7.00–7.40 (m, 4 H, ArH), 7.95 (s, 1 H, pyr-H), D_2O showed two exchangeable protons; ir (Nujol) 3120 (OH) and 1730 cm^{-1} (C=O). A second recrystallization from benzene–EtOH gave 0.35 g of white analytically pure solid **10b**, mp 172.0–173.0° dec.

Anal. Calcd for $C_{18}H_{19}NO_4S$: C, 62.59; H, 5.54; N, 4.06; S, 9.28. Found: C, 62.75; H, 5.62; N, 3.82; S, 9.51.

Acknowledgments. R.A.C. (Lehigh University, Ph.D., 1974) was a recipient of the Hornor and Buch Graduate Research Fellowships which, in part, supported this study.

Registry No.—**1**, 496-31-1; **2a**, 54711-32-9; **2b**, 54711-33-0; **2c**, 54711-34-1; **2d**, 56404-07-0; **2e**, 56404-08-1; **3**, 56404-09-2; **4a**, 54711-35-2; **4b**, 54711-36-3; **4c**, 54711-37-4; **4d**, 56404-10-5; **4e**, 56404-11-6; **5**, 56404-12-7; **6a**, 56404-13-8; **6b**, 56404-14-9; **7**, 56404-15-0; **8**, 56404-16-1; **9**, 56404-17-2; **10a**, 56404-18-3; **10b**, 56404-19-4; salicylaldehyde, 90-02-8; 5-methoxysalicylaldehyde, 672-13-9; 4-methoxysalicylaldehyde, 673-22-3; 3-methoxysalicylaldehyde, 148-53-8; 5-chlorosalicylaldehyde, 635-93-8; 5-nitrosalicylaldehyde, 97-51-8; sulfur, 7704-34-9; triethylamine, 121-44-8; DDQ, 84-58-2; MeOH, 67-56-1; EtOH, 64-17-5; acetonitrile, 75-05-8; *tert*-amyl alcohol, 75-85-4; pyridoxal HCl, 65-22-5.

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Darzens Synthesis of Glycidic Thiol Esters. Formation of a β-Lactone By-product[1]

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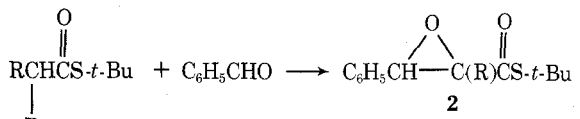
The Darzens condensation has been used in the preparation of glycidic thiol esters. Aliphatic ketones and aromatic and aliphatic aldehydes may be used as substrates. *S*-Benzyl and *S*-*tert*-butyl thiolglycidates were prepared. In general 2-bromothiol esters gave higher yields than the corresponding 2-chlorothiol esters. The low yields obtained with 2-chlorothiol esters are due in part to competing formation of an α-chloro-β-lactone by-product. Results have been obtained that suggest that a carbene intermediate is not involved in the Darzens synthesis of glycidic thiol esters.

A great deal of attention has been given to preparative and mechanistic aspects of the Darzens synthesis of glycidic (oxygen) esters.[2] Recently[1b] we have found that it is also possible to carry out a Darzens synthesis of glycidic thiol esters (**2**). In the formation of the glycidic thiol esters it is important to use nonnucleophilic bases such as sodium hydride or lithium bis(trimethylsilyl)amide and relatively polar aprotic solvents including tetrahydrofuran and dimethylformamide. We have also found that α-bromothiol ester reactants are preferable in most cases to the corresponding α-chlorothiol esters.[1b]



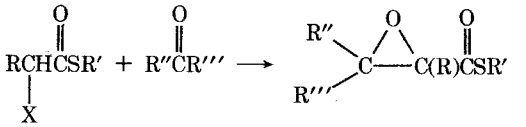
1a, R = H
b, R = CH_3

When these facts are kept in mind the Darzens reaction provides the best available method for the synthesis of S-aliphatic glycidic thiol esters.[3] In this report we would like to comment on the generality of this reaction and also certain mechanistic aspects of the process. At the outset it should be pointed out that even when working within the previously described limits[1b] the proper choice of reaction conditions is critical in obtaining a successful reaction. This situation may be contrasted with the wide variety of conditions successfully employed in the normal Darzens glycidic ester condensation.[2] It is important to understand something about these limitations in order to take full advantage of the Darzens reaction in the synthesis of glycidic thiol esters.

Results and Discussion

In this discussion it will be useful to make reference to the currently accepted mechanism[2b,c,d,h,i,l] for the Darzens reaction (Scheme I). Although we have not carried out an extensive examination of the mechanism of the Darzens synthesis of glycidic thiol esters, we have checked certain points to see if major differences are apparent. It has been argued earlier from a study of the reaction of ethyl 2-chlo-

