in reaching the transition state is dramatically demonstrated by the two equilibria presented in this paper.

Experimental Section

Addition of Difluorocarbene to Cyclohexa-1,3-diene. Sodium iodide (2.9 g, 0.193 mol), 2.2 g of (trifluoromethyl)phenylmercury (0.0063 mol), 10 mg of tetra-*n*-butylammonium iodide, and 10 mg of 18-crown-6 ether were placed in a 25-mL Carius tube in a dry box. The Carius tube was attached to a vacuum line and evacuated, and 0.7 g of cyclohexa-1,3-diene (0.00875 mol) was condensed into the tube from calcium hydride. The tube was sealed in vacuo and heated at 85 °C for 15 h. The tube was cooled in dry ice and opened, and all volatile materials were vacuum transferred to a liquid nitrogen cooled trap. The mixture was separated by GLPC, 20 ft × $^1/_4$ in. 10% TCP on Chrom P, 100 °C, 40 mL min^{-1}, to give only cyclohexa-1,3-diene and **1**, 0.49 g (56% yield): IR ν_{max} 1470 cm^{-1}, $\nu_{C=C}$ weak 1647 cm^{-1}; ^{1}H NMR δ 5.04 (vinyl, complex m, 2 H), 1.0–2.6 (br m, 6 H); ^{19}F ϕ 132.5 (midpoint) (AB, J_{AB} = 148.8 Hz, $\delta\ \nu_{AB}$ = 2390.67 Hz; upfield F br s, downfield F complex m); MS, m/e 130.0593 ± 0.000693 (M$^+$, 5.33 ppm); calcd 130.0594 [dev = 0.0008 (0.6 ppm)]; bp 109–110 °C.

Pyrolysis of 1. Pyrolysis was carried out in the gas phase, in Pyrex vessels heated in a thermostatted salt bath. The apparatus, as well as the gas-handling techniques have been described earlier.[5]

1 was pyrolyzed at 225 °C for 30 min, and the products were condensed into a liquid nitrogen cooled trap and separated by GLPC, 20 ft × $^1/_4$ in., 20% SE 30 on Chrom P 30/80, 105 °C, 40 mL min^{-1} to give recovered **1** and **2**.

2: IR ν_{max} 1125, $\nu_{C=C}$ 1600, 1660 cm^{-1}; NMR (0 °C) ^{1}H NMR δ 5.0–7.0 ppm (overlapping complex m); ^{19}F, ϕ 88.52 (complex dd, J = 9.4, 12.8 Hz); ^{13}C δ 135.56 (t, $^3J_{C-F}$ = 6.71 Hz), 132.86 (t, $^2J_{C-F}$ = 29.9 Hz), 131.81 (S), 123.53 (t, $^1J_{C-F}$ = 29.8 Hz), 123.18 (s), 119.89 (t, $^3J_{C-F}$ = 9.2 Hz), 118.92 (t, $^1J_{C-F}$ = 235 Hz); MS, m/e 130.0594 ± 0.00058 (M$^+$, 4.4 ppm); calcd 130.0594 [dev = 0.00003 (0.2 ppm)]; λ_{max} (EtOH) 224 nm (28 100).

At long pyrolysis time, a third component becomes the dominant product. MS/GC, 20 ft × $^1/_4$ in. 15% ODPN, 60 °C, 30 mL min^{-1} gives an MS almost identical with **2**. An NMR spectrum of the crude pyrolysis mixture gives an additional ^{19}F reasonance ϕ 94.26 (complex t, J = 10 Hz).

Reaction of 7-Methylenebicyclo[4.1.0]hept-2-ene with Diazomethane. To 1.5 g (0.014 mol) of olefin and 0.01 g of palladium diacetate in 5 mL of ethyl ether was added dropwise 30 mL of ethyl ether containing diazomethane prepared from 3.5 g Diazald (0.0163 mol). The reaction, virtually instantaneous as evidenced by the evolution of N$_2$, was filtered and the bulk of the ether was removed by fractional distillation, leaving a yellow oil. This was separated by GLPC, 10 ft × $^1/_4$ in., 10% SE 30 on Chrom P, 130 °C; 50 mL/min, to give starting material plus a single product.

