To what extent this influences the $\alpha'\Delta\delta$ values in *tert*-butyl oxygen esters is not clear based on available information.

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Registry No.—Isobutyryl chloride, 79-30-1; dichloroacetyl chloride, 79-36-7.

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Phase-Transfer Catalyzed Syntheses. 5-Thiacyclohexenecarboxaldehydes and 3,4-Epoxy-2,5-dihydrothiophenes[1]

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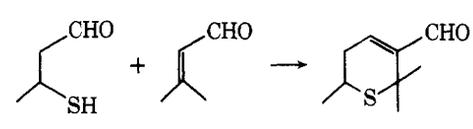
The phase-transfer catalyzed condensation of 3-thioacetoxyaldehydes with acrolein and crotonaldehyde leads to cyclized products **5–9**. Product distributions indicate that no equilibration of intermediates occurs as has been previously noted in pyridine solution. Condensations of α-mercaptocarbonyl compounds with 2-chloroacrylonitrile led to epoxides **11–14** in excellent yields. This reaction may be of some importance in biotin synthesis.

Recently, we have shown that the reaction of 3-mercaptoaldehydes (**1**) with conjugated carbonyl compounds affords, by a conjugate addition–aldol condensation sequence, an excellent route to substituted 5-thiacyclohexene-1-carboxaldehydes (**2**).[3] Compounds related to **2** have previously been shown[4] to be excellent synthons for stereospecific alkene synthesis. However, two drawbacks to the synthesis, as reported,[3] are evident. The first is the difficulty encountered in the purification of mercaptans **1**. Whereas the isomeric 2-mercaptoaldehydes exist largely as dimeric 2,5-dihydroxy-1,4-dithianes[5] which can be purified relatively easily, **1** are polymeric hemithioacetals which are uniformly evil-smelling, viscous oils that decompose (presumbly by dehydration) when distillation is attempted. This leads to complicated mixtures when the preparation of **2** is attempted. Although many examples of **1** are obtained pure enough for direct use in the cyclization, others are not and it was felt that an alternate preparation which avoided this difficulty would be desirable. Replacement of the thiol proton with a suitable protecting group which could be converted into the anion of **1** in situ would achieve this end. Furthermore, as the malodorous properties of most thiols are associated with the SH



1 **2**

Table I. Products and Yields from Crossed Condensations[a,b]

Ester (equiv)	Acceptor (equiv)	Temp, °C	Procedure[c]	Products (%)[d]		
3 (1)	CHO (1)	0	B	5 (13)	7 (8)	8 (79)
6 (1)	CHO (1)	0	A	5 (54)	7 (23)	9 (23)
6 (1)	CHO (1)	−10	A	5 (52)	7 (21)	9 (27)
6 (1)	CHO (2)	0	B	5 (60)	7 (7)	9 (33)
6 (1)	CHO (1)	20	B	5 (61)	7 (10)	9 (29)
6 (2)	CHO (1)	20	B	5 (42)	7 (27)	9 (31)

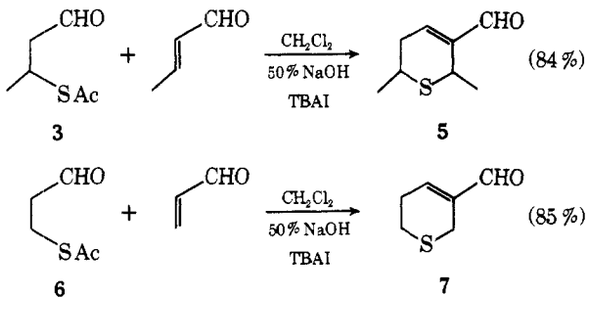
[a] Yields determined by GLC. [b] All reactions carried out using 2 equiv of 50% sodium hydroxide. [c] See Experimental Section. [d] Overall yield in each case was 60–62%.

group, the protected form held the distinctly attractive possibility of being much less noxious to handle. We report here our approach to this problem and some of the unforeseen results that were obtained.