Table I[a]
Glycidic Thiol Esters from α-Halothiol Esters



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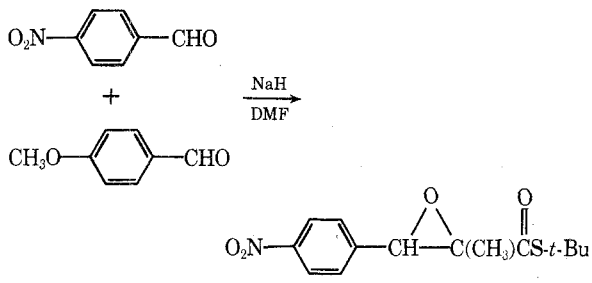
Halo ester	Carbonyl compound	Base	Solvent	Product	R	R'	R''	R'''	Yield, %	Isomer ratio trans:cis
1a	Cyclohexanone	NaH	THF	4	H	*t*-Bu		$-(CH_2)_5-$	69	
1a	Cyclehexanone	NaH	DMF	4	H	*t*-Bu		$-(CH_2)_5-$	28	
$ClCH_2COS$-*t*-Bu (1c)	Cyclohexanone	NaH	THF	4	H	*t*-Bu		$-(CH_2)_5-$	12	
1c	Cyclohexanone	NaH	DMF	4	H	*t*-Bu		$-(CH_2)_5-$	28	
1a	Acetone[b]	NaH	THF	5	H	*t*-Bu	CH_3	CH_3	69	
1a	Acetone[b]	NaH	DMF	5	H	*t*-Bu	CH_3	CH_3	10	
1c	Acetone[b]	NaH	THF	5	H	*t*-Bu	CH_3	CH_3	7	
1c	Acetone[b]	NaH	DMF	5	H	*t*-Bu	CH_3	CH_3	20	
1a	Cyclohexanone	$LiN(SiMe_3)_2$	THF	4	H	*t*-Bu		$-(CH_2)_5-$	92	
1c	Cyclohexanone	$LiN(SiMe_3)_2$	THF	4	H	*t*-Bu		$-(CH_2)_5-$	25	
1a	Acetone[b]	$LiN(SiMe_3)_2$	THF	5	H	*t*-Bu	CH_3	CH_3	60[c]	
1c	Acetone[b]	$LiN(SiMe_3)_2$	THF	5	H	*t*-Bu	CH_3	CH_3	10	
$BrCH_2COSCH_2C_6H_5$ (1d)	Cyclohexanone	$LiN(SiMe_3)_2$	THF	6	H	$C_6H_5CH_2$		$-(CH_2)_5-$	70	
1d	Cyclohexanone	NaH	DMF	6	H	$C_6H_5CH_2$		$-(CH_2)_5-$	10	
1d	Cyclohexanone	NaH	THF	6	H	$C_6H_5CH_2$		$-(CH_2)_5-$	10	
1d	Benzaldehyde	NaH	DMF	7	H	$C_6H_5CH_2$	C_6H_5	H	35[d]	6:4
1a	Benzaldehyde	NaH	DMF	2a	H	*t*-Bu	C_6H_5	H	67[e-g]	3:7
1a	Benzaldehyde	$LiN(SiMe_3)_2$	THF	2a	H	*t*-Bu	C_6H_5	H	59[e]	9:1
1a	Isobutyraldehyde	NaH	DMF	8	H	*t*-Bu	$(CH_3)_2CH$	H	62[f]	4:6
1a	Isobutyraldehyde	$LiN(SiMe_3)_2$	THF	8	H	*t*-Bu	$(CH_3)_2CH$	H	10[h]	9:1
1b	Benzaldehyde	NaH	DMF	2b	CH_3	*t*-Bu	C_6H_5	H	58[e]	9:1
1b	Cyclohexanone	NaH	DMF	9	CH_3	*t*-Bu		$-(CH_2)_5-$ H	60	
$CH_3CH_2CHBrCOS$-*t*-Bu (1e)	Benzaldehyde	NaH	DMF	10	CH_3CH_2	*t*-Bu	C_6H_5	H	59	9:1
$CH_3CHClCOS$-*t*-Bu (1f)	Benzaldehyde	NaH	DMF	2b	CH_3	*t*-Bu	C_6H_5	H	45	All trans
1f	Cyclohexanone	NaH	DMF	9	CH_3	*t*-Bu		$-(CH_2)_5-$	15	

[a] Except where otherwise noted all NaH yields reported in the table were obtained for reactions carried out by adding a mixture of 1 equiv of carbonyl compound and 1 equiv of 2-halothiol ester in DMF (or THF) to 1.3 equiv of NaH in DMF (or THF) at 0° followed by stirring for 30 min at 0° and 30 min at room temperature before work-up. All $LiN(SiMe_3)_2$–THF yields reported in the table were obtained for reactions carried out by adding 1 equiv of base in THF to a mixture of 1 equiv of carbonyl compound and 1 equiv of 2-halothiol ester at 0° followed by stirring for 30 min at 0° and then 30 min at room temperature before work-up. [b] Because of the volatility of acetone, excess (2 equiv) was used and higher yields were thus obtained. [c] A 72% yield was obtained by addition of $LiN(SiMe_3)_2$ to acetone and **1a** at −78° and stirring for 30 min at −78°, followed by warming to room temperature where it was stirred again for 30 min before work-up. [d] No glycidic thiol ester (7) was obtained when the reaction was carried out with $LiN(SiMe_3)_2$ in THF. [e] Reference 1b. [f] No glycidic thiol ester (**2a**) was obtained when the reaction was carried out with NaH in THF. [g] No glycidic thiol ester (**2a**) was obtained when **1c** was used in place of **1a**. [h] A 28% yield was obtained by adding $LiN(SiMe_3)_2$ to isobutyraldehyde and **1a** in THF at −78° and stirring for 30 min at −78°, followed by warming to room temperature where it was stirred again for 30 min before work-up.

rophenylacetate with a mixture of *p*-nitrobenzaldehyde and *p*-methoxybenzaldehyde[2d] that a carbene intermediate is not involved in the Darzens synthesis of glycidic (oxygen) esters. The major Darzens product was that obtained from *p*-nitrobenzaldehyde. If a carbene intermediate were involved the product obtained from *p*-methoxybenzaldehyde would be expected. We thus studied the reaction of a mixture of *p*-nitrobenzaldehyde and *p*-methoxybenzaldehyde with *S-tert*-butyl 2-bromothiolpropionate (**1b**) using NaH in DMF. The product (**3**) resulting from the reaction of *p*-

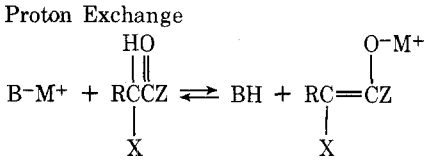


3

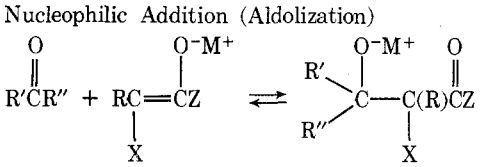
nitrobenzaldehyde was obtained in 75% yield and unreacted *p*-methoxybenzaldehyde (91%) was recovered. No *p*-nitrobenzaldehyde was detected in the reaction mixture. These results suggest that a carbene intermediate is not involved in the mechanism in the formation of glycidic thiol esters. This conclusion is supported by the known high migratory aptitude of the sulfur atom in moving to a carbene center in a Wolff rearrangement process[4] suggesting that if in fact a carbene intermediate was formed in the reaction of **1b** with NaH it would undergo rearrangement preventing formation of the glycidic thiol ester product (**3**). The nature of by-products formed in the Darzens reactions discussed below also tend to support the mechanism in Scheme I.

