51-53] The product of this reaction was the



5-thio-4-aryl-isothiazol-3-yl *O*-(thio ester). The mechanism of this rearrangement has not been investigated, but the authors suggest that it takes place by virtue of the nucleophilic character of the remote carbonyl group, proceeding through a resonance-stabilized ion as shown below.[51-53]



Thiono esters and lactones prepared by the thiolo–thiono rearrangement are listed in Table VI.

G. Transesterification of Thiocarboxylic *O*-Esters and Dithio Esters

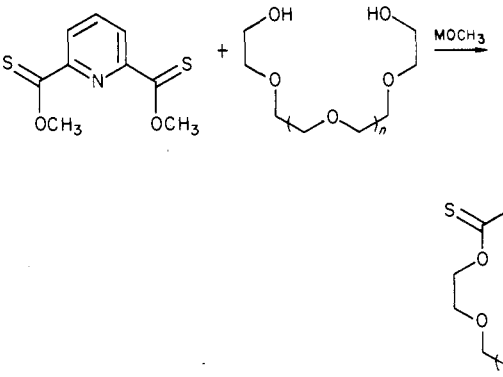
Thiocarboxylic *O*-esters and dithio esters undergo alkoxide-catalyzed transesterification with alcohols just as do their carboxylic ester analogues. The reaction is an equilibrium and can be driven to completion by selective removal of one of the products. A common approach is to use the sodium salt of a dithio ester of mercaptoacetic acid. Treatment with alkoxides gives thiocarboxylic *O*-esters. A mixed anhydride is the presumed intermediate.[1]

$$RC(=S)SCH_2C(=O)O^-Na^+ \rightarrow$$
$$RC(=S)OC(=O)CH_2S^-Na^+ \xrightarrow{R'OH} RC(=S)OR'$$

A novel synthesis involves treatment of a dithio ester containing one α-hydrogen with a Mannich base. Alkylation of the dithio ester produces alcohol which, via transesterification, gives a thiocarboxylic *O*-ester as the product.[54]

$$(CH_3)_2NCH_2OCH_3 + (CH_3)_2CHC(=S)SCH_3 \rightarrow$$
$$(CH_3)_2NCH_2C(CH_3)_2C(=S)OCH_3 + HSCH_3$$

A series of macrocyclic polyether–thiono diester and –thiono tetraester compounds has been prepared by treating *O,O'*-diethyl dithiooxalate and *O,O'*-dimethyl 2,6-pyridinedicarbothioate with various glycols in the presence of metal alkoxide catalysts. The reactions



were driven to completion by removal of the product alcohols by azeotropic distillation, or by absorption in molecular sieves. The metal cation was a template, giving high yields of macrocyclic products. Many of these compounds formed stable crystalline complexes with a variety of organic and inorganic salts.[16]

Thiocarboxylic *O*-esters prepared by transesterification are listed in Table VII.

H. Reactions on Thiocarboxylic *O*-Esters

A considerable number of compounds containing the thiocarboxylic *O*-ester moiety have been prepared by reactions on other portions of the molecule while leaving the thiocarboxylic *O*-ester group intact. These compounds, as well as the synthetic method and references, are grouped together in Table VIII. *Chemical Abstracts* nomenclature is used in lieu of structures in this section.

I. Miscellaneous

A number of new thiocarboxylic *O*-esters have been reported since 1976 where data on their syntheses are lacking. These compounds are summarized in Table IX along with the appropriate references. *Chemical Abstracts* nomenclature is used in this section as well.

III. Reductions of Thiocarboxylic O-Esters

Electroreduction has been applied to thiocarboxylic *O*-esters as a convenient method of generating radical anions for electron spin resonance, polarography, and cyclic voltammetry studies.[12,93] Electroreduction in the presence of alkyl halides gives monothioacetals in low yields.[94]

Radical generation can also be accomplished by treatment of thiocarboxylic *O*-esters with trialkyltin hydride derivatives.[95] This reaction has been developed into a synthetic procedure for the deoxygenation of primary[96] and secondary[22,97] alcohols. The alcohol is first converted to a thiocarboxylic *O*-ester, and is then treated with tri-*n*-butyltin hydride. Good yields of the corresponding alkanes result. Where there is an appropriate leaving group β to the hydroxy group, i.e., phenylsulfonyl, alkenes can be the primary products.[22]

$$C_7H_{15}CH(SO_2C_6H_5)CH(OC(=S)C_6H_5)C_6H_{13} \xrightarrow{Bu_3SnH}$$
$$C_7H_{15}CH=CHC_6H_{13}$$