Results and Discussion

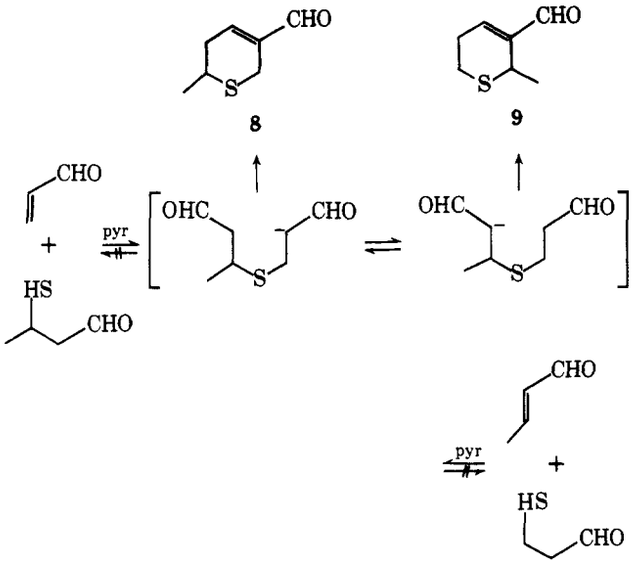
The thiolacetate was an obvious candidate for such a protecting group. 3-Thioacetoxycarbonyl compounds are readily prepared by addition of thiolacetic acid to unsaturated aldehydes and ketones[6] and are prevented from polymerization by virtue of the absence of a sulfhydryl proton. Basic hydrolysis should afford the thiolate ion required for the initiation of the cyclization reaction.

When 3-thioacetoxybutanal (3) was subjected to basic hydrolysis using alcoholic sodium hydroxide, neutralization afforded some 3-mercaptobutanol (4), but a considerable amount of crotonaldehyde was also formed. Acid-catalyzed methanolysis of 3 did afford 4 in good yield, but the problems previously alluded to regarding its purification arose and thus no advantage was gained. However, application of the phase-transfer technique[7] to the basic hydrolysis in the presence of crotonaldehyde as an acceptor molecule led directly to the formation of 4,6-dimethyl-3-thiacyclohexene-1-carboxaldehyde (5) in 84% yield.[8] Similar results were obtained in the condensation of 3-thioacetoxypropanal and acrolein.



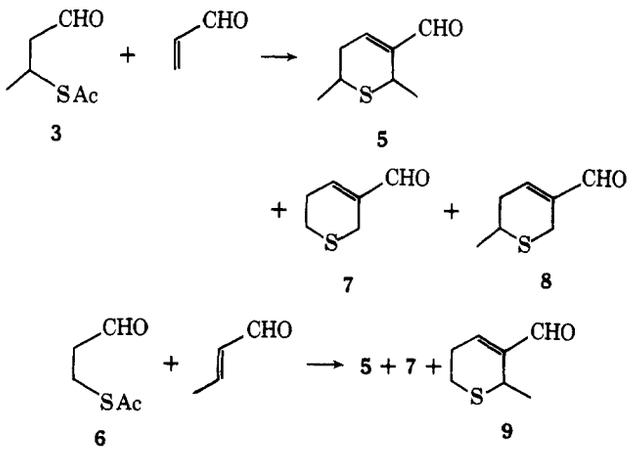
In our previous report,[3] the condensation of 3-mercaptobutanal and acrolein in pyridine solution led to two products—4-methyl-5-thiacyclohexene-1-carboxaldehyde (8) and its 6-methyl isomer (9). These results were rationalized on the basis of an anion equilibration (Scheme I). The absence of 5 and 7 from these reactions strongly suggested that reversal of the conjugate addition was not competing with ring closure in pyridine solution. It was of interest to determine if the same

Scheme I



results would be obtained under the phase-transfer conditions employed in this work. Evidence obtained previously in somewhat related systems[9] suggested that side reactions such as anion transposition are maximized when the rate of ring closure of the carbanionic intermediates is slow. In the system 50% aqueous sodium hydroxide–dichloromethane, the large amount of energy associated with removing water molecules from the strongly hydrogen-bonded aqueous phase suggests that the solvation of the anionic intermediates *in the organic phase* should be minimal and thus the rate of cyclization might increase dramatically. The near absence in these reactions of polymers of acrolein and crotonaldehyde which are usually formed in the presence of aqueous base[10] confirms that the reactions are in fact occurring in the organic phase.

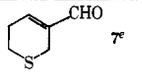
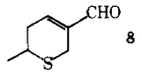
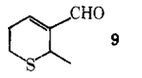
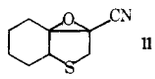
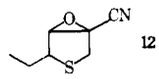
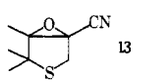
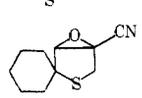
When 3 was condensed with acrolein under phase-transfer conditions, three products were formed, 5, 7, and 8. No trace of 9 could be detected either by NMR or GLC analysis, confirming our hypothesis regarding anion transposition. When the reverse condensation was attempted, a mixture of three materials (5, 7, and 9) was again obtained, now to the exclusion



of 8. Several different sets of reaction conditions were tried in an attempt to maximize the yields of 8 and 9 (Table I). As can be seen, these efforts met with limited success. However, the data obtained allow a possible rationalization of the observed results (Scheme II).