Scheme I

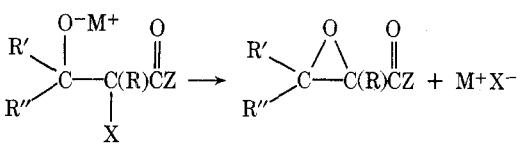
1. Proton Exchange



2. Nucleophilic Addition (Aldolization)



3. Intramolecular Nucleophilic Substitution (Cyclization)



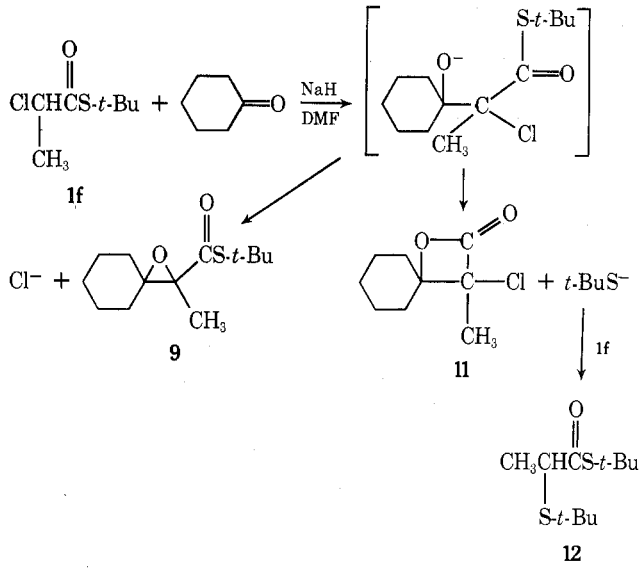
Low yields of thiolglycidates **4** and **5** were obtained in the reaction of cyclohexanone or acetone with *S-tert*-butyl 2-chlorothiolacetate (**1c**) using either the NaH–THF, NaH–DMF, or $LiN(SiMe_3)_2$–THF conditions (Table I). High yields of **4** or **5** were obtained using *S-tert*-butyl 2-bromothiolacetate (**1a**) and NaH or $LiN(SiMe_3)_2$ in THF. Thus with aliphatic ketones as with aromatic aldehydes,[1b] α-bromothiol esters gave higher yields than the corresponding α-chlorothiol esters. However, even when using α-bromothiol esters it is important to be careful in selecting the reaction conditions in order to achieve a satisfactory yield. For example, low yields of **4** or **5** were obtained with α-bromothiol ester **1a** using NaH in DMF. The use of the polar DMF solvent may favor alkylation of acetone or cyclohexanone by **1a**. Intramolecular as well as intermolecular nucleophilic substitution processes are known to proceed more rapidly as the polarity of the solvent is increased.[2i,1] Also in support of this interpretation we have found that the NaH–DMF conditions work well in the reaction of **1a** with benzaldehyde, which may not undergo this alkylation reaction. It is noteworthy that the NaH–DMF conditions were effective in the reaction of cyclohexanone with *S-tert*-butyl 2-bromothiolpropionate (**1b**). In this reaction the alkylation process would occur at a secondary carbon while in the reaction with **1a** a primary carbon is involved. Competing reactions involving alkylation of the ketone substrate have been noted previously in the Darzens synthesis of glycidic (oxygen) esters.[5] This process was shown to be important when α-bromo esters or α-iodo esters were substituted for α-chloro esters. This in part accounts for the preferential use of chloro reactants in the majority of Darzens reactions reported to date.

Another illustration of the need for careful choice of reaction conditions is found in the reaction of *S*-benzyl 2-bromothiolacetate (**1d**) with aldehydes and ketones. In the reaction of **1d** with benzaldehyde a 35% yield of *cis*- and *trans*-*S*-benzyl 3-phenylthiolglycidates (**7**) was obtained using the NaH–DMF conditions although no **7** was found using $LiN(SiMe_3)_2$ in THF. In contrast in the reaction of **1d** with cyclohexanone, a 70% yield of *S*-benzyl thiolglycidate (**6**) was obtained using the $LiN(SiMe_3)_2$–THF conditions although 10% was found using NaH in DMF.

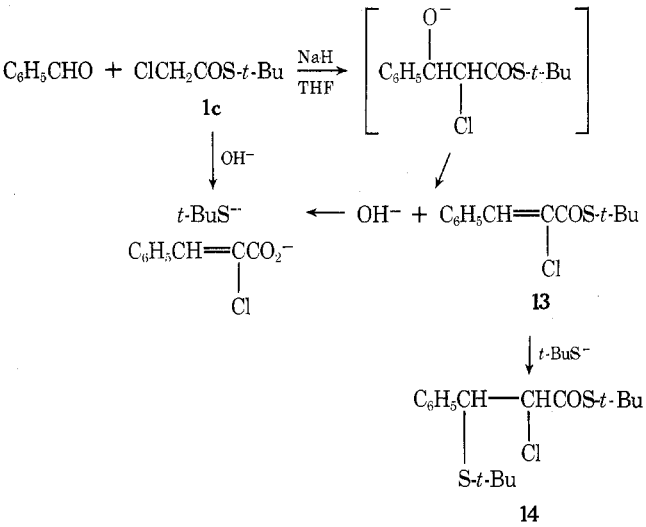
We were interested in learning why α-chlorothiol esters gave low yields in the Darzens synthesis of glycidic thiol esters. In the reaction of cyclohexanone with *S-tert*-butyl 2-chlorothiolpropionate (**1f**) using the NaH–DMF conditions we obtained 15% of thiolglycidate **9**. We also isolated two by-products, *S-tert*-butyl 2-(*tert*-butylthio)thiolpropionate (**12**) and β-lactone **11**. The NMR spectrum of **12** was unusual in that it gave a doublet at δ 1.41 (21 H) and a quartet at δ 3.42 (1 H). This spectra may be explained if we assume that the two *tert*-butyl peaks are superimposed on the methyl doublet. To confirm this interpretation **12** was prepared independently from **1f** and *tert*-butyl mercaptan in DMF solvent using NaH as a base. The structure of β-lactone **11** is based on analytical data and spectral evidence. **11** had a carbonyl absorption at 1820 cm^{-1} in the ir spectrum and an NMR spectrum which showed a singlet at δ 1.75 superimposed on a multiplet between δ 1.35 and 2.15. The mass spectrum gave intense peaks at *m/e* 144 and 146 ($M\cdot^+ - CO_2$) and at 109 [$M\cdot^+ - (CO_2$ and Cl)]. The formation of β-lactone **11** suggests that an intramolecular nucleophilic acyl substitution reaction may compete with the epoxide forming substitution process in the Darzens synthesis of glycidic thiol esters (Scheme II). The liberated *tert*-butyl thiolate anion is then trapped by starting material (**1f**), leading to the formation of **12**.