A rearrangement from the thiocarboxylic *O*-ester to the *S*-ester takes place when *O,O'*-(5,5'-dithiobis(4-

TABLE VI. Thiocarboxylic *O*-Esters by Thiolo-Thiono Rearrangements

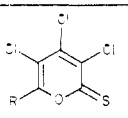
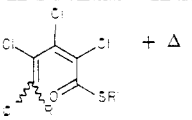
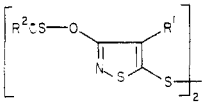
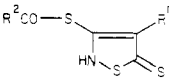
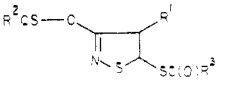
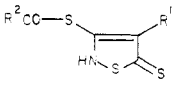
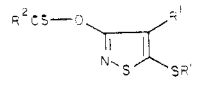
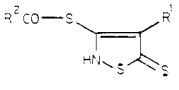
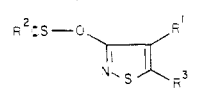
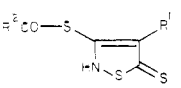
RC(=S)OR'			method	yield, %	mp, °C	ref
						
R			R'			
H			$C(CH_3)_3$	33	81-82	49
C_6H_5			CH_3	93	152	49
C_6H_5			$CH_2CH_2CH_3$	70	152	49
C_6H_5			$C(CH_3)_3$	77	152	49
C_6H_5				82	152	49
C_6H_5S			$C(CH_3)_3$	6	145-146	50
C_6Cl_5S			$C(CH_3)_3$	81	192-194	50
						
R^1	R^2		X			
C_6H_5	C_6H_5		$AlCl_3$	18	209-210	52
C_6H_5	C_6H_5		NBS	64	209-210	51, 52
C_6H_5	C_6H_5		$ZnCl_2$ or BF_3/AcOH	trace	209-210	52
C_6H_5	C_6H_5		$3\text{-}ClC_6H_4CO_3H$	13, 94, 100	209-210	51, 52
C_6H_5	$4\text{-}ClC_6H_4$		$3\text{-}ClC_6H_4CO_3H$	94	236-237	52
C_6H_5	$4\text{-}CH_3C_6H_4$		$3\text{-}ClC_6H_4CO_3H$	12, 73	217-219	52
C_6H_5	$4\text{-}CH_3OC_6H_4$		$3\text{-}ClC_6H_4CO_3H$	30, 70	221-223	52
C_6H_5	$4\text{-}NO_2C_6H_4$		$3\text{-}ClC_6H_4CO_3H$	23	218-220	52
C_6H_5	$4\text{-}CH_3O_2CC_6H_4$		$3\text{-}ClC_6H_4CO_3H$	29, 55	247-248	52
$4\text{-}ClC_6H_4$	C_6H_5		$3\text{-}ClC_6H_4CO_3H$	77	264-266	52
$4\text{-}CH_3C_6H_4$	C_6H_5		$3\text{-}ClC_6H_4CO_3H$	83	232-233	52
						
R^1	R^2	R^3	X			
C_6H_5	$CH_3CH_2CH_2$	C_6H_5	C_6H_5COCl, BF_3/AcOH	27	139-140	52
C_6H_5	$C_6H_5CH=CH$	CH_3	CH_3COCl, BF_3/AcOH	57	183-185	52
C_6H_5	$C_6H_5CH=CH$	C_2H_5	C_2H_5COCl, BF_3/AcOH	57	134-136	52
C_6H_5	$C_6H_5CH=CH$	C_6H_5	C_6H_5COCl, BF_3/AcOH	19	191-192	52
C_6H_5	C_6H_5	CH_3	CH_3COCl, BF_3/AcOH	67	175-176	52
C_6H_5	C_6H_5	C_2H_5	C_2H_5COCl, BF_3/AcOH	70	143-144	52
C_6H_5	C_6H_5	C_6H_5	C_6H_5COCl, BF_3/AcOH	60	171-172	52
C_6H_5	C_6H_5	C_6H_5	C_6H_5COCl, $AlCl_3$	17	171-172	52
C_6H_5	C_6H_5	$4\text{-}CH_3O_2CC_6H_4$	$4\text{-}CH_3O_2CC_6H_4COCl$, BF_3/AcOH	57	180-181	52
						