12: 0.75 g (44% yield); IR (neat, film) 3062, 3030, 2995, 2915, 2850, 1640, 1440, 1047, 1017, 1003, 933, 893, 813, 772, 711 cm^{-1}; ^{1}H NMR δ 5.95 (vinyl, complex m, 1 H), 5.55 (vinyl, complex m, 1 H), 2.00–1.45 (cyclohexyl CH$_2$ and CH, m, 6 H), 0.78–0.58 (cyclopropyl CH$_2$, m, 4 H); ^{13}C δ 47.2, 5.57 (cyclopropyl CH$_2$), 16.54, 19.21 (cyclohexyl CH), 18.10, 22.00 (cyclohexyl CH$_2$), 19.21 (quarternary C), 123.19, 127.19 (vinyl CH); MS, m/e 120.0934 ± 0.0004 (M$^+$, 3.6 ppm); calcd for C_9H_{12}, 120.0939 [dev = 0.0004 (3.9 ppm)].

Pyrolysis of 12. **12** was pyrolyzed at 225 °C for 16 h; the products were condensed into a liquid N$_2$ cooled trap and separated by GLPC, 10 ft × $^1/_4$ in., 10% SE 30 on Chrom P, 150 °C, 50 mL/min to give **13** and **14**.

13: ^{1}H NMR (CDCl$_3$) δ 6.85–4.80 (vinylic H's, complex, 8 H), 0.85 (cyclopropyl CH$_2$, S, 4 H); ^{13}C NMR (CDCl$_3$) δ 15.87 (cyclopropyl CH$_2$), 21.00 (q C), 111.57, 117.67, 132.22, 133.47, 133.71, 143.71 (vinylic C's).

14: ^{1}H NMR (CDCl$_3$) δ 5.74 (vinylic, dd, J = 2.5, 5.4 Hz, 1 H), 5.27 (d, J = 5.4 Hz, 1 H), 3.8–3.1 (m, 1 H), 2.50–1.50 (cyclobutyl CH$_2$ and CH, m, 5 H), 0.70–0.53 (cyclopropyl CH$_2$, m, 4 H); ^{13}C NMR (CDCl$_3$) δ 7.36, 15.25 (cyclopropyl CH$_2$), 25.05, 25.79 (cyclobutyl CH$_2$), 43.41, 45.85 (CH), 132.74, 138.05 (vinyl), the quaternary carbon was not observed.

Acknowledgment. Support of this research, in part, by the National Science Foundation is gratefully acknowledged.

Registry No. **1**, 88703-78-0; **2**, 88703-79-1; **3**, 88703-83-7; **5**, 55758-72-0; **6**, 30915-44-7; **7**, 36398-96-6; **12**, 88703-80-4; **13**, 88703-81-5; **14**, 88703-82-6; 4-bromohepta-1,6-diene, 58794-16-4; 1,3-cyclohexadiene, 592-57-4; diazomethane, 334-88-3; difluorocarbene, 2154-59-8; (trifluoromethyl)phenylmercury, 24925-18-6.

Alkylation and Aldol Condensation Reactions of 1,3-Oxathiolanones[1]

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Received August 2, 1983

Reactions of 2,2,4-trimethyl-1,3-oxathiolan-5-one (**1b**) with alkyl halides in the presence of LDA and HMPA give alkylation products only with very reactive halides. In contast, 2,2-dimethyl-1,3-oxathiolan-5-one (**1a**) affords no alkylation products. Both **1a** and **1b** react with aldehydes and ketones to give diastereomeric mixtures of aldol products. Conjugated enones afford predominantly 1,2- or 1,4-addition depending on the structure of the reactants.

Recently, we described the reduction of substituted 1,3-oxathiolan-5-ones (**1**) as a preparative route to 2-mercaptoaldehydes[4] which are of value in the preparation of 2,5-dihydrothiophenes and their derived products.[5] Compounds **1** were prepared from the corresponding 2-mercaptoacids. When this preparation is used, access to **1** which bear complex substituents with further function-

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(1) Presented in part at the annual meeting of the Chemical Institute of Canada, Calgary, June, 1983.

(2) NSERC postgraduate scholarship holder, 1981–present.

(3) Taken in part from M.S. thesis of M.A.S., University of Windsor, 1982.