A large number of products were obtained in the reaction of benzaldehyde with *S-tert*-butyl 2-chlorothiolacetate (**1c**) using NaH in THF. We were able to isolate 2-chlorocinnamic acid along with *erythro*- and *threo*-*S-tert*-butyl 3-*tert*-butylthio-2-chloro-3-phenylthiolpropionate (**14**). The isolation of **14** suggests that aldol condensation involving formation of an α-chloro α,β-unsaturated thiol ester derivative such as **13** is another important competing process in the Darzens synthesis of glycidic thiol esters (Scheme III). A similar side reaction has been observed previously in the Darzens reaction of benzaldehyde with ethyl chloroacetate leading to the formation of ethyl 2-chlorocinnamate.[6] α-Chloro ketones are also known to undergo this elimina-

Scheme II



Scheme III



tion process.[7] This reaction may be particularly important with thiol esters, since the acidity of protons adjacent to a thiol ester group is substantially greater than protons α to the (oxygen) ester.[8] A competing elimination process of this type may be used to explain the result that no thiolglycidate **2a** was obtained in the reaction of benzaldehyde with *S-tert*-butyl 2-chlorothiolacetate (**1c**) using NaH in DMF. In this connection it is interesting that under the same conditions 45% of thiolglycidate **2b** was obtained in the reaction of benzaldehyde with *S-tert*-butyl 2-chlorothiolpropionate (**1f**), a reaction which would not be expected to undergo this elimination process. Thiolglycidate **2a** may be obtained in 67% yield from *S-tert*-butyl 2-bromothiolglycidate (**1a**) and benzaldehyde using NaH in DMF.[1b] When the chlorine is replaced by the bromine leaving group, intramolecular substitution (step 3, Scheme I) is able to compete with the side reaction involving proton abstraction.

Experimental Section

General. Infrared spectra were recorded on a Perkin-Elmer Model 457 spectrometer. Nuclear magnetic resonance spectra were recorded on a Varian Associates Model A-60A spectrometer using tetramethylsilane (Me_4Si) as an internal standard. Mass spectral analysis was performed on a Varian MAT CH-5 spectrometer. THF was dried over sodium metal–anthracene complex and distilled prior to use. DMF was initially refluxed with a mixture of potassium hydroxide and calcium oxide overnight. It was then distilled and the distillate was dried over P_2O_5, distilled again, and finally stored over molecular sieves [type 4A (4–8 mesh)]. Benzene was dried over sodium metal while ether was dried over $LiAlH_4$. Both were distilled prior to use. Elemental analysis were performed by M-H-W Laboratories, Garden City, Mich. Melting points and boiling points are uncorrected. The petroleum ether had a boiling point range of 60–110°. The silica gel used in column chromatography was Baker reagent grade (60–200 mesh). Aldehydes and ketones were purified by distillation.

***S-tert*-Butyl 2-Bromothiolacetate (1a).** Pyridine (40 g, 0.51 mol) in chloroform (50 ml) and *tert*-butyl mercaptan (45 g, 0.50 mol) in chloroform (50 ml) were added separately and simultaneously over a 30-min period to a stirred solution of 2-bromoacetyl bromide[9] (101 g, 0.50 mol) in chloroform (150 ml) at 0°. The reaction mixture was stirred for an additional 90 min at 0° and then for 1 hr at room temperature. The chloroform was removed under reduced pressure and the residue was dissolved in ether (300 ml) and extracted once with cold water (200 ml). The water layer was reextracted with ether (150 ml) and the combined ether layers were dried (Na_2SO_4) and concentrated. The residue was purified by fractional distillation to give **1a** as a colorless oil: bp 58–60° (1.3 mm) (63 g, 0.30 mol, 60%); $n^{26}D$ 1.5077; NMR (CCl_4) δ 3.88 (s, 2 H), 1.48 (s, 9 H); ir (thin film) 1690 cm^{-1} (broad).

Anal. Calcd for $C_6H_{11}OSBr$: C, 34.13; H, 5.25; S, 15.19; Br, 37.85. Found: C, 34.23; H, 5.36; S, 15.00; Br, 38.07.

The following 2-halothiolacetates were prepared using a similar procedure.

***S*-Benzyl 2-bromothiolacetate (1d)** was obtained as a colorless oil from 2-bromoacetyl bromide and benzyl mercaptan: 60%; bp 114–116° (0.3 mm); $n^{27}D$ 1.5980; NMR (CCl_4) δ 7.15 (s, 5 H), 4.03 (s, 2 H), 3.80 (s, 2 H); ir (thin film) 1690 cm^{-1} (broad).

Anal. Calcd for C_9H_9OSBr: C, 44.09; H, 3.70; S, 13.08; Br, 32.60. Found: C, 44.12; H, 3.82; S, 12.88; Br, 32.79.