R^1	R^2	R^3	X			
C_6H_5	$4\text{-}ClC_6H_4$	C_6H_5CO	C_6H_5COCl, BF_3/AcOH	62	181-182	52
C_6H_5	$4\text{-}CH_3OC_6H_4$	C_6H_5CO	C_6H_5COCl, BF_3/AcOH	42	205-206	52
C_6H_5	$4\text{-}CH_3C_6H_4$	C_6H_5CO	C_6H_5COCl, BF_3/AcOH	57	170	52
C_6H_5	$4\text{-}NO_2C_6H_4$	C_6H_5CO	C_6H_5COCl, BF_3/AcOH	59	183-185	52
$4\text{-}CH_3C_6H_4$	$4\text{-}ClC_6H_4$	C_6H_5CO	C_6H_5COCl, BF_3/AcOH	63	164-166	52
C_6H_5	CH_3	CH_3	CH_3I	34	146-147	51, 53
C_6H_5	CH_3	CH_3	CH_2N_2	83	146-147	51, 53
C_6H_5	CH_3	C_2H_5	$(C_2H_5)_3O^+BF_4^-$	68	121-122	53
C_6H_5	C_6H_5	CH_3	CH_2N_2	97	207-208	51, 53
C_6H_5	C_6H_5	C_2H_5	$(C_2H_5)_3O^+BF_4^-$	82	183-185	51, 53
						
R^1	R^2	R^3	X			
$4\text{-}ClC_6H_4$	C_6H_5	C_2H_5S	$(C_2H_5)_3O^+BF_4^-$	88	205-206	51, 53
$4\text{-}CH_3C_6H_4$	C_6H_5	CH_3S	CH_2N_2	93	198-199	51, 53
C_6H_5	C_6H_5	Tl^+S^-	$C_2H_5O^-Tl^+$	88-100	198-199	52
C_6H_5	$C_6H_5CH=CH$	Tl^+S^-	$C_2H_5O^-Tl^+$	88-100	198-199	52
C_6H_5	$4\text{-}ClC_6H_4$	Tl^+S^-	$C_2H_5O^-Tl^+$	88-100	198-199	52
C_6H_5	$4\text{-}NO_2C_6H_4$	Tl^+S^-	$C_2H_5O^-Tl^+$	88-100	198-199	52
C_6H_5	CH_3	H	$3\text{-}ClC_6H_4CO_3H$ (2 equiv)	52	123-124	52
C_6H_5	$CH_3CH_2CH_2$	H	$3\text{-}ClC_6H_4CO_3H$ (2 equiv)	48	74-75	52

TABLE VI (*Continued*)

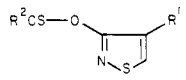
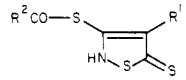
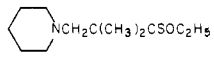
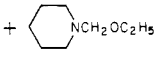
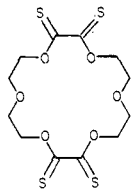
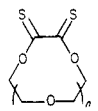
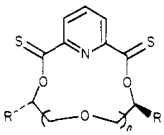
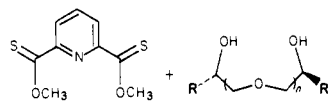
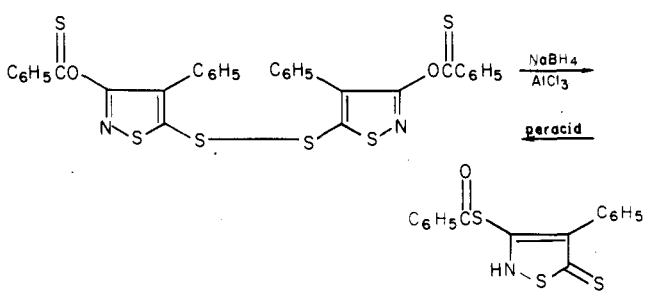
RC(=S)OR′			method	yield, %	mp, °C	ref
C_6H_5	C_6H_5	H	3-$ClC_6H_4CO_3H$ (2 equiv)	56	141-143	52
C_6H_5	4-$CH_3OC_6H_4$	H	3-$ClC_6H_4CO_3H$ (2 equiv)	43	167-169	52
			 + X			
R^1	R^2		X			
C_6H_5	4-$CH_3C_6H_4$		3-$ClC_6H_4CO_3H$ (2 equiv)	19	176-177	52
C_6H_5	4-$NO_2C_6H_4$		3-$ClC_6H_4CO_3H$ (2 equiv)	46	229-231	52
C_6H_5	4-$CH_3O_2CC_6H_4$		3-$ClC_6H_4CO_3H$ (2 equiv)	37	232-233	52
4-ClC_6H_4	CH_3		3-$ClC_6H_4CO_3H$ (2 equiv)	43	126-128	52