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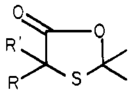
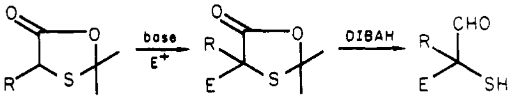
Table I. Yields of Alkylation and Condensation Products



			product			
entry	compd	E	No.	R	R′	% yield
1	**1b**	MeI	**2a**	Me	Me	90
2	**1b**	$PhCH_2$	**2b**	Me	$PhCH_2$	65
3	**1b**	$CH_2=CHCH_2Br$	**2c**	Me	$CH_2=CHCH_2$	62
4	**1a**	$PhCH_2Br$	**2d**	$PhCH_2$	$PhCH_2$	9
5	**1a**	BuI	**3b** + **4b**			
6	**1a**	BuI	**2e** + **3a** + **4a**			
7	**1a**	$Me_2C=O$	**2e**	H	$Me_2C(OH)$	63
8	**1b**	$Me_2C=O$	**2f**	Me	$Me_2C(OH)$	86
9	**1b**	MeCHO	**2g**	Me	MeCH(OH)	54
10	**1a**	PhCHO	**2h**	H	PhCH(OH)	63
10a	**1a**	PhCHO	**2h**	H	PhCH(OH)	67
11	**1b**	PhCHO	**2i**	Me	PhCH(OH)	70
12	**1a**	$CH_2=CHAc$	**2j**	H	$CH_2=CHC(OH)Me$	63
			2k	H	$AcCH_2CH_2$	
13	**1b**	$CH_2=CHAc$	**2l**	Me	$AcCH_2CH_2$	59
14	**1a**	cyclohexenone	**2m**	H	1-hydroxycyclohex-3-en-1-yl	73
15	**1b**	cyclohexenone	**2n**			
			2o	Me Me	3-oxocyclohexyl }	67

ality at C4 is difficult. However, the direct homologation of an electrophile which has the required functionality already in place with the anion of **1** would solve many of these difficulties [eq 1]. Such an approach requires a



(1)

1a, R = H
b, R = Me

2

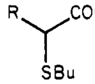
knowledge of the scope and limitations of the reactions of **1** with various electrophiles. In this report our observations on the reactions of **1a** and **1b** with alkyl halides and aldehydes and ketones are recorded.

In 1976 Schultz[6] reported that the condensation of **1b** with 2-cyclohexenone at ambient temperature led to 1,4-addition. A significant difference between **1b** and the molecule in which the sulfur atom had been replaced by oxygen was observed, in that the latter gave only 1,2-addition. This is in contrast to the results recently obtained from simple 2-alkoxy esters and 2-alkylthio esters[6] which afforded products of 1,2- and 1,4-addition depending on the reaction temperature.

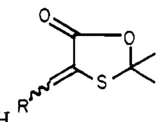
A very recent report,[7] which appeared after our alkylation experiments on **1a** and **1b** had been completed, notes that the alkylation of potassium enolates of 2-alkylthio aldehydes was successful only with very reactive alkyl halides. As is outlined below, our results are in concert with that report.

Results

Alkylation of **1a** or **1b** requires the formation of its anion. The effect of the sulfur atom in **1** is to make the adjacent protons more acidic than the corresponding protons in butyrolactone. Thus the base system which has been used successfully[8] to deprotonate butryolactone (LDA/HMPA) was used in the reactions of **1a** and **1b**. Using these conditions, alkylation of **1b** gave excellent yields of **2** when reactive halides are used (Table I). Less reactive alkylating agents (EtBr, BuBr, BuI) led to mixtures of products. The two major products in the mixture obtained from **1b** and BuI were tentatively identified as 2-(butylthio)propionic acid (**3b**) and its butyl ester (**4b**)



3a, R = H; R′ = H
b, R = Me; R′ = H
4a, R = H; R′ = Bu
b, R = Me; R′ = Bu



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by comparison of the GC retention times and NMR spectra of the mixture with those of authentic samples. The same result was obtained from all alkyl halides used when HMPA was omitted from the reaction mixture. Increasing the temperature from −78 to −45 °C did not significantly affect these results.

Alkylation of **1a** at −78 °C failed with all alkyl halides tried. Raising the temperature to −45 °C led to a complex mixture of products which appeared to contain **3a** and **4a**. Also isolated was compound **2e**. When benzyl bromide was used, GC/MS of the crude reaction product showed the absence of monoalkylated product but the presence of a 9% (isolated) yield of the dibenzylated material (m/z 312). The use of increased amounts of base and alkylating agent led mainly to the formation of *trans*-stilbene. The spectroscopic data for products **2** are summarized in Tables II and III.

