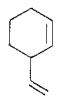
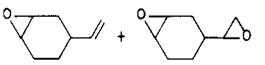
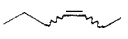
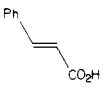
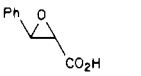
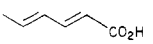
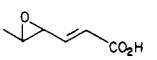
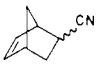
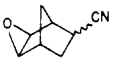
Table I. Reaction of Alkenes with Potassium Hydrogen Persulfate

entry	alkene	method[a]	reactn time, h	$KHSO_5$,[b] equiv	product		yield,[c] %
1	cyclohexene	B	5	2	1,2-epoxycyclohexane (4)		62
2	cycloheptene	B	4	2	1,2-epoxycycloheptane (5)		91
3	cyclooctene	A	4	1.5	1,2-epoxycyclooctane (6)		94
4	cyclodecene $E + Z$	A or B	5	2	no reaction		
5		B	5	1	 7 (46%) 8 (21%)[d]		
		B	5	2	7 (40%) 8 (60%)[d]		
		B	5	5	8		78
6		B	5	2		9	63
7		C or B	5	2		10	10[e]
8		C	1	2		11	84
9		A	3	1.5		12	93

[a] All the reactions were performed at room temperature: method A, oxone in water added to alkene in methanol, uncontrolled pH; method B, same as A, but pH 6; method C, oxone and alkene in water, pH 6. [b] An excess of potassium hydrogen persulfate is necessary, due to competitive peroxide decomposition.[7] [c] Yields are given for isolated epoxides unless noted otherwise. [d] The ratio 7/8 were evaluated by ^1H NMR and GLC coupled with a mass spectrometer; when 1 equiv of $KHSO_5$ was used, 4-vinylcyclohexene was also present in the reaction mixture. [e] Yields evaluated by ^1H NMR.

AG CH-9100 Herisau combi titrator. Oxone is a stable powder containing 2 mol of $KHSO_5$, 1 mol of K_2SO_4, and 1 mol of $KHSO_4$ and is sold in Europe by Aldrich. Cyclohexene, cycloheptene, cyclooctene, cyclododecene, 4-vinylcyclohexene, *trans*-cinnamic acid, and sorbic acid were commercial products. 2-Cyanobicyclo[2.2.1]hept-5-ene and 4-thiatricyclo[5.2.1.$0^{2,6}$]dec-8-ene were prepared following reported procedures.[6,8]

All the epoxides, but the sulfone **3**, were known compounds and had spectral data that where identical with those given in the literature[2,9–11] or with those of commercial samples.

Epoxy sulfone 3 obtained in 86% yield (method A) after column chromatography; recrystallized (CH_3CO_2Et/*n*-hexane, 4/1): mp 241–242 °C; ^1H NMR ($CDCl_3$) δ 3.27 (br s, 2 H), 2.65–3.65 (m, 8 H), 1.5–1.8 (m, 1 H), 0.8–1.1 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 48.4, 48.2, 38.2, 37.7, 26.8; IR ($CHCl_3$) 2960, 1315, 1215, 1140, 850 cm^{-1}.

Anal. Calcd for $C_9H_{12}O_3S$: C, 53.98; H, 6.04; S, 16.01. Found: C, 53.73; H, 5.99; S, 16.02.

Typical Procedures. Method A. A solution of oxone (4.62 g, 15 mmol of $KHSO_5$) in water (20 mL) was added in one portion to a solution of cyclooctene (1.1 g, 10 mmol) in methanol (20 mL). The reaction mixture was then magnetically stirred during 4 h at room temperature. After addition of water (50 mL), the solution was extracted with methylene chloride (2 × 20 mL). The extracts were dried ($MgSO_4$) and the solvent removed in vacuo, affording 1.19 g (94%) of 9-oxabicyclo[6.1.0]nonane (**6**) having spectra identical with those of a commercial sample (mp after sublimation 56 °C, lit.[12] mp 56–57 °C).