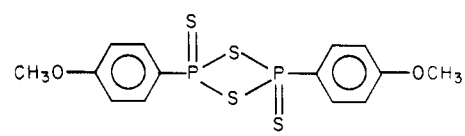
TABLE VII. Thiocarboxylic *O*-Esters by Transesterification

RC(=S)OR′	method	yield, %	mp, °C	ref
4-$(CH_3)_3CC_6H_4{}^{13}CSOCD_3$	$R^{13}CS_2CH_2CO_2Na + CD_3ONa$			47
2,4,6-$((CH_3)_3C)_3C_6H_2C^{33}SOCD_3$	$RC^{33}S_2CH_2CO_2Na + CD_3ONa$			47
$(C_2H_5)_2NCH_2C(CH_3)_2CSOCH_3$	$(CH_3)_2CHCS_2CH_3 + (C_2H_5)_2NCH_2OCH_3$			54
$(C_2H_5)_2NCH_2C(CH_3)_2CSOCH_3$ + HCl	$(CH_3)_2CHCS_2CH_3 + (C_2H_5)_2NCH_2OCH_3$ + HCl			54
$(C_2H_5)_2NCH_2C(CH_3)_2CSOC_2H_5$	$(CH_3)_2CHCS_2CH_3 + (C_2H_5)_2NCH_2OC_2H_5$			54
$(C_2H_5)_2NCH_2C(CH_3)_2CSOC_2H_5$ + HCl	$(CH_3)_2CHCS_2CH_3 + (C_2H_5)_2NCH_2OC_2H_5$ + HCl			54
	$(CH_3)_2CHCS_2CH_3$ + 			54
	$C_2H_5OC(S)CSOC_2H_5 + O(CH_2CH_2OH)_2 + C_2H_5OK$	10	169.5-170	16
	$C_2H_5OC(S)CSOC_2H_5 + HO(CH_2CH_2O)_{n+1}OH + C_2H_5OK$			
n = 3		5	108.5	16
n = 4		14	136-137	16
	 + CH_3OM			
R n				
H 2		71	140-141	16
H 3		39	124-125	16
H 4		26	124-125	16
H 5		10	51	16
CH_3 3		30, 69	63.5-64	16

phenylisothiazol-3-yl)) bis(benzenecarbothioate) (Table VI) is reduced by sodium borohydride/aluminum chloride.[52] The product, *S*-(4-phenyl-5-thioxo-3-isothiazol-3-yl) benzenecarbothioate, gives its predecessor by a reverse rearrangement when treated with 3-chloroperbenzoic acid.



A new method of preparing ethers from esters has been recently described.[39] This process consists of conversion of the ester to the thiono ester using Lawesson's reagent,[37] followed by reductive desulfurization with Raney nickel. The method gives good



1

$$RC(=O)OR' \xrightarrow{1} RC(=S)OR' \xrightarrow[Ni]{Raney} RCH_2OR'$$

yields of the ether for a variety of systems. Thiocarboxylic *O*-esters, available by other methods, also undergo the reduction.[16,40] The Raney nickel reduction must be carried out in anhydrous alcohol-free solvents, or aldehydes and acetals are the major products. The conditions are very mild (anhydrous ether at −30 to −10 °C), and the reaction is fast (just minutes to comple-