***S*-Phenyl 2-bromothiolacetate** was obtained as colorless plates (decomposes on standing) from 2-bromoacetyl bromide and benzenethiol: 59% mp 38–39° from benzene–petroleum ether; NMR (CCl_4) δ 7.30 (s, 5 H), 3.93 (s, 2 H); ir (KBr) 1695 cm^{-1} (broad).

Anal. Calcd for C_8H_7OSBr: C, 41.57; H, 3.05; S, 13.87; Br, 34.58. Found: C, 41.69; H, 3.09; S, 13.64; Br, 34.53.

***S*-Benzyl 2-chlorothiolacetate** was obtained as a colorless oil from 2-chloroacetyl chloride[9] and benzyl mercaptan: 73%; bp 100–101° (0.1 mm); $n^{26}D$ 1.5782; NMR (CCl_4) δ 7.16 (s, 5 H), 4.03 (s), and 3.99 (s) (4 H); ir (thin film) 1680 cm^{-1} (broad).

Anal. Calcd for C_9H_9OSCl: C, 53.86; H, 4.52; S, 15.98; Cl, 17.66. Found: C, 54.04; H, 4.58; S, 16.16; Cl, 17.54.

***S-tert*-Butyl 2-Bromothiolpropionate (1b).** Pyridine (12.6 g, 0.16 mol) in chloroform (25 ml) and *tert*-butyl mercaptan (14.4 g, 0.16 mol) in chloroform (25 ml) were added separately and simultaneously over a 30-min period to a stirred solution of 2-bromopropionyl bromide[10] (37.5 g, 0.17 mol) in chloroform (50 ml) at 0°. The reaction mixture was stirred for an additional 90 min at 0° and for 1 hr at room temperature. The chloroform was evaporated and ether (200 ml) and water (100 ml) were added. The water layer was extracted with additional ether (100 ml) and the combined ether layers were extracted with 5% $NaHCO_3$ (2 × 50 ml), dried (Na_2SO_4), and concentrated to give an oil which was purified by fractional distillation, bp 68–71° (0.6 mm). **1b** was obtained as a colorless oil (26.7 g, 0.12 mol, 74%): $n^{26}D$ 1.4965; NMR (CCl_4) δ 4.31 (q, 1 H, J = 7 Hz), 1.77 (d, 3 H, J = 7 Hz), 1.48 (s, 9 H); ir (thin film) 1690 cm^{-1} (broad).

Anal. Calcd for $C_7H_{13}OSBr$: C, 37.34; H, 5.82; S, 14.24; Br, 35.49. Found: C, 37.35; H, 5.63; S, 14.06; Br, 35.72.

***S-tert*-Butyl 2-Bromothiolbutyrate (1e).** Using the same procedure **1e** was prepared from 2-bromobutyryl bromide[10] and *tert*-butyl mercaptan: 63%; $n^{26}D$ 1.4940; NMR (CCl_4) δ 4.11 (t, 1 H, J = 7 Hz), 1.97 (m, 2 H), 1.49 (s, 9 H), 1.03 (t, 3 H, J = 7 Hz); ir (thin film) 1685 cm^{-1} (broad).

Anal. Calcd for $C_8H_{15}OSBr$: C, 40.17; H, 6.32; S, 13.41. Found: C, 40.33; H, 6.32; S, 13.55.

***S-tert*-Butyl 2-Chlorothiolpropionate (1f).** Using the procedure described by Dawson[11] for the preparation of *S-tert*-butyl 2-chlorothiolacetate, **1f** was synthesized from *tert*-butyl mercaptan and 2-chloropropionyl chloride:[9] 70%; bp 105° (35 mm); $n^{29}D$ 1.4734; NMR (CCl_4) δ 1.50 (s, 9 H), 1.65 (d, 3 H, J = 7 Hz), 4.32 (q, 1 H, J = 7 Hz); ir (thin film) 1680 cm^{-1} (broad).

Anal. Calcd for $C_7H_{13}OSCl$: C, 46.52; H, 7.27; S, 17.74; Cl, 19.61. Found: C, 46.34; H, 7.32; S, 17.61; Cl, 19.84.

Reaction of 1b with *p*-Nitrobenzaldehyde and Anisal-

dehyde. A 54% NaH dispersion in mineral oil (0.49 g, 11 mmol) was washed with hexane (3 × 10 ml) under nitrogen atmosphere and dry DMF (25 ml) was added. A mixture of anisaldehyde (1.36 g, 10 mmol), *p*-nitrobenzaldehyde (1.51 g, 10 mmol), and **1b** (2.25 g, 10 mmol) in DMF (15 ml) was added to the NaH at 0° over a period of 10 min. After the addition the reaction was stirred at 0° for 30 min and then at room temperature for 75 min. The reaction mixture was extracted with petroleum ether (3 × 50 ml). The combined petroleum ether extracts were washed with water (2 × 50 ml), dried (Na_2SO_4), and concentrated to give an oil that solidified on standing. Water (100 ml) was added to the DMF extract and this was extracted with ether (3 × 50 ml). The combined ether extracts were reextracted with water (2 × 25 ml), dried (Na_2SO_4), and concentrated to give an oil. NMR analysis indicated that the oil obtained from both the ether and petroleum ether extractions contained substantial amounts of anisaldehyde and *trans*- and *cis*-*S*-*tert*-butyl 2-methyl-3-*p*-nitrophenyloxiranecarbothioate (**3**). The fractions were thus combined and subjected to column chromatography on silica gel eluting with 1:3 benzene–petroleum ether. The trans isomer was the first product eluted from the column (1.36 g, 4.6 mmol, 46%). Recrystallization (benzene and hexane) gave faint yellow plates: mp 107–108°; NMR (CCl_4) δ 8.23 (d, 2 H, J = 9 Hz), 7.49 (d, 2 H, J = 9 Hz), 4.17 (s, 1 H), 1.48 (s, 9 H), 1.23 (s, 3 H); ir (KBr) 1660 cm^{-1}.

Anal. Calcd for $C_{14}H_{17}O_4NS$: C, 56.93; H, 5.80; N, 4.74; S, 10.86. Found: C, 56.91; H, 5.78; N, 4.74; S, 10.95.