Method B. A solution of cycloheptene (960 mg, 10 mmol) in methanol (20 mL) was added in 5 min to a solution of oxone (6.15 g, 20 mmol of $KHSO_5$) in water (50 mL). Before the addition was started the pH was adjusted to 6 and it was monitored with a pH electrode and kept at this value during the entire reaction by dropwise addition of KOH (1 M in water). The reaction mixture was stirred for an additional 4 h and extracted with methylene chloride (2 × 20 mL). The organic layer was dried ($MgSO_4$) and the solvent was removed on a rotatory evaporator. The residue was bulb-to-bulb distilled at 85 °C (50 mm) to give 1.02 g (91%) of 8-oxabicyclo[5.1.0]octane (**5**), giving spectra identical with those of a sample prepared by a reported procedure.[13]

Method C. A solution of oxone (6.15 g, 20 mmol of $KHSO_5$) in water (20 mL) was added in one portion to a solution of sorbic acid (1.12 g, 10 mmol) in water (20 mL) while the pH was kept at 6 by addition of aqueous 1 M KOH. After 1 h of stirring, the pH remained constant without KOH addition. The solution was acidified to pH 1 (12 N HCl) and continuously extracted with ether during one night. The ether extract was dried ($MgSO_4$) and the solvent was removed, affording 1.10 g (84%) of 4,5-epoxy-2-hexenoic acid (**11**) pure by ^1H NMR. A sample purified by crystallization (CCl_4/*n*-hexane) had mp 82 °C (lit.[2] mp 81–83 °C).

Registry No. **1**, 2434-67-5; **2**, 83947-07-3; **3**, 95722-43-3; **4**, 286-20-4; **5**, 286-45-3; **6**, 286-62-4; **7**, 106-86-5; **8**, 106-87-6; **9**, 53897-32-8; **10**, 1566-68-3; **11**, 74923-21-0; **12**, 18776-20-0; $KHSO_5$, 10058-23-8; (*Z*)-cyclododecene, 1129-89-1; 4-vinylcyclohexene, 100-40-3; sorbic acid, 110-44-1; cyclohexene, 110-83-8; cycloheptene, 628-92-2; cyclooctene, 931-88-4; (*E*)-cyclododecene, 1486-75-5; 3-heptene, 592-78-9; *trans*-cinnamic acid, 140-10-3; bicyclo[2.2.1]hept-5-ene-2-carbonitrile, 95-11-4.

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Diels–Alder and Retro-Diels–Alder Reactions: From *N'*-(Thioacyl)formamidines to Thio Amide Vinylogues

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As part of our continuing study of the chemistry of sulfur-containing heterocycles, we have developed and generalized the cyclocondensation reactions of *N'*-(thio-

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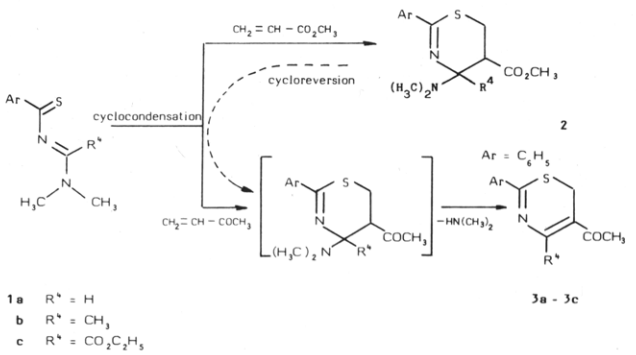
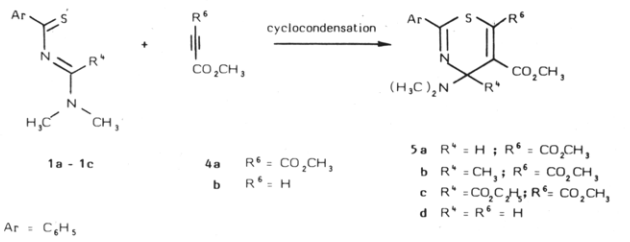
Scheme I



Scheme II



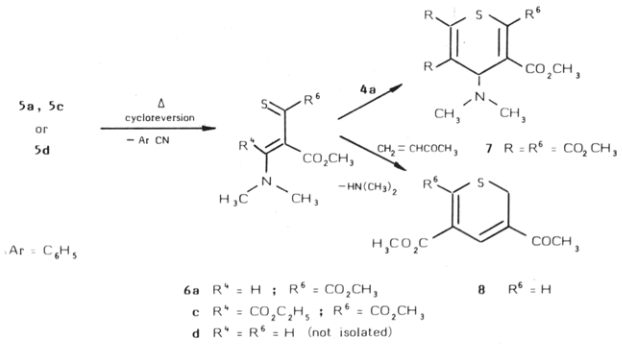
acyl)formamidines and characterized the products of thermolysis of the adducts obtained.