TABLE VIII. Thiocarboxylic *O*-Esters by Reactions on Thiocarboxylic *O*-Esters

thiocarboxylic *O*-ester/method	yield, %	mp, °C	ref
2-amino-3-(6,7-dihydro-9-methoxy-7-thioxo-5*H*-furo[3,2-*g*][1]benzopyran-5-yl)-1-propene-1,1,3-tricarbonitrile/9-methoxy-7*H*-furo[3,2-*g*][1]benzopyran-7-thione + ammonia			55
O-[5-(benzoylthio)-4-phenyl-3-isothiazolyl] benzenecarbothioate/*O*-(5-mercapto-4-phenyl-3-isothiazolyl) benzenecarbothioate, thallium(1+) salt + benzoyl chloride	38	171–172	52
O-[5-(benzoylthio)-4-phenyl-3-isothiazolyl] 4-chlorobenzenecarbothioate/*O*-(5-mercapto-4-phenyl-3-isothiazolyl) 4-chlorobenzenecarbothioate, thallium(1+) salt + benzoyl chloride	47	181–182	52
O-[5-(benzoylthio)-4-phenyl-3-isothiazolyl] 4-nitrobenzenecarbothioate/*O*-(5-mercapto-4-phenyl-3-isothiazolyl) 4-nitrobenzenecarbothioate, thallium(1+) salt + benzoyl chloride	41	183–185	52
O-[5-(benzoylthio)-4-phenyl-3-isothiazolyl] 3-phenyl-2-propenethioate/*O*-((5-mercapto-4-phenyl-3-isothiazolyl) 3-phenyl-2-propenethioate, thallium(1+) salt + benzoyl chloride	25	191–192	52
5-bromo-6-(1,2-diphenylethyl)-7,8-dihydroxy-2*H*-1-benzopyran-2-thione/4-bromo-7*H*-furo[3,2-*g*][1]benzopyran-7-thione + aluminum chloride			55
O-butyl 4-[4-[(4,6-dichloro-2-pyridinyl)oxy]phenoxy]-2-pentenethioate/*O*-butyl 3,4-dibromopentanethioate + substituted phenoxide ion			56
O-butyl 4-[4-[4-(trifluoromethyl)phenoxy]phenoxy]-2-pentenethioate/*O*-butyl 3,4-dibromopentanethioate + substituted phenoxide ion			56
O,O-diethyl *trans*-2-butenebis(thioate)/*O,O*-diethyl (±)-3,5-bis(ethoxythiocarbonyl)-4-thiaheptanebis(thioate) + heat	40	61–62	4
O,O-diethyl butanebis(thioate)/*O,O*-diethyl (±)-3,5-bis(ethoxythiocarbonyl)-4-thiaheptanebis(thioate) + heat	40		4
(6,7-dihydro-9-methoxy-7-thioxo-5*H*-furo[3,2-*g*][1]benzopyran-5-yl)-propanedinitrile/9-methoxy-7*H*-furo[3,2-*g*][1]benzopyran-7-thione + propanedinitrile + ammonia			55
6-(1,2-diphenylethyl)-7,8-dihydroxy-2*H*-1-benzopyran-2-thione/7*H*-furo[3,2-*g*][1]benzopyran-7-thione + aluminum chloride			55
O-ethyl *trans*-2-butenethioate/*O,O*-diethyl (±)-3,5-bis(ethoxythiocarbonyl)-4-thiaheptanebis(thioate) + heat	42	bp 61 (12 mm)	4
O-ethyl *trans*-2-butenethioate/*O*-ethyl 3-(1-piperidyl)butanethioate + heat		bp 61 (12 mm)	4
O-ethyl 4-[4-[(4,6-dichloro-2-pyridinyl)oxy]phenoxy]-2-pentenethioate/*O*-ethyl 3,4-dibromopentanethioate + substituted phenoxide ion			56
O-ethyl 3,3-difluoro-2-(trifluoromethyl)propenethioate/*O*-ethyl bis(trifluoromethyl)ethanethioate + boron trifluoride–triethylamine			26