The cis isomer (0.87 g, 2.9 mmol, 29%) was obtained after further elution with benzene–petroleum ether (1:3). Recrystallization from hexane gave faint yellow plates: mp 81–82°; NMR (CCl_4) δ 8.23 (d, 2 H, J = 9 Hz), 7.60 (d, 2 H, J = 9 Hz), 4.04 (s, 1 H), 1.70 (s, 3 H), 1.22 (s, 9 H); ir (KBr) 1670 cm^{-1}.

Anal. Calcd for $C_{14}H_{17}O_4NS$: C, 56.93; H, 5.80; N, 4.74; S, 10.86. Found: C, 57.10; H, 5.68; N, 4.81; S, 10.65.

Finally anisaldehyde (1.24 g, 91%) was recovered by further elution with benzene–petroluem ether (1:3). *p*-Nitrobenzaldehyde was not detected in the NMR spectrum of the crude reaction mixture nor was any isolated from the chromatography column.

***S*-*tert*-Butyl 1-Oxaspiro[2.5]octane-2-carbothioate (4).** A 57% sodium hydride dispersion in mineral oil (0.558 g, 13 mmol) was washed with hexane (4 × 15 ml) under nitrogen atmosphere and anhydrous THF (15 ml) was added. A mixture of cyclohexanone (0.98 g, 10 mmol) and **1a** (2.11 g, 10 mmol) in THF (10 ml) was added at a rate of approximately 1 ml/min to the stirred mixture of NaH in THF at 0°. After the addition the reaction was stirred at 0° for an additional 30 min and then at room temperature for 30 min before filtering through a sintered glass funnel (coarse). The filtrate was added to a mixture of cold water (200 ml) and ether (150 ml). The ether layer was separated and the water layer was extracted again with ether (75 ml). The combined ether extracts were dried (Na_2SO_4) and concentrated to give an oil which was purified by careful column chromatography on silica gel eluting with petroleum ether followed by benzene–petroleum ether (1:1). **4** was obtained as an oil (1.58 g, 6.9 mmol, 69%). Short-path distillation (130–135° bath temperature, 0.6 mm) gave a colorless oil which crystallized on standing overnight under reduced pressure. Recrystallization (hexane) gave colorless plates: mp 31–32°; NMR (CCl_4) δ 3.12 (s, 1 H), 1.45 (s) superimposed on 1.59 (broad singlet), 19 H; ir (KBr)[12] 1665 (strong), 1695 cm^{-1} (medium).

Anal. Calcd for $C_{12}H_{20}O_2S$: C, 63.11; H, 8.83; S, 14.04. Found: C, 63.23; H, 8.90; S, 14.24.

Reaction of Benzaldehyde with *S*-*tert*-Butyl 2-Chlorothiolacetate (1c). Using the same NaH–THF procedure benzaldehyde was allowed to react with **1c**[11] to give an oil after evaporation of the ether extract. The NMR spectrum of this oil indicated the presence of a large number of products. It was subjected to column chromatography on silica gel eluting with petroleum ether. A product crystallized from fraction 5 that was purified by recrystallization from hexane to give one of the diastereoisomers of **14**: 6%; mp 75–76°; NMR (CCl_4) δ 7.53–7.18 (m, 5 H), 4.30 and 4.27 (AB quartet, 2 H, J_{AB} = 10 Hz), 1.50 (s, 9 H), 1.20 (s, 9 H); ir (KBr) 1670 cm^{-1}.

Anal. Calcd for $C_{17}H_{25}OS_2Cl$: C, 59.19; H, 7.31; S, 18.59; Cl, 10.28. Found: C, 59.46; H, 7.54; S, 18.39; Cl, 10.09.

From fraction 8 a product crystallized after standing for several days. It was purified by recrystallization from hexane to give the other diastereoisomer of **14**: 4%; mp 90–91°; NMR (CCl_4) δ 7.70–7.20 (m, 5 H), 4.54 and 4.34 (AB quartet, 2 H, J_{AB} = 6.5 Hz), 1.41 (s, 9 H), 1.24 (s, 9 H); ir (KBr) 1660 cm^{-1}.

Anal. Calcd for $C_{17}H_{25}OS_2Cl$: C, 59.19; H, 7.31; S, 18.59; Cl, 10.28. Found: C, 59.35; H, 7.44; S, 18.45; Cl, 10.50.

The basic water layer that remained after the initial ether extraction was acidified with 10% HCl and extracted with ether. Evaporation of this ether extract gave an oil that partially crystallized on standing. Separation of the residual oil from the solid and recrystallization from benzene–hexane gave *trans*-(*Z*)-2-chlorocinnamic acid: 10%; mp 137–139° (lit.[13] 137°). This material was identical (mixture melting point and ir spectrum) with authentic *trans*-(*Z*)-2-chlorocinnamic acid (mp 138–139°) that was prepared by autoxidation of 2-chlorocinnamaldehyde.[9]

***S*-*tert*-Butyl 2-Methyl-1-oxaspiro[2.5]octane-2-carbothioate (9).** A 57% sodium hydride dispersion in mineral oil (0.558 g, 13 mmol) was washed with hexane (4 × 15 ml) under nitrogen atmosphere and dry DMF (20 ml) was added. The mixture was cooled to 0°. Cyclohexanone (0.98 g, 10 mmol) and **1b** (2.25 g, 10 mmol) in dry DMF (10 ml) was added dropwise over a period of 10–15 min. The reaction mixture was stirred for an additional 30 min at 0° and then at room temperature for 30 min before it was filtered through a sintered glass funnel (coarse). The filtrate was extracted with petroleum ether (2 × 150 ml) and the combined petroleum ether extracts were washed with water (2 × 50 ml), dried (Na_2SO_4), and concentrated (below 40°) to give an oil which was chromatographed on silica gel eluting with petroleum ether followed by benzene–petroleum ether (1:1) to give the product (1.4 g, 6.0 mmol, 60%). An analytical sample of **9** was obtained as a faint yellow oil after short-path distillation (118–120° bath temperature, 0.2 mm): $n^{26}D$ 1.4874; NMR (CCl_4) δ 1.40 (s, 3 H), 1.45 (s, 9 H), 1.60 (broad singlet, 10 H); ir (thin film) 1670 cm^{-1}.