Diels–Alder reactions of azadienes affording either the corresponding heterocyclic compounds or their cycloreversion products have been recently reported.[1] However, there have been few reports concerning heteroazadienes containing an atom of oxygen[2] or sulfur.[3] In the course of a preliminary study,[4] we showed that it was possible to obtain 4,5-dihydro-6*H*-1,3-thiazines **2** or 6*H*-1,3-thiazines **3** from *N'*-(thioacyl)formamidines **1** via a 4 + 2 cyclocondensation reaction using various acrylic compounds (Scheme I). Yields of compounds **3a** and **3b** were optimized (98% yield) by carrying out the reaction in an autoclave (140 °C) in the presence of methyl vinyl ketone. An acid catalyst is needed in order to obtain **3c** from **1c**. The conversion of 4,5-dihydro-6*H*-1,3-thiazine (**2**) to 6*H*-1,3-thiazine (**3a**) proceeds via a cycloreversion reaction on heating **2** (autoclave 140 °C) in the presence of excess methyl vinyl ketone (Scheme I).

We have extended the scope of this investigation by studying the cyclocondensation reactions between *N'*-(thioacyl)formamidines and acetylenic compounds. At room temperature, compounds **1** react stoechiometrically with dimethyl acetylenedicarboxylate (**4a**, $R^6 = CO_2CH_3$), affording 4*H*-1,3-thiazines **5** (Scheme II). The reactivity of **1** depends on the nature of the substituent R^4 (**1b** > **1a** > **1c**). 4*H*-Thiazine compounds are thus obtained in excellent yields. We did not obtain five-membered heterocycles as has been observed for 1-thia-3-aza-1,3-butadienes substituted in position 4 by an aromatic[3a] or electron-attracting group.[3b]

An increase in the reaction temperature gives rise to the thermolysis of the 4*H*-1,3-thiazines via a cycloreversion-type reaction.[5] Thus, on heating **5a** in refluxing methylene chloride, benzonitrile ($\bar{\nu}_{CN}$ (CCl_4) = 2220 cm^{-1}) is liberated and the thio amide vinylogue **6a** is isolated (Scheme III), in which the functional groups in positions 2 and 3 are those of acetylene **4a**. In this cycloreversion reaction the formation of the nitrile instead of the starting acetylene is in agreement with the literature.[6]

Scheme III



The 4*H*-thiopyran **7** can be obtained directly by prolonged heating of *N'*-(thioacyl)formamidine (**1a**) in excess **4a** (Scheme III). The reaction of thio amide vinylogues[7] with acetylenic compounds such as dimethyl acetylenedicarboxylate is well-known.[8]

Heating **5b** in refluxing toluene does not give the corresponding thio amide vinylogue **6b**. However, under these conditions the cycloreversion of **5c** to **6c** is observed but thio amide vinylogue **6c** is not isolated; the reaction instead gives a product of cyclic rearrangement (the tertiary amine effect),[9] which is the object of a further study.

The reaction of methyl propiolate (**4b**) with **1a** affords 4*H*-1,3-thiazine (**5d**). On heating a solution of **5d**, we did not observe the amine transposition reported for the 4*H*-thiopyran homologues[8] but instead observed a cycloreversion reaction liberating thioaldehyde **6d**. This compound, on addition of methyl vinyl ketone, affords the 2*H*-thiopyran **8** ($J_{H^4-H^6}$ = 0.5 Hz). The position of the methoxycarbonyl group in **8** confirms the direction of the addition of **4b** to **1a**. In this case the yield is superior to that obtained for the addition of unsymmetrical acetylenic compounds to 1-amino-2-azadienes.[10]

The cyclocondensation reaction of *N'*-(thioacyl)formamidines **1** is general and leads specifically to functionalized 4,5-dihydro-6*H*-1,3-thiazines and 6*H*-1,3-thiazines.[11] The thermolysis of **5** is a novel example of the application of cycloreversion reactions in organic synthesis,[12] linking the chemistry of *N'*-acylthio imines **1** to that of functionalized thio amide vinylogues **6**.

