and the overall temperature factor obtained from Wilson's statistics. The structure was solved by the direct method, using the MULTAN 78 series of programs.[19] The atomic scattering factors were from the tables of Cromer and Weber.[20]

An E map calculated with 244 signed E's ($|E| \geq 1.74$), which gave a combined figure of merit of 2.4255, revealed the position of all the expected nonhydrogen atoms.

Refinements were carried out by the block-diagonal least-squares method by using isotropic temperature factors for the hydrogen atoms placed in calculated positions and anisotropic temperature factors for the remaining atoms. In the course of the refinement, the O(34) atom was divided into two parts according to the populations estimated by the peak height in a difference Fourier map. The final R value was 0.0527 for the observed reflections.

In final refinements, the following weights were used for the observed reflections: $w = 1.0$ for $F_0 < 30.0$, $w = 900/F_0^2$ for $F_0 \geq 30.0$.

All structure-solving programs were from the computer center of Kyushu University with the Universal Crystallographic Computation Program System (UNICS II).[21]

Registry No. **1ak**, 65007-17-2; **1al**, 86259-46-3; **1bl**, 86259-47-4; **1ck**, 86259-44-1; **1cl**, 86259-45-2; **4ck**, 86259-48-5; **4cl**, 86259-49-6; **5ak**, 86259-42-9; **5ck**, 86259-43-0; **6ak**, 86259-50-9; **6ck**, 86259-51-0; **7al**, 86259-52-1; **7bl**, 86259-53-2.

Supplementary Material Available: Tables of final positional and final thermal parameters of nonhydrogen atoms, hydrogen atom parameters, interatomic distances, and interatomic angles for 1cl, MMPI EFF conformation of 1cl, and elemental analysis of 4ck, 4cl, 5ak, 5ck, 6ak, 6ck, 7al, and 7bl (8 pages). Ordering information is given on any current masthead page.

(19) Main, P.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J. P.; Woolfson, M. M. "MULTAN 78, a System of Computer Programs for Automatic Solution of Crystal Structures from X-ray Diffraction Data"; University of York: England, 1978.

(20) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. 4, pp 72-98.

(21) (a) Sakurai, T.; Iwasaki, J.; Kobayashi, K.; Bando, Y.; Nakamichi, Y. *Rikagaku Kenkyusho Hookoku* **1974**, *50*, 74-91. (b) Kawano, S. *Koho, Computer Center of Kyushu University* **1980**, *13*, 39-50.

Flash Vacuum Thermolysis of Functionalized γ-Sultines

Rob M. J. Liskamp, Henk J. Blom, Rutger J. F. Nivard, and Harry C. J. Ottenheijm*

Department of Organic Chemistry, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands

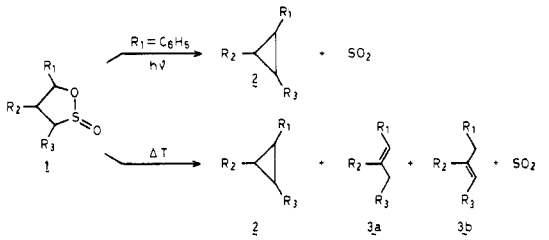
Received November 19, 1982

The flash vacuum thermolysis (FVT) of the 4-benzamido γ-sultines **5a** and **5b** is shown to lead to a mixture of the N-allyl amide **6** and enamides **7** and **8**, the allyl amide being the main product. This reaction involves a novel migration of the benzamido group, which is proposed to proceed as depicted in path c of Scheme IV. This proposed mechanism features heterolytic bond fission, accompanied by neighboring group participation. Support for this proposal has been found by flash vacuum thermolysis (FVT) of **5a**-d_2 (Scheme IV).