ethyl 3-(1,1-dimethylethyl)-5-(ethoxythioxomethyl)benzoate/*O,O*-diethyl 5-(1,1-dimethylethyl)-1,3-benzenedicarbothioate + silver nitrate			12
O-ethyl ethanethioate/*O*-ethyl 2-(trimethylsilyl)ethanethioate + hydroxide ion + methanol			28
ethyl 3-(ethoxythioxomethyl)benzoate/*O,O*-diethyl 1,3-benzenedicarbothioate + silver nitrate			12
ethyl 3-ethoxy-3-thioxopropanoate/*O*-ethyl 3-amino-3-ethoxy-2-propenethioate + water			13
O-ethyl 3-(ethylthio)-3-thioxopropanethioate/*O,O*-diethyl propanebis(thioate) + sodium ethanethioate			13
O-ethyl 3-(1-piperidyl)butanethioate/*O*-ethyl *trans*-2-butenethioate + piperidine	93	oil	4
O-methyl 4-[4-[(4,6-dichloro-2-pyridinyl)oxy]phenoxy]-2-pentenethioate/*O*-methyl 3,4-dibromopentanethioate + substituted phenoxide ion			56
O-methyl ethanethioate/*O*-methyl 2-(trimethylsilyl)ethanethioate + hydroxide ion + methanol			28
O-1-methylethyl ethanethioate/*O*-1-methylethyl 2-(trimethylsilyl)-ethanethioate + hydroxide ion + methanol			28
O-methyl 2-methoxy-4,5-dimethyl-3,6-dihydro-2*H*-thiin-2-carbothioate/*O,O*-dimethyl dithiooxalate + 2,3-dimethylbutadiene	100	oil	57
O-methyl 3-methoxy-2-thiabicyclo[2.2.1]hept-5-ene-*endo*-3-carbothioate/*O,O*-dimethyl dithiooxalate + cyclopentadiene	50	oil	57
O-methyl 3-methoxy-2-thiabicyclo[2.2.1]hept-5-ene-*exo*-3-carbothioate/*O,O*-dimethyl dithiooxalate + cyclopentadiene	30	oil	57
O-[5-(methylthio)-4-phenyl-3-isothiazolyl] benzenecarbothioate *S*-oxide/*O*-[5-(methylthio)-4-phenyl-3-isothiazolyl] benzenecarbothioate + 3-chloroperbenzoic acid	99	221–225	53
O-methyl 4,5,10-trimethoxy-3,6,11-trithia-*exo*-2,7-*exo*-9,12-tetracyclo[6.4.1.$0^{2,7}$.$0^{9,12}$]tridec-4-ene-*endo*-10-carbothioate/*O,O*-dimethyl dithiooxalate + tetracyclo[2.2.$0^{2,3}$.$0^{5,6}$]heptane	87	132	57, 58
O-methyl 3,7,8-trimethoxy-2,6,9-trithia-*exo*-5,10-tricyclo[6.2.1.$0^{5,10}$]undec-7-ene-*endo*-3-carbothioate/*O,O*-dimethyl dithiooxalate (2 equiv) + cyclopentadiene	60	77	57
O-methyl 3,7,8-trimethoxy-2,6,9-trithia-*exo*-5,10-tricyclo[6.2.1.$0^{5,10}$]undec-7-ene-*exo*-3-carbothioate/*O,O*-dimethyl dithiooxalate (2 equiv) + cyclopentadiene	33	56–58	57
O-[4-phenyl-3-isothiazolyl] benzenecarbothioate/*O,O*-[dithiobis(4-phenyl-3,5-isothiazolediyl)] benzenecarbothioate + 3-chloroperbenzoic acid	12	142–144	52
3a,6,7,7a-tetrahydro-2-phenyl-6-thioxo-4,7-ethenopyrano[3,4-*c*]pyrrole-1,3(2*H*,4*H*)-dione/2*H*-pyran-2-thione + *N*-phenyl-2,5-dihydropyrrole	40		59