Anal. Calcd for $C_{13}H_{22}O_2S$: C, 64.42; H, 9.15. Found: C, 64.28; H, 9.34.

The following glycidic thiol esters were prepared using the same procedure.

***S*-Benzyl 3-Phenyloxiranecarbothioate (7).** A 6:4 mixture of *trans*- and *cis*-**7** was obtained from benzaldehyde, **1d**, and NaH in DMF in 35% yield after column chromatography. Fractional recrystallization from hexane gave pure *trans*-**7**: mp 65–66°; NMR (CCl_4) δ 7.29 (s, 10 H), 4.10 (s, 2 H), 3.97 (d, 1 H, J = 1.5 Hz), 3.52 (d, 1 H, J = 1.5 Hz); ir (KBr) 1660 cm^{-1}. The 1.5-Hz epoxide proton coupling constant is consistent with the trans stereochemical assignment.[14]

Anal. Calcd for $C_{16}H_{14}O_2S$: C, 71.08; H, 5.22; S, 11.86. Found: C, 71.36; H, 5.16; S, 12.03.

***S*-*tert*-Butyl 3-Isopropyloxiranecarbothioate (8).** A 6:4 mixture of *cis*- and *trans*-**8** was obtained from isobutyraldehyde, **1a**, and NaH in DMF in 62% yield after column chromatography. The mixture was subjected to short-path distillation (bath temperature 95–98°, 0.6 mm) followed by preparative thin layer chromatography (Merck silica gel GF-254) developing six times with benzene–hexane (3:7). The cis (*Z*) isomer traveling with the lower R_f was obtained essentially pure: NMR (CCl_4) δ 3.35 (d, 1 H, J = 4.5 Hz), 2.65 (doublet of doublets, 1 H, J = 4.5, 8.0 Hz), 1.75 (m, 1 H), 1.45 (s, 9 H), 1.08 (d, 3 H, J = 6.0 Hz), 0.86 (d, 3 H, J = 6.5 Hz); ir (thin film) 1670, 1690 cm^{-1}. The 4.5-Hz epoxide proton coupling constant is consistent with the cis stereochemical assignment.[14]

Anal. Calcd for $C_{10}H_{18}O_2S$: C, 59.37; H, 8.97; S, 15.85. Found: C, 59.62; H, 9.23; S, 15.61.

The trans isomer [δ 3.11 (d, J = 1.5 Hz), 2.83 (doublet of doublets, J = 1.5, 6.0 Hz)] traveling with the higher R_f was obtained with a small amount of cis impurity.

***S*-*tert*-Butyl (*E*)-2-Ethyl-3-phenyloxiranecarbothioate (10).** A 9:1 mixture of *trans*- and *cis*-**10** was obtained from benzaldehyde, **1e**, and NaH in DMF in 59% yield after column chromatography. The product was subjected to short-path distillation (140–145° bath temperature, 0.2 mm) to give **10** as a colorless oil (purification by thin layer chromatography on silica gel using petroleum ether as eluent did not result in any change in the spectral data): $n^{23}D$ 1.5253; NMR (CCl_4) δ 7.23 (s, 5 H), 4.03 (s, 1 H), 1.48 (s) superimposed on 2.30–1.10 (m) (11 H), 1.10–0.70 (m, 3 H); ir (thin film) 1675 cm^{-1}. The chemical shift value of δ 1.48 for the *tert*-butyl group is in agreement with the trans stereochemical assignment.[15]

Anal. Calcd for $C_{15}H_{20}O_2S$: C, 68.14; H, 7.63; S, 12.13. Found: C, 68.16; H, 7.64; S, 12.33.

Reaction of 1f with Cyclohexanone. Cyclohexanone was allowed to react with **1f** using the NaH–DMF procedure to give an oil which was purified by column chromatography on silica gel eluting with petroleum ether, followed by benzene–petroleum ether (1:4). Fractions 3–6 contained **12** (34%). This material gave the same NMR and ir spectrum as authentic **12** prepared as described below. Fractions 8–10 contained β-lactone **11** (11%) obtained as a solid (mp 66–68°). This was recrystallized from ben-

zene–hexane to give **11** as colorless plates: mp 69–70°; NMR (CCl_4) δ 1.75 (s) superimposed on a multiplet between δ 1.35 and 2.15; ir (KBr) 1820 cm^{-1} (strong); mass spectrum *m/e* (rel intensity) 146 (27), 144 (78) ($M^+ - CO_2$), 109 (98) [$M - (CO_2 + Cl)$], 92 (50), 90 (100), 81 (88), 79 (83), 68 (90), 67 (85), 55 (73). Molecular ion peaks at *m/e* 188 and 190 were not observed.

Anal. Calcd for $C_9H_{13}O_2Cl$: C, 57.29; H, 6.96; Cl, 18.79. Found: C, 57.48; H, 7.08; Cl, 19.00.

Fractions 12–14 contained glycidic thiol ester **9** (15%). Fraction 11 was a mixture of **9** and **11**.

***S-tert*-Butyl 2-(*tert*-Butylthio)thiolpropionate (12).** a mixture of *tert*-butyl mercaptan (2.0 g, 22 mmol) and **1f** (3.6 g, 20 mmol) in DMF (5 ml) was added to sodium hydride (24 mmol or 1.06 g of a 54% dispersion in mineral oil washed three times with hexane) in DMF (15 ml] at 0°. The reaction was allowed to stir for 30 min at 0° and 30 min at room temperature before water (25 ml) was added. The product was extracted into petroleum ether (3 × 50 ml) and the combined petroleum ether extracts were washed with water (2 × 25 ml), dried (Na_2SO_4), and concentrated. The residue was purified by short-path distillation to give **12** as a colorless oil (3.5 g, 15 mmol, 75%): $n^{28}D$ 1.4884; NMR (CCl_4) δ 1.35 (s) and 1.48 (s) (21 H), 3.42 (q, 1 H, J = 7.5 Hz); ir (thin film) 1670, 1690 cm^{-1} (shoulder).