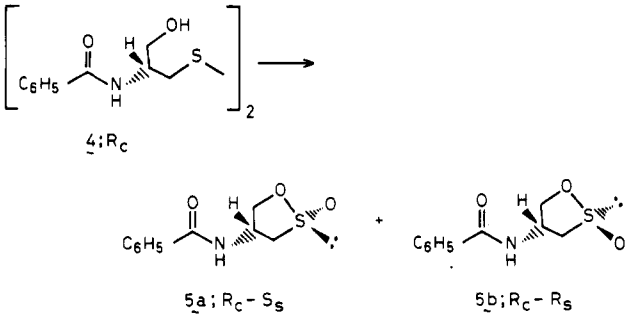
During the last decade several aspects of the chemistry of cyclic sulfinate esters (sultines) received incidental attention, but all those studies[1,2] concerned sultines containing only phenyl or simple alkyl substituents or sultines condensed with aromatic rings. Recently, we reported[3] for the first time an efficient route to functionalized cyclic sulfinate esters, viz., the N-protected β-amino γ-sultines, and showed that nucleophilic ring-opening reactions can be performed by selective cleavage of either the S–O or the C–O bond.

Durst et al. have studied the photochemical[4] and thermolytic[5] breakdown of nonfunctionalized γ-sultines **1**. Photolysis was only observed with sultines having a γ-phenyl substituent and gave phenylcyclopropanes **2**

Scheme I



Scheme II



(Scheme I). Thermolysis gave the alkenes **3a** and **3b** beside **2**.[6] The authors assumed that thermolysis of **1** proceeds via an intermediate diradical by consecutive cleavage of the C–O and C–S bond.[5] It seemed worthwhile

(1) Squires, T. G.; Venier, C. G.; Hodgson, B. A.; Chang, L. W.; Davis, F. A.; Panunto, T. W. *J. Org. Chem.* **1981**, *46*, 2373. Hanson, G.; Kemp, D. S.; *Ibid.* **1981**, *46*, 5441. Pirkle, W. H.; Hoekstra, M. S. *J. Am. Chem. Soc.* **1976**, *98*, 1832. Harpp, D. N.; Vines, S. M.; Montillier, J. P.; Chan, T. H. *J. Org. Chem.* **1976**, *41*, 3987. Sharma, N. K.; De Reinach-Hirtzbach, F.; Durst, T. *Can. J. Chem.* **1976**, *54*, 3012 and references cited therein. Kroll, J. O.; Wojcicki, A. *J. Organomet. Chem.* **1974**, *66*, 95. Henrick, K.; Johnson, B. L. *Aust. J. Chem.* **1972**, *25*, 2263. Thomasson, J. E.; Robinson, P. W.; Ross, D. A.; Wojcicki, A. *Inorg. Chem.* **1971**, *10*, 2130. Applequist, D. E.; McKenzie, L. F. *J. Org. Chem.* **1977**, *42*, 1251. King, J. F.; de Mayo, P.; McIntosh, C. L.; Piers, K.; Smith, D. J. H. *Can. J. Chem.* **1970**, *48*, 3704.

(2) Harpp, D. N.; Steliou, K.; Chan, T. H. *J. Am. Chem. Soc.* **1978**, *100*, 1222.

(3) Liskamp, R. M. J.; Zeegers, H. J. M.; Ottenheijm, H. C. J. *J. Org. Chem.* **1981**, *46*, 5408.

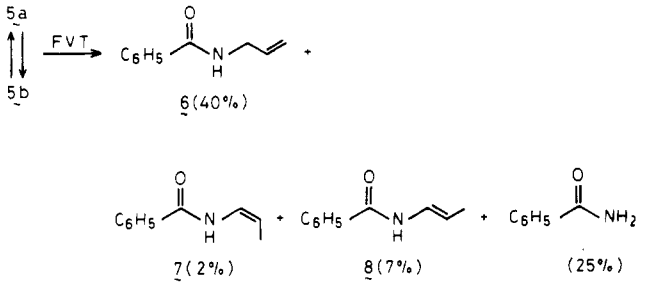
(4) Durst, T.; Huang, J. C.; Sharma, N. K.; Smith, D. J. H. *Can. J. Chem.* **1978**, *56*, 512.