We next turned our attention to the use of simple carbonyl compounds as the electrophilic species. As indicated in Table I (entries 7–11), these reactions are successful for both **1a** and **1b**. Where possible, **2** are obtained as mixtures of diastereomers, the ratios of which have been determined by integration of the appropriate ^1H NMR signals in the crude reaction products. In general, these ratios lie in the range of 1:1 to 7:3. Chromatographic separation of the stereoisomers was not attempted but assignments in the ^1H NMR spectra could easily be made based on the relative intensities of the absorptions. HMPA has no effect on the yields from these condensations but in one case (entry 10, Table I) a significant change in the diasteromeric

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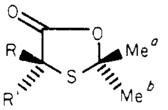
Table II. Physical and Spectroscopic Properties of Products

compd	bp, °C/mm; [mp], °C	IR, cm^{-1} ^{a}	^{1}H NMR, δ ^{b}
2a	[52-54]^c 86-90/24	1765, 1745 1175, 1078	1.78 (s, 6 H), 1.68 (s, 6 H)
2b	[54-55]^c	1743, 1215 1112, 1080	7.32 (s, 5 H), 3.10 (ABq, 2 H, *J* = 14 Hz), 1.70 (s, 3 H), 1.68 (s, 3 H), 1.20 (d, 2 H, *J* = 7 Hz)
2c	113-115/26	1750, 1225 1175, 1070	6.25-4.98 (ABXm, 3 H), 2.60 (d, 2 H, *J* = 7 Hz), 1.75 (s, 6 H), 1.63 (s, 3 H)
2d	[158-160]^c	1742, 1265 1215, 695	7.32 (s, 10 H), 3.21 (ABq, 4 H, *J* = 14 Hz), 0.84 (s, 6 H)
2e	[96-97]^c	1760 sh, 1738 1245, 1160	4.27 (s, 1 H), 3.71 (s, 1 H), 1.78 (s, 6 H), 1.38 (s, 3 H), 1.31 (s, 3 H)
2f	90-95/1.3	1750,^{d} 1740 1250, 1180	3.22 (s, 1 H), 1.77 (s, 6 H), 1.73 (s, 3 H), 1.40 (s, 3 H), 1.28 (s, 3 H)
2g	122-125/53	1740, 1260	4.01 (q, 1 H, *J* = 6 Hz), 3.52 (br s, 1 H), 1.78 (s, 3 H), 1.74 (s, 3 H), 1.70 (s, 3 H), 1.25 (d, 3 H, *J* = 6 Hz)
		1218, 1090	4.05 (q, 1 H, *J* = 6 Hz), 3.52 (br s, 1 H), 1.56 (s, 9 H), 1.19 (d, 3 H, *J* = 6 Hz)
2h^f	[109-120]	1755, 1220 1180, 700	7.33 (s, 5 H), 5.42 (d, 1 H, *J* = 3 Hz), 4.51 (d, 1 H, *J* = 3 Hz), 4.30 (OH), 1.87 (s, 3 H), 1.82 (s, 3 H)
	(not distilled)	1740, 1225 1180, 700	7.33 (s, 5 H), 5.03 (d, 1 H, *J* = 8 Hz), 4.42 (d, 1 H, *J* = 8 Hz), 3.00 (OH), 1.80 (s, 3 H), 1.72 (s, 3 H)
2i	(not distilled)	1704, 1260	7.40 (m, 5 H), 5.07 (s, 1 H), 4.70 (br s, 1 H), 1.79 (s, 3 H), 1.66 (s, 3 H), 1.19 (s, 3 H)
		1175, 1075	7.40 (m, 5 H), 4.93 (s, 1 H), 4.70 (br s, 1 H), 1.65 (s, 3 H), 1.43 (s, 3 H), 1.19 (s, 3 H)
2j^f	[44-69]	1740, 1245	6.50-5.07 (m, 3 H), 4.30 (s, 3 H), 3.43 (br s, 1 H), 1.77 (s, 3 H), 1.47 (s, 3 H)
		1220, 1100	6.50-5.07 (m, 3 H), 4.32 (s, 1 H), 3.93 (br s, 1 H), 1.77 (s, 3 H), 1.38 (s, 3 H)
2l	136-142/0.5	1775,^{d} 1717 1245, 1180	2.87-2.40 (m, 2 H), 2.15 (s, 3 H), 2.27-1.90 (m, 2 H), 1.77 (s, 6 H), 1.65 (s, 3 H)
2m^f	115-130/0.7	1735, 1220 1080, 990	6.17-5.53 (m, 2 H), 4.33 (s, 1 H), 3.25 (br s, 1 H), 2.53-1.47 (m, 6 H), 1.75 (s, 6 H)
	[92-120]^c	1750,^{d} 1230 1180, 990	6.13-5.40 (m, 2 H), 4.27 (s, 1 H), 3.67 (br s, 1 H), 2.53-1.47 (m, 6 H), 1.73 (s, 6 H)
2n^f	[93-115]^e	1750, 1210 1225, 1070	6.17-5.33 (m, 2 H), 3.40 (br s, 1 H), 2.47-1.47 (m, 6 H), 1.78 (s, 3 H), 1.73 (s, 6 H)
2o^{f,g}	134-146/0.9	1750,^{d} 1248 1175, 975	2.70-1.88 (m, 9 H), 1.78 (s, 3 H), 1.73 (s, 6 H)