Experimental Section

^1H NMR spectra were recorded on 60-MHz (Perkin-Elmer R 24) and 250-MHz (Bruker) instruments. ^{13}C NMR spectra were determined on a 90-MHz (Bruker WH 90) spectrometer. Me_4Si was used as internal reference. Mass ion kinetic energy (MIKE) and collision ion detection (CID) MIKE mass spectra were re-

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corded on a Varian MAT 311 spectrometer. Column chromatography was carried out on silica gel (Merck Art. 9385, Kieselgel 60). Melting points were determined on an RCH (C. Reichert) microscope with a Kofler heating stage.

General Procedure for the Preparation of 6*H*-1,3-Thiazines 3a and 3b. A mixture of **1a** or **1b** (4.85 mmol) in 30 mL of benzene and 3 mL of freshly distilled methyl vinyl ketone was heated at 140 °C (autoclave) for 5 h with stirring. The thiazine obtained was purified on a silica gel column (elutant, 80/20 petroleum ether/ethyl acetate; yield, 98%). Cycloreversion of **2** to **3a** was carried out with an identical procedure to the previous one, **1a** being replaced by **2** (yield, 98%).

5-Acetyl-2-phenyl-6*H*-1,3-thiazine (3a): ^{1}H and ^{13}C NMR spectra were in agreement with data given in the literature.[13]

5-Acetyl-4-methyl-2-phenyl-6*H*-1,3-thiazine (3b): mp 75–77 °C; ^{1}H NMR ($CDCl_3$) δ 2.4 (6 H, s, CH_3, $COCH_3$), 3.61 (2 H, s, CH_2); ^{13}C NMR ($CDCl_3$) δ 25.1 (t, C^6, $J_{^{13}C-H}$ = 145 Hz), 113.6 (s, C^5), 154 (s, C^4), 164.9 (s, C^2). Anal. Calcd for $C_{13}H_{13}NOS$: C, 67.50; H, 5.66; S, 13.86. Found: C, 67.93; H, 5.63; S, 13.94.

5-Acetyl-4-(ethoxycarbonyl)-2-phenyl-6*H*-1,3-thiazine (3c). To a solution of 1.14 g (4.3 mmol) of **1c** in 30 mL of CH_2Cl_2 were added at 0 °C 2 mL of methyl vinyl ketone and 0.4 g (3 mmol) of $AlCl_3$. Stirring of the reaction mixture was continued at 0 °C for 3 h and then at room temperature for 12 h. After hydrolysis (40 mL of H_2O) and decanting off the aqueous phase the thiazine was purified on a column of silica gel (elutant, 80/20 petroleum ether/ethyl acetate; crystallization from ethanol): mp 66–67 °C; yield 80%; ^{1}H NMR ($CDCl_3$) δ 1.37 (3 H, t, CH_3), 2.42 (3 H, s, $COCH_3$), 3.69 (2 H, s, CH_2), 4.38 (2 H, q, CH_2); ^{13}C NMR ($CDCl_3$) δ 24.5 (t, C^6, $J_{^{13}C-H}$ = 144 Hz), 118.6 (s, C^5), 144 (s, C^4), 165.8 and 167 (2 s, $C^{4'}$ and C^2), 198.3 (s, $C^{5'}$). Anal. Calcd for $C_{15}H_{15}NO_3S$: C, 62.26; H, 5.22; S, 11.08. Found: C, 62.00; H, 5.22; S, 10.96.

General Procedure for the Preparation of 4-(Dimethylamino)-2-phenyl-4*H*-1,3-thiazines. 1 (5 mmol) was added at room temperature to the acetylenic compound (5 mmol) in 20 mL of CH_2Cl_2, and the reaction was followed by TLC. The 4*H*-1,3-thiazine was purified on a silica gel column (elutant; 60/40 petroleum ether/ethylacetate, crystallization from methanol).