(5) Durst, T.; Finlay, J. D.; Smith, D. J. H. *J. Chem. Soc., Perkin Trans. 1* **1979**, 950. Durst, T.; Gimbarzevsky, B. P. *J. Chem. Soc., Chem. Commun.* **1975**, 724. Jung, F.; Sharma, N. K.; Durst, T. *J. Am. Chem. Soc.* **1973**, *95*, 3420.

(6) Photochemical and thermolytic breakdown of γ-lactones, which are carbon counterparts of γ-sultines, yield also **2** and **3**. See: Givens, R. S.; Oettle, W. F. *J. Org. Chem.* **1972**, *37*, 4325.

0022-3263/83/1948-2733$01.50/0

Scheme III



to investigate whether thermolysis of N-protected β-amino γ-sultines leads to functionalized analogues of **2** and **3**.

Results and Discussion

The N-protected amino γ-sultines **5a** and **5b** were prepared from *N*-benzoyl-L-cystinol (**4**) by treatment with *N*-chlorosuccinimide and AcOH[3] (Scheme II). The two diastereomers **5a** and **5b** were readily separated by silica gel chromatography. Their thermolytic behavior was studied by flash vacuum thermolysis (FVT) at 0.05 mmHg through a quartz tube heated by a tube furnace. The products were collected on a cold finger and analyzed by thin-layer chromatography, ^{1}H NMR spectroscopy, and mass spectroscopy.

Interestingly, the sultines **5a** and **5b** epimerize at the sulfur atom at 130 °C, which is the preheating temperature of the samples.[7] As a consequence, thermolysis of **5a** and **5b** gave identical reaction mixtures. At 700 °C the compounds fragmented as shown in Scheme III. At higher temperatures a considerable amount of unidentifiable products was formed whereas at 650 °C the starting material was not completely converted. Other variations in reaction conditions yielded invariably the allyl amide **6** as the main product: when the reaction tube was filled with quartz wool (600 °C, 0.05 mmHg) or quartz chips (625 °C, 0.09 mmHg, N_2 flow) causing a longer contact time, compound **6** was isolated in yields of 45% and 50%, respectively.

In variation with the results of Durst et al.[5] (Scheme I), we could not detect cyclopropane derivatives.

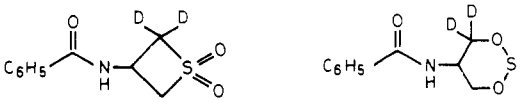
The formation of **6** via an intermediate biradical (**9**) and a cyclopropane derivative (**10**), as proposed by Durst et al.[5] for nonfunctionalized γ-sultines (Scheme I), could be ruled out by the following experiment. Thermolysis of benzamidocyclopropane[8] **10** at 700 °C yielded a mixture of **7** and **8**; none of the allyl amide **6** could be detected. Conclusive evidence which allowed us to rule out pathway a for the formation of **6** as well as of **7** and **8** was obtained by thermolysis of the labeled sultine **5a**-d_2 (Scheme IV). Thermolysis of **5a**-d_2 at 700 °C gave the compounds **6**-d_2, **7**-d_2, and **8**-d_2, all having the label at the terminal carbon atom. These structures were secured by ^{1}H NMR spectroscopy. Pathway a fails to explain these results, as the intermediacy of **10** would inevitably lead to scrambling of the label in **6**-d_2, **7**-d_2, and **8**-d_2.

Apparently, the formation of **6**–**8** by thermolysis of **5** involves migration of the amide function. Pathways b and c (Scheme IV) might explain this rearrangement. Path b features intramolecular nucleophilic attack by the amide *nitrogen* on the C–S bond leading to the aziridine intermediate **11**; expulsion of SO_2 give **6**-d_2. Alternatively, intramolecular nucleophilic attack on the C–O bond by the amide *oxygen* (path c) gives the oxazoline intermediate **12**. Extrusion of SO_2 from the latter yields **13**, which gives **6**-d_2 via a Claisen-type rearrangement.[9] Compounds **7**-d_2 and **8**-d_2 may have been formed in their turn from **6**-d_2 by a hydrogen shift. This was substantiated as follows: thermolysis of **6**-d_2 at 700 °C gave a mixture of **7**-d_2 and **8**-d_2 and starting material.