[a] In CHCl$_3$ unless otherwise noted; four strongest peaks listed. [b] In CDCl$_3$. [c] From hexane. [d] Neat. [e] From ether. [f] Two diastereomers. [g] Contaminated with **2n**.

Table III. ^{13}C NMR Data for Products^{a,b,c}



compd	C2	C4	C5	CH$_3$	CH$_3$ ^{b}	R	R′
1a	88.9	33.3	172.7	30.7	30.7		
1b	86.0	42.4	174.6	31.3	30.9	17.9	
2a	84.5	52.8	177.8	32.6	32.6	30.2	30.2
2b	84.4	59.4	176.5	31.8	33.5	29.8	136.3, 131.0, 128.0, 127.1, 47.0
2c	84.5	57.2	176.3	32.6	33.4	28.5	132.7, 119.8, 45.7
2d	85.1	67.3	176.0	32.1			136.0, 131.5, 128.0, 127.2, 47.0
2e	86.3	58.5	174.0	31.0	32.6		72.5, 28.3, 25.5
2f	84.5	65.7	177.1	31.7	34.0	(28.6)	74.6, (25.2), (24.8)
2g	85.2	62.8	176.8	32.0	33.8	24.7	72.4, 18.5
2h	87.5	58.3	172.9	32.7	31.5		141.0, 128.0, 128.2, 125.7, 72.0
2i	85.8	63.5	176.8	31.6	33.7	25.7	130.1, 128.4, 128.1, 127.7, 77.9
2j	86.5	58.1	173.4	31.1	32.7		141.2, [139.6], 115.1, 74.2, [26.8], 23.7
2l	84.6	57.0	176.6	32.4	33.3	(29.2)	206.3, (29.8), 39.6, 34.8
2m	86.5	58.2	173.3	32.2	32.7		133.3, 128.5, 71.2, 30.9, 25.1, 18.2
2m	86.5	58.2	173.2	31.2	32.6		133.0, 128.8, 71.0, 34.9, 25.0, 18.4
2n	85.2	62.5	176.1	32.1	34.2	28.5	209.4, 46.5, 44.0, 40.7, 26.5, 24.3

[a] In CDCl$_3$. [b] Values in parentheses may be interchanged. [c] Values in brackets due to minor diastereomer.

ratio of the products was noted when HMPA was omitted. Compounds **2e** and **2f** show ^{1}H NMR spectra which are complicated by the presence of diasterotopic methyl groups. In addition, some of the hydroxy esters do not show a molecular ion in their EI mass spectra. The FI mass spectra do show molecular ions in all cases. The highest peak observed corresponds to complete loss of the side chain.