TABLE IX. Thiocarboxylic *O*-Esters Prepared with No Synthetic Data Available

thiocarboxylic *O*-ester	ref
O-*trans*-[2-(acetyloxy)cyclohexyl] benzenecarbothioate	60
O-[2,3-bis(acetyloxy)propyl] ethanethioate	61
3-(aminomethylene)-2 (3*H*)-furanthione	62, 63
3-(aminomethylene)-5-phenyl-2 (3*H*)-furanthione	62–65
4-bromo-7*H*-furo[3,2-*g*][1]benzopyran-7-thione	66
4-bromo-9-methoxy-7*H*-furo[3,2-*g*][1]-benzopyran-7-thione	55, 66
O-butyl 3,4-dibromopentanethioate	56
O-butyl ethanethioate	67
O-butyl 2,3,3-trichloropropanethioate	68
O-(4-cyanophenyl) 4-pentylbenzenecarbothioate	69
O-decyl 2,3,3-trichloropropenethioate	70
O-(3,4-dichlorophenyl) 3,5-bis(1,1-dimethylethyl)-4-hydroxybenzenecarbothioate	71
O-[2-(diethylamino)ethyl] 4-aminobenzenecarbothioate	72
O-[2-(diethylamino)ethyl] 4-aminobenzenecarbothioate picrate	72
O-[2-(diethylamino)ethyl] 4-(dimethylamino)benzenecarbothioate	72
O,*O*-diethyl butanebis(thioate)	73
O,*O*-diethyl heptanebis(thioate)	73
O,*O*-diethyl hexanebis(thioate)	73
O,*O*-diethyl pentanebis(thioate)	73
O-[2-(dimethylamino)ethyl] 4-methylbenzenecarbothioate	74
3-((dimethylamino)methylene)-5-phenyl-2(3*H*)-furanthione	75
O-methyl (2,6-dimethylphenyl)-aminoethanethioate	76
O,*O*-bis[3-[[3-[[2-[2,4-bis(1,1-dimethylpropyl)-phenoxy]-1-oxobutyl]amino]benzoyl]amino]-4,5-dihydro-5-oxo-1-(2,4,6-trichlorophenyl)-1*H*-pyrazol-4-yl] 1,4-benzenedicarbothioate	77
3,4-diphenyl-6-selenophene-2-yl-2*H*-pyran-2-thione	78
3,4-diphenyl-6-(2-thienyl)-2*H*-pyran-2-thione	78
O-ethyl 2-[1-[(4-chloro-2-nitrophenyl)(amino]-phenoxy]propanethioate	79
O-ethyl 5-chloro-2-oxo-3(2*H*)-benzothiazole-ethanethioate	80
O-ethyl cyclopropanecarbothioate	81
O-ethyl 3,4-dibromopentanethioate	56
O-ethyl 4-(1,1-dimethylethyl)benzenecarbothioate	82
O-ethyl 3-methylbenzenecarbothioate	83
O-ethyl 2-methylpropanethioate	84
O-ethyl 2-[4-[[2-nitro-4-(trifluoromethyl)-phenyl]amino]phenoxy]propanethioate	79
O-ethyl octanethioate	84
O-ethyl (5-phenyl-3*H*-1,2-dithiol-3-ylidene)-ethanethioate	85
O-ethyl 1a,2,7,7a-tetrahydro-1*H*-cyclopropa-[*b*]naphthalene-1-carbothioate	81
O-ethyl 2,3,3-trichloropropanethioate	68, 70
O-ethyl tridecanethioate	84
6-fluoro-2*H*-1-benzopyran-2-thione	86
8-fluoro-2*H*-1-benzopyran-2-thione	86
6-fluoro-7-nitro-2*H*-1-benzopyran-2-thione	86
7*H*-furo[3,2-*g*][1]benzopyran-7-thione	66
O-heptyl 2,3,3-trichloropropenethioate	70
O-hexyl 2,3,3-trichloropropenethioate	70
4-methoxy-7*H*-furo[3,2-*g*][1]benzopyran-7-thione	66
9-methoxy-7*H*-furo[3,2-*g*][1]benzopyran-7-thione	55, 66
4,9-dimethoxy-7*H*-furo[3,2-*g*][1]-benzopyran-7-thione	66
O-methyl 5-(aminosulfonyl)-2-methoxybenzenecarbothioate	87
O-methyl 3,4-dibromopentanethioate	56
O-[5-methyl-2-(1-methylethenyl)cyclohexyl] benzenecarbothioate	88
O-(4-methylphenyl) propanethioate	89
O-methyl 2,3,3-trichloropropanethioate	70
O-methyl-d_3 ethanethioate	67
O-pentyl 2,3,3-trichloropropenethioate	68, 70
O-[3-(phenoxyphenyl)methyl] 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropane-carbothioate	90
6,6'-(1,4-phenylene)bis(2*H*-pyran-2-thione)	91
O-propyl ethanethioate	67
O-propyl 2,3,3-trichloropropenethioate	70
O-octyl 2,3,3-trichloropropenethioate	70
2-oxabicyclo[3.3.1]nonane-3-thione	92