At present we have no conclusive evidence permitting a choice between pathways b and c. However, we are inclined to favor pathway c for two reasons. First, in **5** the C–O bond is more polarized than the C–S bond, and thus more susceptible to a nucleophilic attack. Second, attack by the amide nitrogen on the C–S bond (path b) would lead to a strained transition state, in which the nucleophile and the leaving group hardly can take apical positions.

The formation of benzamide (Scheme III) can be explained as depicted in Scheme V. This mechanism is analogous to the well-documented[10] thermolytic fragmentation of amides having a C(O)–N–C–C–H moiety. As this fragmentation is in competition with path c and/or path b, the occurrence of benzamide explains the relatively low yields of compounds **6**–**8**.

The mechanisms as depicted in paths b and c (Scheme IV) deserve some further comment. First, one might argue that, prior to attack by N or O, the sultine **5a**-d_2 rearranges to the sulfone **14** or or the sulfoxylate **15**. However, the



formation of **6**-d_2 excludes the intermediacy of these structures in any conceivable mechanism, as they would lead to an allyl amide, **6**, having a scrambled label.[11]

Second, the proposed mechanistic pathways b and c (Scheme IV) involve *heterolytic* bond fissions, whereas radical pathways are rather generally encountered in pyrolytic reactions.[15] However, there is limited evidence for the occurrence of charged intermediates in thermolysis.[15,16] These examples concern polar molecules containing moieties which are able to accommodate charge, as is the case with **5** too. Heterolytic bond fission is expected to take place primarily at the polar surface of the reaction tube.[17] Loss of deuterium, when observed in pyrolytic reactions, can be expected also to occur in a surface process.

We argued that as a consequence, loss of deuterium in the conversion of **5a**-d_2 into **6**-d_2 might be indicative of the reaction to take place, at least partly, at the surface and would thus support the proposed polar mechanism. Therefore, we determined by mass spectroscopy the per-

(7) This clean epimerization is of practical value. Earlier[3] we have shown that the enantiomer of **5a** having the S_cR_s configuration can be converted into a cysteinol monooxo dithioacetal, which is the characteristic moiety of sparsomycin. This synthesis starts from the expensive D-cystine and yields the S_cS_s sultine beside the desired S_cR_s sultine. The S_cS_s sultine can be recycled now by a thermally induced epimerization.

(8) Kishner, A. B. *Chem. Zentralbl.* **1905**, *1*, 1704.

(9) This type of Claisen rearrangement has been reported before, e.g.: Black, D. S. C.; Wade, A. M. *J. Chem. Soc. Chem. Commun.* **1970**, 871. See also: Rhoads, S. J.; Raulins, N. R. *Org. React.* **1975**, *22*, 1.

(10) Bailey, W. J.; Bird, C. N. *J. Org. Chem.* **1958**, *23*, 996.

(11) In addition, the rearrangement of **5a**-d_2 into **14** or **15** is considered to be unprobable as it has been shown that sultines can be prepared from cyclic sulfones under thermolytic[12] or photochemical conditions[13] and that cyclic sulfoxylates rearrange to sultines.[2,14]

(12) Dittmer, D. C.; Henion, R. S.; Takashina, N. *J. Org. Chem.* **1969**, *34*, 1310. King, J. F.; de Mayo, P.; McIntosh, C. L.; Piers, K.; Smith, D. J. H. *Can. J. Chem.* **1970**, *48*, 3704. Dittmer, D. C.; Nelson, T. R. *J. Org. Chem.* **1976**, *41*, 3044.

(13) Hall, C. R.; Smith, D. J. H. *Tetrahedron Lett.* **1974**, 3633.