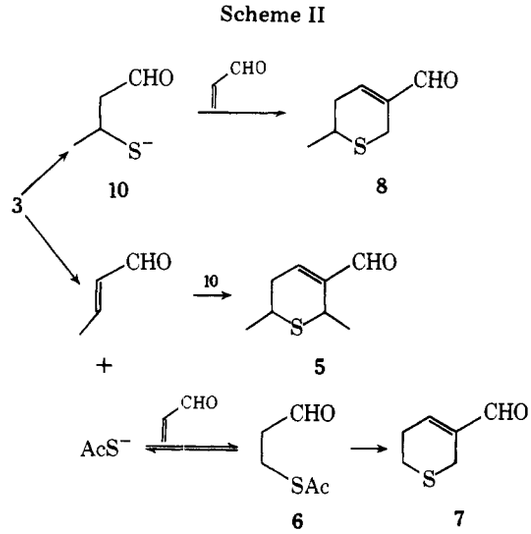
The formation of significant amounts of 5 and 7 and the absence of the products of alternate ring closure seem to exclude the possibility of direct anion equilibration. A more

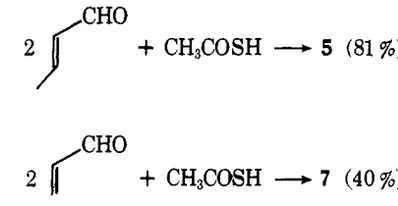
Table II. Spectral Data for Previously Unreported Compounds

Compd	n^{25}D or mp, °C	Infrared, cm^{-1} [a]	m/e (100%) [b]	^{1}H NMR [c,d]
 7 [e]	1.5365	2700 (w), 1690 (vs), 1648 (m)	128	9.33 (s, 1), 6.83 (m, 1), 3.26 (m, 2), 2.70 (m, 4)
 8	1.5316	2715 (w), 1688 (vs), 1647 (s) 1647 (s)	Found 142.0453 Calcd 142.0452	9.50 (s, 1), 6.88 (m, 1), 3.30 (m, 2) 2.95 (m, 1), 2.56 (m, 2), 1.28 (d, 3, J = 6.7 Hz)
 9	1.5413	2720 (w), 1690 (vs), 1649 (s)	Found 142.0453 Calcd 142.0452	9.40 (s, 1), 6.85 (m, 1), 3.70 (m, 1) 2.78 (m, 4), 1.45 (d, 3, J = 6.7 Hz)
 11	61–63	2244 (m), 1451 (vs), 1265 (s) 1250 (m), 944 (s), 912 (s), 870 (s)	Found 181.0561 Calcd 181.0561	3.23 (s, 2), 3.15 (m, 1), 1.75 (m, 8)
 12	1.5080	2240 (w), 910 (s), 855 (m)	Found 155.0405 Calcd 155.0405	3.86 (s, 1), 3.56 (m, 1), 3.27 (d, 2, J = 3 Hz), 1.6 (m, 2), 1.00 (t, 3, J = 7 Hz)
 13	36–37	2242 (w), 1463 (s), 1169 (s), 1137 (s), 941 (vs), 871 (s)	Found 169.0559 Calcd 169.0561	3.35 (s, 2), 1.58 (s, 3), 1.45 (s, 3) 1.40 (s, 3)
 14	110–112	2242 (w), 1450 (m), 1260 (w) 1165 (w), 1150 (w), 1110 (w), 970 (m), 950 (s), 910 (vs), 855 (m)	Found 195.0718 Calcd 195.0718	3.75 (s, 1), 3.48 and 3.32 (AB q, 2, J = 14 Hz), 1.70 (m, 10)

[a] In chloroform solution. [b] In all cases, the molecular ion is the base peak. [c] In deuteriochloroform solution. [d] Tabulation follows the order chemical shift (δ), multiplicity, number of protons, coupling constant. [e] Reference 3.