4-(Dimethylamino)-5,6-bis(methoxycarbonyl)-2-phenyl-4*H*-1,3-thiazine (5a): mp 90 °C; yield 81%; ^{1}H NMR ($CDCl_3$) δ 2.45 (6 H, s, NCH_3), 3.88 (6 H, s, OCH_3), 5.80 (H, s, CH); mass spectrum, *m/z* 334 (M^+), MIKE *m/z* 231, 199, CID MIKE *m/z* 231, 216, 199, 188, 184, 172, 155, 141, 129, 113, 104, 98, 88, 84, 73, 60, 47, 44. Anal. Calcd for $C_{16}H_{18}N_2O_4S$: C, 57.46; H, 5.42; N, 8.37; S, 9.59. Found: C, 57.31; H, 5.45; N, 8.36; S, 9.33.

4-(Dimethylamino)-5,6-bis(methoxycarbonyl)-4-methyl-2-phenyl-4*H*-1,3-thiazine (5b): mp 101–102 °C; yield 81%; ^{1}H NMR ($CDCl_3$) δ 1.60 (3 H, s, CH_3), 2.40 (6 H, s, NCH_3), 3.88 (6 H, s, OCH_3); ^{13}C NMR ($CDCl_3$) δ 80 (s, C^4), 151 (s, C^2). Anal. Calcd for $C_{17}H_{20}N_2O_4S$: C, 58.60; H, 5.78; N, 8.04; S, 9.20. Found: C, 58.45; H, 5.83; N, 8.09; S, 9.00.

4-(Dimethylamino)-4-(ethoxycarbonyl)-5,6-bis(methoxycarbonyl)-2-phenyl-4*H*-1,3-thiazine (5c): mp 83–84 °C; yield 91%; ^{1}H NMR ($CDCl_3$) δ 1.27 (3 H, t, CH_3), 2.48 (6 H, s, NCH_3), 3.90 (6 H, s, OCH_3), 4.27 (2 H, q, CH_2); ^{13}C NMR ($CDCl_3$) δ 85.4 (s, C^4). Anal. Calcd for $C_{19}H_{22}N_2O_6S$: C, 56.14; H, 5.45; S, 7.89. Found: C, 56.14; H, 5.47; S, 7.99.

4-(Dimethylamino)-5-(methoxycarbonyl)-2-phenyl-4*H*-1,3-thiazine (5d): mp 75–77 °C; yield 80%; ^{1}H NMR ($CDCl_3$) δ 2.45 (6 H, s, NCH_3), 3.84 (3 H, s, OCH_3), 6.02 (H^4, s, CH), 7.93 (H^6, s, CH); ^{13}C NMR ($CDCl_3$) δ 72.2 (d, C^4, $J_{^{13}C-H}$ = 160 Hz), 116.6 (s, C^5), 132 (d, C^6, $J_{^{13}C-H}$ = 160 Hz), 154.3 (s, C^2), 164 (s, $C^{5'}$). Anal. Calcd for $C_{14}H_{16}N_2O_2S$: C, 60.84; H, 5.83; N, 10.14; S, 11.60. Found: C, 60.90; H, 5.99; N, 10.02; S, 11.57.

3-(Dimethylamino)-1,2-bis(methoxycarbonyl)-2-propene-1-thione (6a). **5a** (3 mmol) was heated for an hour in 30 mL of CH_2Cl_2. The reaction product was purified on a column of silica gel (elutant, 50/50 petroleum ether/ethyl acetate; crystallization from ethanol): mp 135 °C; yield 83%; ^{1}H NMR ($CDCl_3$) δ 3.13 (3 H, s, NCH_3), 3.50 (3 H, s, NCH_3), 3.73 (3 H, s, OCH_3), 3.83 (3 H, s, OCH_3), 8.24 (H, s, CH); ^{13}C NMR ($CDCl_3$) δ 114.0 (s, C^2), 162.1 (d, C^3, $J_{^{13}C-H}$ = 176 Hz), 206.3 (s, C^1); mass spectrum, *m/z* 231 (M^+), MIKE *m/z* 231, 199, CID MIKE *m/z* 231, 216, 199, 188, 172, 155, 141, 129, 113, 104, 98, 88, 84, 73, 60, 47, 44. Anal. Calcd for $C_9H_{13}NO_4S$: C, 46.73; H, 5.66; N, 6.05; S, 13.86. Found: C, 46.81; H, 5.63; N, 5.83;, S, 13.65.