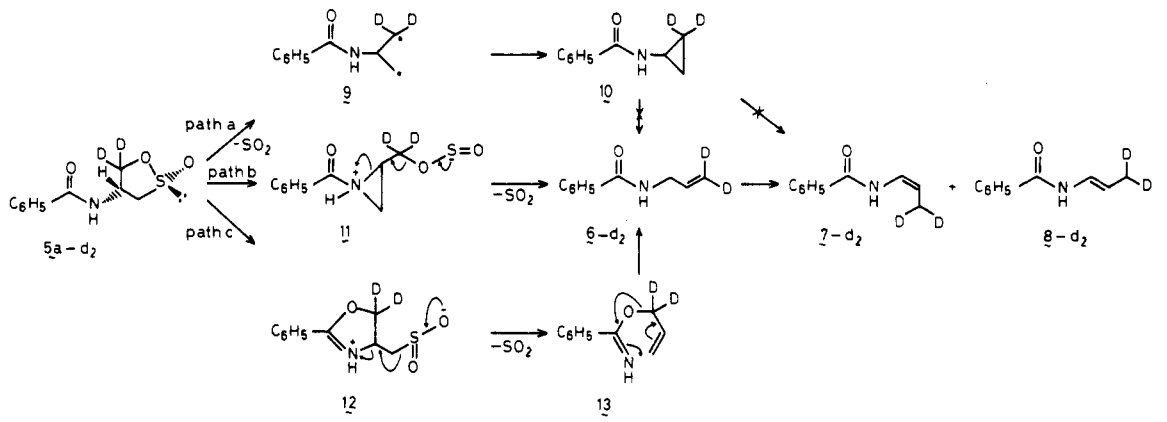
(14) Carlsen, L.; Snijder, J. P. *J. Org. Chem.* **1978**, *43*, 2216.

(15) Brown, R. F. C. *Org. Chem. (N.Y.)* **1980**, *41*, 44.

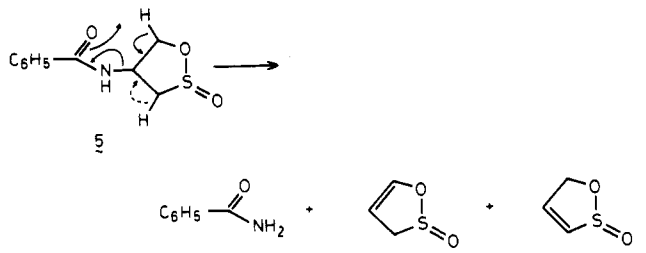
(16) Cameron, T. B.; El-Kabbani, F. M.; Pinnick, H. W. *J. Am. Chem. Soc.* **1981**, *103*, 5414.

(17) Wertz, D. H.; Allinger, N. L. *J. Org. Chem.* **1977**, *42*, 698.

Scheme IV



Scheme V



centage of monodeuterated (d_1) and nondeuterated (d_0) compounds **5a**-d_2 and **6**-d_2 relative to the corresponding dideuterated (d_2) compounds. For **5a**-d_2 and **6**-d_2 the ratios $d_2/d_1/d_0$ were found to be 100/26/2 and 100/41/6, respectively. This loss of deuterium is significant and suggests that the mechanism for the conversion of **5** into **6** is a polar one.

Conclusions

The above findings suggest that thermolysis of **5a** or **5b** involves a novel migration of the benzamide group to yield **6–8**. The proposed mechanisms (Scheme IV) feature neighboring group participation by the amide nitrogen (path b) or amide oxygen (path c) in the heterolytic fission of the C–S or C–O bond, respectively. We favor pathway c above pathway b for the aforementioned reasons. Support has been found for the heterolytic nature of the bond fission. Whereas thermolysis of nonfunctionalized γ-sultines leads to cyclopropanes among other products,[5] we could not detect benzamidocyclopropane in the reaction mixture. Experiments to refine the proposed mechanism are being sought.