Scheme II





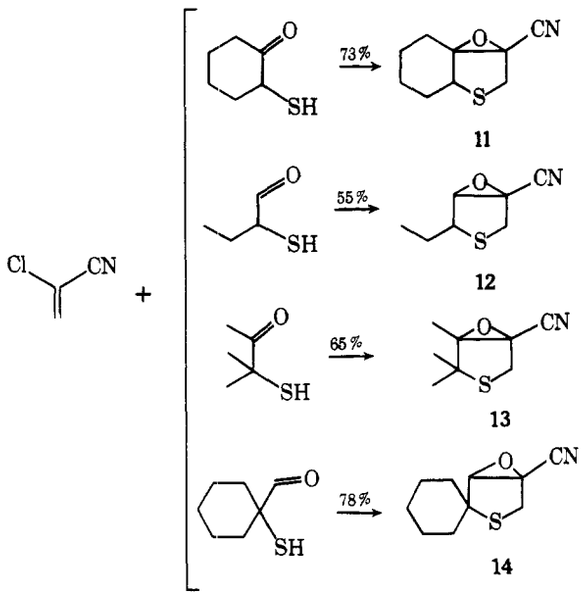
acceptable explanation assumes that the initial reaction between base and thiol ester **3** occurs in the organic phase and involves an elimination–hydrolysis competition leading to some crotonaldehyde and some of the desired anion **10**. Condensation of **10** with acrolein leads to **8** only, while condensation with the crotonaldehyde leads to **5**. Thiolacetate ion adds to acrolein forming **6** which then suffers hydrolysis and condensation with acrolein leading to **7**. Because of the relatively low concentrations of both **6** and crotonaldehyde, the rate of bimolecular reaction between these two would be expected to be very low, accounting for the absence of **9** from the mixture. Why the yield of **9** from the reaction of **6** and crotonaldehyde should be so much lower than that of **8** from **5** and acrolein is not immediately obvious.

In order that the above scheme can operate, it is necessary that the phase-transfer catalyzed addition of thiolacetic acid to crotonaldehyde and acrolein occur. In order to verify this, the reaction between 2 equiv of acceptor, 1 equiv of thiolacetic acid, and 2 equiv of 50% sodium hydroxide was carried out under the standard conditions. In each case, the expected condensation products were obtained. Unfortunately, neither cinnamaldehyde nor acrylonitrile could be induced to react.

Currently there is much interest in devising improved methods for the preparation of biotin and related molecules.[11] These contain a reduced thiophene ring, bearing heteroatom substituents at positions 3 and 4. An obvious possibility for the synthesis of these compounds involves the epoxidation of 2,5-dihydrothiophenes, but this route has proved abortive owing to the very facile oxidation of the sulfur atom.[12] It occurred to us that the incorporation of a leaving group adjacent to the anion-stabilizing group in the acceptor molecule might lead to an intramolecular Darzen's condensation and the desired epoxides. This type of reaction has been noted previously under non-phase-transfer conditions.[11]

In the event, reaction of a variety of α-mercaptocarbonyl compounds with 2-chloroacrylonitrile led to the ready formation of epoxides **11**, **12**, **13**, and **14**, in excellent yields.

The NMR spectra of epoxides **11**–**14** (Table II) require some comment. The spectra of **11** and **13** show a clean singlet for the diastereotopic methylene protons adjacent to sulfur, indicating an accidental degeneracy. The corresponding absorption for **12** appears to be a doublet. This doublet may be due to a long-range coupling through sulfur to the methine proton at C_5 or it may be the center two lines of an AB quartet of which the outer lines are too weak to be seen. In the case of **14**, a clear AB quartet is observable whose calculated coupling constant is 14 Hz. These differences may be ascribed to minor differences in the ring geometries in the four compounds. It should be noted that a similar complexity of the analogous protons in the dihydrothiophene related to **14** has been observed.[14]



Conclusion

To our knowledge, the results described constitute the first report of the successful condensation of reactive aliphatic aldehydes in the presence of strong aqueous base.[10] The application of the phase-transfer technique to these molecules will undoubtedly have considerable future use. Also, the consecutive liberation of a reactive functional group and its utilization under the same reaction conditions is an attractive feature which should find wide application in other systems. We are currently exploring some of these, as well as methods for improving the selectivity for hydrolysis of the thiol esters. These will form the basis of future reports.