4-(Dimethylamino)-2,3,5,6-tetrakis(methoxycarbonyl)-4*H*-thiopyran (7). A mixture of 1 g (4.3 mmol) of **6a** and 610 mg (4.3 mmol) of **4a** in 30 mL of CH_2Cl_2 was heated at reflux for 48 h. After evaporation of the solvent, the reaction product was purified on a column of silica gel (elutant, 50/50 petroleum ether/ethyl acetate; crystallization from ethanol): mp 92–93 °C; yield 83%; ^{1}H NMR ($CDCl_3$) δ 2.28 (6 H, s, $(CH_3)_2$), 3.81 (6 H, s, OCH_3), 3.84 (6 H, s, OCH_3), 5.00 (H^4, s, CH); ^{13}C NMR ($CDCl_3$) δ 59.7 (d, C^4, $J_{^{13}C-H}$ = 150 Hz), 125.9 (s, C^3–C^5), 133 (s, C^2–C^6). Anal. Calcd for $C_{15}H_{19}NO_8S$: C, 48.24; H, 5.13; N, 3.75; S, 8.58. Found: C, 48.24; H, 5.08; N, 3.66; S, 8.59.

3-Acetyl-5-(methoxycarbonyl)-2*H*-thiopyran (8). A mixture of 500 mg (1.8 mmol) of **5d** and 3 mL of methyl vinyl ketone was heated at reflux for 3 h. After evaporation of the excess methyl vinyl ketone, the reaction product was purified on a column of silica gel (elutant, 50/50 petroleum ether/ethyl acetate; crystallization from 90/10 petroleum ether/ethanol): mp 35 °C; yield 98%; ^{1}H NMR ($CDCl_3$) δ 2.45 (3 H, s, $COCH_3$), 3.66 (2 H, s, CH_2), 3.84 (3 H, s, OCH_3), 7.50 and 8.00 (H^4 and H^6, $J_{H^4-H^6}$ = 0.50 Hz); ^{13}C NMR ($CDCl_3$) δ 21.7 (t, C^2, $J_{^{13}C-H}$ = 146 Hz), 122.5 and 124.6 (2 s, C^3 and C^5), 132.9 and 145.8 (C^4, $J_{^{13}C-H}$ = 163 Hz and C^6, $J_{^{13}C-H}$ = 178 Hz). Anal. Calcd for $C_9H_{10}O_3S$: C, 54.52; H. 5.08; S, 16.17. Found: C, 54.40; H, 5.05; S, 15.52.

Registry No. **1a**, 52421-65-5; **1b**, 67229-59-8; **1c**, 87108-97-2; **2a**, 72856-29-2; **3a**, 72856-35-0; **3b**, 95482-64-7; **3c**, 87109-03-3; **4a**, 762-42-5; **4b**, 922-67-8; **5a**, 95482-65-8; **5b**, 95482-66-9; **5c**, 95482-67-0; **5d**, 95482-68-1; **6a**, 95482-69-2; **7**, 95512-41-7; **8**, 95482-70-5; CH_2=$CHCOCH_3$, 78-94-4.

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Reaction of β-Nitroenamines with Electrophilic Reagents. Synthesis of β-Substituted β-Nitroenamines and 2-Imino-5-nitro-4-thiazolines

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β-Nitroenamines are useful synthetic intermediates, and their reactivity is of interest in connection with that of β-aminoenones. The reaction of β-nitroenamines with carbon nucleophiles has been studied extensively.[1–8] In contrast, the reaction of primary and secondary β-nitroenamines with electrophiles has been little studied.[9–11] In a previous paper, we reported a convenient synthesis of the primary and secondary β-nitroenamines (1) from nitroacetone and ammonia and/or primary amines using titanium(IV) chloride as a catalyst.[12] In this paper, we

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