In addition, we plan to study the FVT of other functionalized sultines and sultones. Presently, the influence of the N-protecting group on the behavior of sultines in FVT is under investigation. Also, synthetic applications of this route to allyl amides **6** are being studied.[18] Finally, the synthesis of sparsomycin starting from a sultine[3,19] can now be optimized by making use of the finding that sultines **5a** and **5b** undergo a clean epimerization at 120–130 °C.[7]

Experimental Section

^{1}H NMR spectra were measured on a Varian Associates Model T-60 or a Bruker WH-90 spectrometer with Me_4Si as an internal standard. IR spectra were measured with a Perkin-Elmer spectrophotometer, Model 997. Mass spectra were obtained with a double-focusing Varian Associates SMI-B spectrometer and with a Finnigan 3100 gas chromatograph/mass spectrometer.

Melting points were taken on a Köfler hot stage (Leitz–Wetzlar) and are uncorrected. Thin-layer chromatography (TLC) was carried out by using Merck precoated silica gel F254 plates (thickness 0.25 mm). Spots were visualized with a UV lamp or Cl_2–TDM.[20] For column chromatography Merck silica gel H (Type 60) was used. The Miniprep LC (Jobin–Yvon) was used for preparative HPLC.

Flash vacuum thermolysis (FVT) was carried out in standard equipment in a horizontal assembly as described in Chapter II of ref 15. The quartz tube (outer diameter 1.75 cm) was heated over a length of 17.5 cm. The products were collected on a cold finger cooled with 2-propanol/CO_2. The preheating temperature was 130 °C. The reported yields are after HPLC column chromatography.

***N*-Benzoyl-L-cystinol (4).** *N*-Benzoyl-L-cystine methyl ester (10.0 g, 21 mmol) was reduced with lithium borohydride [sodium borohydride (4.75 g, 125 mmol) and lithium iodide (21.34 g, 125 mmol)] in 500 mL of DME as described earlier for the preparation of benzyloxycarbonyl-L-cystinol. The workup had to be slightly modified, however, due to the poor solubility of the reaction products in DME. The pH was adjusted to 5 by addition of an aqueous solution 1 N HCl to the stirred and cooled (0 °C) solution. DME was evaporated in vacuo, and the residue was dissolved in 500 mL of methanol/water (1/1, v/v) and then oxidized with iodine as described[3] for benzyloxycarbonyl-L-cystinol. Subsequently, the methanol was evaporated in vacuo, and water and dichloromethane were added. The aqueous phase was extracted five times with 400-mL portions of dichloromethane.

The collected organic layers were dried (Na_2SO_4), and residual iodine was removed by stirring with $Na_2S_2O_5$. The residue was recrystallized from methanol/water to give **4**: 56% yield; mp 194 °C; R_f 0.27 (eluent MeOH/CH_2Cl_2, 1/9 v/v); NMR (CD_3OD) δ 3.00 (ABX, 2 H, $CHCH_2S$), 3.63 (d, 2 H, CH_2OH), 4.11–4.52 (m, 1 H, $CHCH_2OH$), 7.20–7.89 (m, 5 H, C_6H_5); IR (KBr) 3380, 3300, 1640, 1530 cm^{-1}. Anal. Calcd for $C_{20}H_{24}N_2O_4S_2$: C, 57.12; H, 5.75; N, 6.56. Found: C, 56.75; H, 5.79; N, 6.51.

***N*-Benzoyl-L-dideuteriocystinol (4-d_2).** This compound was prepared as has been described for the preparation of **4**. Instead of sodium borohydride, sodium borodeuteride was used. The compound was obtained in 60% yield and was identical in every aspect with **4**, except for the CH_2OH signal in the NMR spectrum (residual protons, ca. 18% by integration). Anal. Calcd for $C_{20}D_4H_{20}N_2O_4S_2$: C, 56.58; N, 6.60. Found: C, 56.58; N, 6.46.