TABLE X. Reductions of Thiocarboxylic *O*-Esters

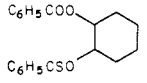
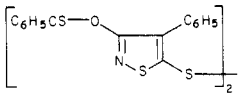
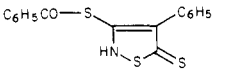
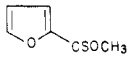
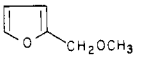
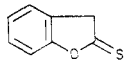
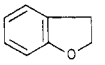
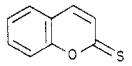
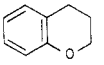
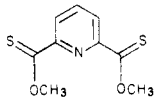
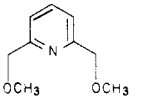
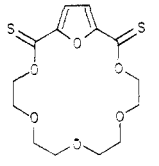
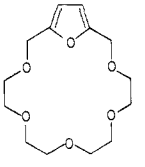
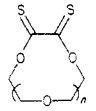
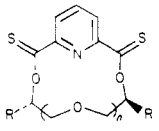
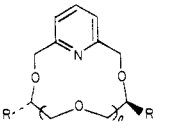
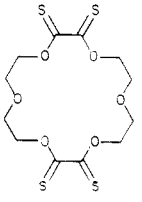
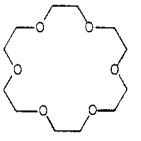
thiocarboxylic *O*-ester	method	product	yield, %	ref
$C_2H_5OOCCSOC_2H_5$	electroreduction	radical anion		93
$C_2H_5OSCCSOC_2H_5$	electroreduction	radical anion		93
$4\text{-}CH_3OOCC_6H_4CSOCH_3$	electroreduction	radical anion		12
$4\text{-}CH_3OSCC_6H_4CSOCH_3$	electroreduction	radical anion		12
$3\text{-}C_2H_5OOCC_6H_4CSOC_2H_5$	electroreduction	radical anion		12
$3\text{-}C_2H_5OSCC_6H_4CSOC_2H_5$	electroreduction	radical anion		12
$5\text{-}(CH_3)_3C\text{-}3\text{-}C_2H_5OOCC_6H_3CSOC_2H_5$	electroreduction	radical anion		12
$5\text{-}(CH_3)_3C\text{-}3\text{-}C_2H_5OSCC_6H_3CSOC_2H_5$	electroreduction	radical anion		12
$C_6H_5CSOCH_3$	electroreduction + CH_3I	$C_6H_5CH(OCH_3)SCH_3$	25	94
$HCSOC_2H_5$	$(C_4H_9)_3SnH$	radical		95
$HCSOC(CH_3)_3$	$(C_4H_9)_3SnH$	radical		95
$CH_3CSOC_2H_5$	$(C_4H_9)_3SnH$	radical		95
$C_6H_5CSOC_2H_5$	$(C_4H_9)_3SnH$	radical		95
$C_6H_5CSOCH_2CH(CH_3)CH_2CH_3$	$(C_4H_9)_3SnH$	radical		95
$C_6H_5CSOC_{18}H_{37}$	$(C_4H_9)_3SnH$	$C_{18}H_{38}$		96
				97
$C_6H_5CSOCH(C_6H_{13})CH(C_7H_{15})SO_2C_6H_5$	$(C_4H_9)_3SnH$	*trans*-$C_7H_{15}CH{=}CHC_6H_{13}$	61	22
$C_6H_5CSOCH_3$	$LiAlH_4$	$C_6H_5CH_3$	6	40
		$C_6H_5CH_2SH$	14	40
		trans-$C_6H_5CH{=}CHC_6H_5$	13	40
		$C_6H_5CH_2CH_2C_6H_5$	1	40
$C_6H_5CSOCH_3$	$LiAlH_4/BF_3$	$C_6H_5CH_3$	1	40
		trans-$C_6H_5CH{=}CHC_6H_5$	18	40
		$C_6H_5CH_2CH_2C_6H_5$	1	40
$C_6H_5CSOCH_3$	$NaBH_4$	$C_6H_5CH_3$		40
		trans-$C_6H_5CH{=}CHC_6H_5$		40
		$C_6H_5CH_2CH_2C_6H_5$		40

TABLE X (*Continued*)

thiocarboxylic *O*-ester	method	product	yield, %	ref
	$NaBH_4/AlCl_3$		86	34
$(CH_3)_3CCSOC_2H_5$	Raney nickel	$(CH_3)_3CCH_2OC_2H_5$		39
trans-$C_6H_5CH{=}CHCSOC_2H_5$	Raney nickel	$C_6H_5(CH_2)_3OC_2H_5$		40
$C_6H_5CSOCH_3$	Raney nickel	$C_6H_5CH_2OCH_3$		39
$C_6H_5CSOC_2H_5$	Raney nickel	$C_6H_5CH_2OC_2H_5$		39
$C_6H_5CSOCH(CH_3)_2$	Raney nickel	$C_6H_5CH_2OCH(CH_3)_2$		39
$C_6H_5CSOCH_2CH_2C_6H_5$	Raney nickel	$C_6H_5CH_2OCH_2CH_2C_6H_5$		40
$C_6H_5CSOC_6H_5$	Raney nickel	$C_6H_5CH_2OC_6H_5$		39
$4\text{-}CH_3OC_6H_4CSOCH_3$	Raney nickel	$4\text{-}CH_3OC_6H_4CH_2OCH_3$		39
				39
	Raney nickel			40
				40
$C_2H_5OSCCSOC_2H_5$	Raney nickel	$C_2H_5OCH_2CH_2OC_2H_5$	23	40
$O(CH_2CSOC_2H_5)_2$	Raney nickel	$O(CH_2CH_2OC_2H_5)_2$		39
			18	40
			17	39
 $n = 3$ $n = 4$	Raney nickel	 $n = 3$ $n = 4$	52 45	16 16
	Raney nickel			
R n H 2 H 3 H 4 H 5 CH_3 3			40 56 76 40 56	16 16 16 16 16
	Raney nickel		21	16

tion). All necessary hydrogen for the reduction is absorbed on the nickel surface. A large excess of nickel is required to effect the reduction. The Raney nickel desulfurization reaction has been employed on macrocyclic systems containing up to four thiocarboxylic *O*-ester moieties in the ring with good success.[16]

O-Methyl benzenecarbothioate has been reduced with lithium aluminum hydride (LAH), LAH/boron trifluoride, and sodium borohydride. In each case, complex mixtures of products were obtained, including toluene, benzyl mercaptan, stilbene, and 1,2-diphenylethane.[40]

Reductions of specific compounds and the procedure used for each are listed in Table X.

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