Reaction of **1a** with methyl vinyl ketone at −78 °C led predominantly to the 1,2-addition product **2j**. The presence of **2k** in the reaction mixture could not be conclusively established. Compound **1b**, under the same conditions, afforded exclusively the 1,4-addition product **2l**. Using 2-cyclohexenone as the electrophile gave the opposite result. With **1a** exclusive 1,2-addition occurred to give **2m**, but with **1b** a 5:2 ratio of 1,2- to 1,4-addition products (**2n**,**2o**) was obtained. If the reaction of either **1a** or **1b** was allowed to warm to room temperature before quenching, only decomposition of the starting heterocycle was observed. The same result was obtained if a solution of the anion was allowed to warm above −20 °C in the absence of an electrophile. In the case of **2m**, one diastereomer fortuitously crystallized from the reaction mixture.

Discussion

The formation of **2e** during the attempted alkylation of **1a** with unreactive halides is a curious result. None of **2f** could be detected in the reactions of **1b** and, under the same conditions, none of **2e** is formed from **1a**. The sole result in the latter case is the decomposition of **1a** when the temperature is allowed to rise above −45 °C. It seems clear that the 2-hydroxypropyl group must be derived from the acetal protecting group of **1a** but how this occurs is unknown at this time. Another surprising result in the light of Schultz's work[6] is our inability to isolate meaningful products from **1a** and **1b** at reaction temperatures above −40 °C. At this time we have no explanation for this discrepancy.

To date we have made no attempt to examine the effect of reaction variables on the relative amounts of the two diastereomers of **2g**–**2o**. For the carbonyl addition reactions, if one assumes a transition state similar to that proposed by Heathcock[9] wherein the oxygen-bound lithium atom of the enolate is coordinated to the carbonyl of the electrophile, one would expect that the *pref*[10] configuration should be the dominant isomer. In principle this information should be readily accessible from the proton and carbon NMR spectra. It is interesting to note that, although the ^{1}H NMR spectra clearly show the presence of two diasteromers where these are possible, the ^{13}C NMR spectra, run at 22.64 MHz, do not show two peaks for the chiral carbons. The absorptions at ca. 60 and 74 ppm are broadened. In some cases, two peaks for the carbons attached to the acyclic chiral center could be observed (Table III). Further work designed to verify the stereostructures of the major isomers and alter the diastereomeric ratios is planned. It is interesting that the ring *gem*-dimethyl groups which are diastereotopic in all cases except **1a** occur as a clear singlet in the proton spectra. Two signals are seen in the carbon spectra as expected (Table III).

The ratios of 1,2- to 1,4-addition products in entries 12–15 (Table I) seem in accord with established precedents. Thus increasing steric bulk at the anionic center favors the product with less steric congestion at the adjacent carbon. This in turn implies that both modes of addition are reversible, a fact that is supported by the formation of product when the reaction temperature is kept below −78 °C but not when the reaction is warmed to room temperature before quenching.

Table IV. Elemental Analyses

compd	calculated C	calculated H	found C	found H
2a	52.47	7.45	52.55	7.42
2b	66.06	6.82	66.11	6.86
2c	58.03	7.57	57.94	7.62
2d	73.04	6.45	73.17	6.30
2e	50.50	7.42	50.05	7.50
2f	52.92	7.90	52.03	7.78
2g	50.50	7.42	50.98	7.73
2h	60.48	5.92	60.72	6.03
2i	61.88	6.39	61.73	6.30
2j	53.44	6.98	53.13	6.99
2l	55.53	7.46	55.03	7.48
2m	57.87	7.06	58.08	7.08
2n	59.48	7.49	59.61	7.66
2o	59.48	7.49	59.44	7.60

Conclusions

The results obtained here serve to indicate that alkylation reactions on the oxathiolanone ring system are severely limited in scope. However carbonyl addition reactions are much more successful and allow the introduction of various types of substituents at the 4-position. Preliminary work indicates that elimination of the elements of water from the adducts of **1a** occurs as expected and these products (**5**) are potentially useful Michael acceptors. Reactions of acyl halides and epoxides with **1** are under examination. Manipulation of the oxidation state of sulfur in **1** may also affect the mode of reaction. These facts combined with the established reduction of **1** to 2-mercaptoaldehydes[4] make this heterocycle both an interesting and potentially useful area of investigation.