Experimental Section

Melting points are uncorrected. Infrared spectra were obtained on a Beckman IR-12 instrument; NMR spectra were run on a JEOLCO C60HL spectrometer and are reported in parts per million downfield from Me_4Si as an internal standard. Mass spectra were run on a Varian-MAT CH5-DF spectrometer under the control of an INCOS computer. Gas chromatographic analyses were performed on an F and M Model 720 instrument, using the following columns; column A, 10 ft × 0.375 in. 20% SE-30 on Chromosorb W; column B, 10 ft × 0.375 in. 20% Carbowax 20M on Chromosorb W; column C, 10 ft × 0.25 in. 20% SE-30 on Chromosorb W. Preparative TLC was performed on 2 mm thick silica gel G.F. plates using 5% ether in petroleum ether as the eluting solvent.

Materials. Crotonaldehyde and acrolein were distilled just prior to use. Compounds 3 and 6 were prepared as outlined in the literature.[6]

General Procedures for Phase-Transfer Catalyzed Reactions. Procedure A. In a 250-mL round-bottom flask fitted with a magnetic stirrer, reflux condenser, nitrogen inlet, and addition funnel were placed 15 mL (0.185 mol) of 50% aqueous sodium hydroxide solution, 100 mL of methylene chloride, and 100 mg of tetra-*n*-butylammonium iodide (TBAI). The system was purged with nitrogen and cooled to the desired temperature. The mixture was stirred vigorously while 0.1 mol of the thiol ester was added rapidly. A pale yellow color developed immediately. After 1–2 min, the acceptor molecule (0.1 mol) was added rapidly. (Note that when acrolein was the acceptor, the ensuing reaction was vigorously exothermic.) The solution was stirred for 3 h, and then allowed to warm to room temperature overnight. After 1 h at reflux (40 °C), the cooled solution was diluted with water, the organic layer separated, and the aqueous phase extracted twice with ether. The combined organic layers were washed with water until the washings were neutral and dried over sodium sulfate and the solvent was removed to give the product(s) which were treated as outlined below. Infrared and NMR spectral data are collected in Table II.

Procedure B. The same general procedure was used except that the thioester and acceptor were added simultaneously to the cooled, stirred mixture containing the base and ammonium salt.

4,6-Dimethyl-5-thiacyclohex-1-enecarboxaldehyde (5). Using procedure A, 84% of 5 was obtained from 3 and crotonaldehyde which was identical in all respects with an authentic sample[3,15] (GLC, column C, 180 °C).

5-Thiacyclohex-1-enecarboxaldehyde (7). Using procedure A, a yellow oil was obtained from 6 and acrolein which showed only one peak on GLC analysis (column C, 180 °C). An analytical sample showed $n^{25}D$ 1.5365; *m/e* 128 (100%); 2,4-DNP mp 250–251 °C (lit.[16] 247–248 °C). Spectral data are included in Table II. This compound should be stored in ether solution to avoid decomposition.

4-Methyl-5-thiacyclohex-1-enecarboxaldehyde (8). Using procedure B, a mixture of 5, 7, and 8 in 70% yield was obtained when 3 was condensed with acrolein. These were separated by GLC (column B, 180 °C) and identified by their spectral characteristics.

6-Methyl-5-thiacyclohex-1-enecarboxaldehyde (9). The series of experiments outlined in Table I were performed. In each case, the product mixture was separated into three components by GLC (columns A or B) and identified by their spectral characteristics.

Reaction of thiolacetic acid and crotonaldehyde. The reaction was carried out in the usual fashion by adding the acceptor to a vigorously stirred mixture of 2 equiv of 50% sodium hydroxide, 1 equiv of thiolacetic acid, TBAI, and methylene chloride over a period of 30 min at 0 °C. The mixture was stirred for an additional 2.5 h at 0 °C and then refluxed for 20 min. The organic layer was separated, diluted with ether, washed thoroughly with water, dried, and evaporated. Aldehyde 5 (81%) was obtained as the only product.

Reaction of Thiolacetic Acid and Acrolein. Substituting acrolein for the crotonaldehyde in the above experiment afforded aldehyde 7 (41%).

Synthesis of Epoxynitriles 11, 12, and 13. The following procedure is representative. Sodium hydroxide (50%, 10 mL), methylene chloride (40 mL), and TBAI (150 mg) were cooled (ice–salt bath) in a round-bottom flask fitted with magnetic stirrer, two addition funnels, and a reflux condenser with a nitrogen inlet. 3-Mercapto-3-methyl-2-butanone[17] (2.63 g) in 5 mL of methylene chloride and 2-chloroacrylonitrile (1.75 g) in 5 mL of the same solvent were added simultaneously from the two funnels over a period of 1 h while the mixture was vigorously stirred. The reaction mixture was worked up as usual and the product was purified by preparative TLC to give 65% of pure nitrile 13.

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References and Notes

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