Anal. Calcd for $C_{11}H_{22}OS_2$: C, 56.36; H, 9.46; S, 27.36. Found: C, 56.26; H, 9.69; S, 27.50.

Lithium bis(trimethylsilyl)amide in THF was prepared according to literature methods.[16] *n*-Butyllithium (32 ml of a 1.59 *M* hexane solution) was added slowly over a 15-min period to hexamethyldisilazane (11 ml, 53 mmol) in anhydrous ether (15 ml) under nitrogen atmosphere. The mixture was refluxed for 30 min, the ether was evaporated, and anhydrous THF (50 ml) was added to the residue, all of which dissolved to give a 0.80 *M* solution of $LiN(SiMe_3)_2$. The molarity of this solution was determined by the titration of a 10-ml aliquot with *tert*-butyl alcohol using 4-phenylazodiphenylamine as indicator.[2k]

S-Benzyl 1-Oxaspiro[2.5]octane-2-carbothioate (6). Cyclohexanone (0.98 g, 10 mmol) and **1d** (2.45 g, 10 mmol) were mixed with dry THF (5–10 ml) at 0° under nitrogen atmosphere. To this solution was added $LiN(SiMe_3)_2$ in dry THF (12.5 ml of a 0.80 *M* solution, 10 mmol) over a period of 15 min. The reaction mixture was stirred at 0° for 30 min and at room temperature for an additional 30 min before it was poured into ice water (200 ml) and ether (150 ml). The ether layer was separated and the water layer was extracted again with ether (100 ml). The combined ether layers were dried (Na_2SO_4) and concentrated to give an oil which was purified by column chromatography on silica gel (60 g) eluting with petroleum ether followed by benzene–petroleum ether (1:1) to obtain the product, **6** (1.84 g, 7.0 mmol, 70%) as an oil that crystallized on standing overnight under reduced pressure. Recrystallization (hexane) gave pale yellow needles: mp 32–33°; NMR (CCl_4) δ 7.13 (s, 5 H), 3.98 (s, 2 H), 3.20 (s, 1 H), 1.50 (broad singlet, 10 H); ir (KBr) 1675 (strong), 1695 cm^{-1} (medium).

Anal. Calcd for $C_{15}H_{18}O_2S$: C, 68.67; H, 6.91; S, 12.22. Found: C, 68.76; H, 6.88; S, 12.07.

***S-tert*-Butyl 3,3-Dimethyloxiranecarbothioate (5).** In a similar way **5** was prepared from acetone (2 equiv), **1a** (1 equiv), and $LiN(SiMe_3)_2$ (1 equiv) in THF in 60% yield after column chromatography. The addition of the reactants in the manner described by Borch[2k] involving initial addition of $LiN(SiMe_3)_2$ (1 equiv) to (**1a**) (1 equiv) at −78° followed by the addition of acetone (2 equiv) gave only a 40% yield. This same addition procedure carried out at 0° also gave a 40% yield. However, the addition of base (1 equiv) to **1a** (1 equiv) and acetone (2 equiv) in THF at −78°, stirring for 30 min at −78°, followed by warming to room temperature and stirring for an additional 30 min gave a higher yield (72%) of **5**. The product was obtained as a faint yellow oil after short-path distillation (85–90° bath temperature, 0.6 mm): $n^{25}D$ 1.4702; NMR (CCl_4) δ 3.10 (s, 1 H), 1.40 (s, 9 H), 1.30 (s, 6 H); ir (thin film) 1670 (strong), 1695 cm^{-1} (medium).

Anal. Calcd for $C_9H_{16}O_2S$: C, 57.41; H, 8.57; S, 17.03. Found: C, 57.57; H, 8.79; S, 16.89.

Schotten–Baumann Preparation of 6. Using essentially the same procedure reported[3c] for the preparation of *S*-phenyl 3-methyl-3-phenylthioglycidate, sodium 1-oxaspiro[2.5]octane-2-carboxylate[17] was converted to **6** in 22% yield using oxalyl chloride, pyridine, and benzyl mercaptan. Recrystallization (hexane) gave pure **6** as pale yellow needles (mp 31–32°). This material was identical with **6** prepared from cyclohexanone and **1d** using the $LiN(SiMe_3)_2$–THF Darzens procedure described earlier. The mixture melting point for these two products was not depressed.

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Registry No.—**1a,** 32797-86-7; **1b,** 53635-53-3; **1c,** 56377-45-8; **1d,** 56377-46-9; **1e,** 56403-12-4; **1f,** 56377-47-0; *trans*-**3,** 56403-10-2; *cis*-**3,** 56377-35-6; **4,** 56377-48-1; **5,** 56377-49-2; **6,** 56377-50-5; *trans*-**7,** 56377-37-8; *cis*-**7,** 56377-38-9; *trans*-**8,** 56377-39-0; *cis*-**8,** 56377-40-3; **9,** 56377-54-9; *trans*-**10,** 56377-41-4; *cis*-**10,** 56377-42-5; **11,** 56377-55-0; **12,** 56377-56-1; **14** isomer 1, 56377-43-6; **14** isomer 2, 56377-44-7; *tert*-butyl mercaptan, 75-66-1; 2-bromoacetyl bromide, 598-21-0; benzyl mercaptan, 100-53-8; *S*-phenyl 2-bromothiolacetate, 56377-57-2; benzenethiol, 108-98-5; *S*-benzyl 2-chlorothiolacetate, 56377-58-3; 2-chloroacetyl chloride, 79-04-9; 2-bromopropionyl bromide, 563-76-8; 2-bromobutyryl bromide, 26074-52-2; 2-chloropropionyl chloride, 7623-09-8; *p*-nitrobenzaldehyde, 555-16-8; anisaldehyde, 123-11-5; cyclohexanone, 108-94-1; benzaldehyde, 100-52-7; isobutyraldehyde, 78-84-2; $LiN(SiMe_3)_2$, 4039-32-1; acetone, 67-64-1.

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