Experimental Section

Melting points are corrected; boiling points are uncorrected. Infrared spectra were run either as neat liquids or in $CHCl_3$ solution. ^{1}H NMR spectra were run at 60 MHz in $CDCl_3$ solution and ^{13}C NMR spectra were run in the same solvent at 22.64 MHz in the FT mode using a flip angle of 45°. Gas chromatographic analyses were performed by using either 5% SE-30 or 5% OV-101 on Chromosorb W columns; solvents were removed at reduced pressure and the drying agent used was anhydrous $MgSO_4$. Mass spectra were run on a Varian MAT CH-5 DF instrument in either an electron-impact (EI) or field-ionization (FI) mode. Microanalyses (Table IV) were performed by the Guelph Chemical Laboratories Ltd., Guelph Ontario or by Canadian Microanalytical Services, Vancouver, B.C.

2-(Butylthio)propionic Acid (3b). To a stirred solution of 0.01 mol of thiolactic acid in 2.5 mL of Et_3N was added BuI (1.84 g, 0.01 mol). A mild exotherm was noted and a white precipitate formed. After 15 min, 3 N NaOH (10mL) was added and the mixture was washed with ether (3 × 50 mL). The aqueous phase was acidified with HCl and extracted with $CHCl_3$, and the organic extracts were dried and evaporated to give **3b** (1.2 g, 72%): IR (neat) 3000, 1710, 1455, 1238 cm^{-1}; ^{1}H NMR 12.10 (s, 1 H), 3.36 (q, 1 H, J = 7 Hz), 2.65 (t, 2 H, J = 7 Hz), 1.42 (d, 3 H, J = 7 Hz), 1.87–1.07 (m, 4 H), 0.88 (br t, 3 H, J = 7 Hz).

Butyl 2-(Butylthio)propionate (4b). Compound **3b** (0.8 g, 5 mmol) was stirred with 5.5 mmol of BuI and 7 mmol of K_2CO_3 in acetone solution for 3 days. The mixture was acidified with 10% HCl and then extracted with $CHCl_3$. The extracts were washed with 3 N NaOH (20 mL), dried, and evaporated. Distillation afforded 0.45 g (42%) of **4b**: bp 115–117 °C (6mm); IR (neat) 2980, 2950, 1735, 1165 cm^{-1}; ^{1}H NMR 4.10 (t, 2 H, J = 7 Hz), 3.37 (q, 1 H, J = 7 Hz), 2.77 (t, 2 H, J = 7 Hz), 1.42 (d, 3 H, J = 7 Hz), 1.9–1.17 (m, 8 H), 0.91 (br t, 3 H), 0.88 (br t, 3 H).

General Procedure for the Alkylation of 1b. A solution of **1b** (0.018 mol) in 5 mL of dry THF was added over 10 min to a stirred solution of LDA in 5–10 mL of the same solvent at −78 °C. The mixture was stirred at this temperature for 45 min and then a solution of the alkyl halide (0.018 mol) in 5 mL of THF containing 0.022 mol of HMPA was added dropwise. After 3 h at −78 °C the reaction was quenched at −78 °C with saturated NH_4Cl solution and extracted with ether. The extracts were

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washed with water, dried, and evaporated to afford either liquid or solid product. The physical and spetroscopic characteristics are given in Tables II and III.

General Procedure for the Aldol Reactions. A solution of 0.017 mol of LDA in 20 mL of THF was cooled to −78 °C and a solution of **1a** in 10 mL of THF was added. The solution became orange and was stirred at −78 °C for 30 min. The electrophile (0.017 mol) in 10 mL of THF was added and the solution stirred at −78 °C for 3–4 h. The reaction was quenched without warming by the addition of saturated NH_4Cl, allowed to warm to room temperature, and acidified with 10% HCl, and the organic material was extracted into ether (3 × 50 mL). The extracts were washed with 10% HCl and water, dried, and evaporated before distillation or recrystallization. The physical and spectroscopic properties of the products are given in Tables II and III.

Acknowledgment. The financial support of the Natural Sciences and Engineering Research Council of Canada in the form of operating grants and a scholarship (to P.M.) made this work possible. We would like to thank Dr. P. M. Beaumier for the GC/MS results at a critical time in the work.

Registry No. **1a**, 35350-46-0; **1b**, 60822-65-3; **2a**, 87602-19-5; **2b**, 88802-41-9; **2c**, 88802-42-0; **2d**, 88802-43-1; **2e**, 88802-44-2; **2f**, 88802-45-3; **2g** (isomer 1), 88802-46-4; **2g** (isomer 2), 88802-47-5; **2h** (isomer 1), 88802-48-6; **2h** (isomer 2), 88825-33-6; **2i** (isomer 1), 88802-49-7; **2i** (isomer 2), 88802-50-0; **2j** (isomer 1), 88802-51-1; **2j** (isomer 2), 88802-52-2; **2k**, 88802-53-3; **2l**, 88802-54-4; **2m** (isomer 1), 88802-55-5; **2m** (isomer 2), 88802-56-6; **2n** (isomer 1), 88802-57-7; **2n** (isomer 2), 88802-58-8; **2o** (isomer 1), 88802-59-9; **2o** (isomer 2), 88802-60-2; **3b**, 88802-61-3; **4b**, 88802-62-4; CH_3I, 74-88-4; $PhCH_2Br$, 100-39-0; $CH_2{=}CHCH_2Br$, 106-95-6; $CH_3(CH_2)_3I$, 542-69-8; CH_3CHO, 75-07-0; PhCHO, 100-52-7; $CH_2{=}CHC(O)CH_3$, 78-94-4; Me_2CO, 67-64-1; cyclohexenone, 930-68-7; thiolactic acid, 79-42-5.

One-Step Synthesis of 3,8-Methano-1-aza[10]annulene Derivatives via Diels–Alder Reaction of Benzocyclopropene with 1,2,4-Triazines[1]

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Received September 20, 1983

A new approach to the synthesis of 3,8-methano-1-aza[10]annulene derivatives based on the Diels–Alder reaction of benzocyclopropene with electron-deficient 1,2,4-triazines was developed. The exceptionally electron-deficient triazines **4a** and **4b** yielded azaannulenes **6a** and **6b** under normal conditions, while the less activated triazines **4c** and **4d** required ultrahigh pressure (15 kbar) to produce annulenes **6c** and **6d**. Both the disubstituted and monosubstituted annulenes **6c** and **6d** were quite unstable. The cyanoannulene **6b** was, however, converted into other stable annulene derivatives including the 2,9-disubstituted compound **6j**.

3,8-Methano-1-aza[10]annulene (**1**), as yet not synthesized, is a bridged methylene homologue of isoquinoline.

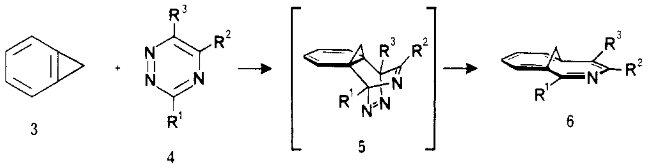
1

The preparation of annulene **1** and derivatives thereof is of interest in order to study the physical properties and reactions of this class of heterocycles. Moreover, the substitution of this bridged heterocyclic system for the isoquinoline moiety of natural products and medicinal agents would lead to novel structures with potentially interesting biological activities.

Recently, the synthesis of some 10-alkoxy-3,8-methano-1-aza[10]annulenes **2** was independently achieved by three groups of investigators.[2] Unfortunately, further study of these novel heterocycles was hampered by the lengths and low overall yields of the published synthetic routes. We have also reported preliminary studies on a novel, one-step synthesis of carboxylic ester derivatives of this class of annulenes, which provided the opportunity for preparing substantial quantities of these substances.[3] We now describe in more detail the preparations, physical properties, and reactions of these heteroannulenes.

2; $R = CH_3, C_2H_5$

Scheme I



a, $R^1,R^2,R^3 = CO_2Et$
b, $R^1 = CN$; $R^2,R^3 = CO_2Et$
c, $R^1 = H$; $R^2,R^3 = CO_2Et$
d, $R^1 = CO_2Et$; $R^2,R^3 = H$
e, $R^1 = CO_2K$; $R^2,R^3 = CO_2Et$
f, $R^1 = CO_2H$; $R^2,R^3 = CO_2Et$
g, $R^1 = CO_2Me$; $R^2,R^3 = CO_2Et$
h, $R^1 = OEt$; $R^2,R^3 = CO_2Et$
i, $R^1 = CN$; $R^2 = CO_2H$; $R^3 = CO_2Et$
j, $R^1 = CN$; $R^2 = H$; $R^3 = CO_2Et$

Results and Discussion

Prior to our investigations of azaannulene synthesis, several reports on the synthesis of pyridines from 1,2,4-

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