4-Benzamido-1,2-oxothiolane 2-Oxide (5a,b). Compounds **5a** and **5b** were prepared from *N*-benzoyl-L-cystinol (**4**; 3.50 g, 8.33 mmol) and *N*-chlorosuccinimide (3.34 g, 25 mmol) in 150 mL of glacial acetic acid as has been reported earlier[3] for other N-protected amino sultines. HPLC (eluent MeOH/CH_2Cl_2, 5/95 v/v) gave **5a** (43%), which was homogeneous by TLC (MeOH/CH_2Cl_2, 1/9 v/v). Compound **5b** thus obtained was still con-

(18) For a recent synthesis of the allyl amide portion of griseoviridine, see: Meyers, A. I.; Lawson, J. P.; Corver, D. R. *J. Org. Chem.* **1981**, *46*, 3119.

(19) Ottenheijm, H. C. J.; Liskamp. R. M. J.; van Nispen, S. P. J. M.; Boots, H. A.; Tijhuis, M. W. *J. Org. Chem.* **1981**, *46*, 3273.

(20) von Arx, E.; Faupel, M.; Brugger, M. *J. Chromatogr.* **1976**, *120*, 224.

taminated with succinimide; both compounds have nearly identical R_f values on TLC. Purification was achieved by repeated extraction of a dichloromethane solution of the mixture with 0.1 N $NaHCO_3$ solution. After the mixture was dried (Na_2SO_4) and the solvent evaporated, sultine **5b** was obtained in 32% yield.

5a: R_f 0.77 (eluent MeOH/CH_2Cl_2, 1/9 v/v); NMR ($CDCl_3$) δ 3.06 and 3.32 (AB part of ABX spectrum, J_{AX} = 1.2 Hz, J_{BX} = 6.3 Hz, J_{AB} = 13.2 Hz, 2 H, CH_2S), 4.67 and 4.84 (AB part of ABX spectrum, J_{AX} = 1.7 Hz, J_{BX} = 5.4 Hz, J_{AB} = 9.9 Hz, 2 H, CH_2O), 5.22-5.60 (m, 1 H, $CHCH_2O$), 7.17-8.11 (m, 6 H, C_6H_5 and NH); IR (KBr) 3280, 1640, 1535, 1060 cm^{-1}; mass spectrum, m/e 225 (M^+), 161 ($-SO_2$). Anal. Calcd for $C_{10}H_{11}NO_3S$: C, 53.32; H, 4.92; N, 6.22. Found: C, 53.12; H, 4.86; N, 6.19.

5b: R_f 0.40 (eluent MeOH/CH_2Cl_2, 1/9 v/v); NMR ($CDCl_3$) δ 3.24 and 3.60 (AB part of ABX spectrum, J_{AX} = 3 Hz, J_{BX} = 6.6 Hz, J_{AB} = 14 Hz, 2 H, CH_2S), 4.60 and 4.89 (AB part of ABX spectrum, J_{AX} = 1.5 Hz, J_{BX} = 4.6 Hz, J_{AB} = 10 Hz, 2 H, CH_2O), 5.00-5.29 (m, 1 H, $CHCH_2O$), 6.87 (d, 1 H, NH), 7.16-7.84 (m, 5 H, C_6H_5); IR (KBr) 3300, 1650, 1530, 1030 cm^{-1}; mass spectrum, 225 (M^+), 161 ($-SO_2$). Anal. Calcd for $C_{10}H_{11}NO_3S$: C, 53.32; H, 4.92; N, 6.22. Found: C, 53.26; H, 4.90; N, 6.22.

4-Benzamido-5,5-dideuterio-1,2-oxothiolane 2-Oxide (5a,b-d_2). The synthesis of **5a**-d_2 and **5b**-d_2 from **4**-d_2 was carried out as described above for **5a** and **5b**, yielding the compounds in 43% and 29%, respectively.

5a-d_2: R_f 0.77 (eluent MeOH/CH_2Cl_2, 1/9 v/v); NMR ($CDCl_3$) δ 3.06 and 3.32 (AB part of ABX spectrum, J_{AX} = 1.2 Hz, J_{BX} = 6.3 Hz, J_{AB} = 13.2 Hz, 2 H, CH_2S), 4.55-5.02 (residual protons CH_2O; 15% by integration), 5.44 (d of t, 1 H, $CHCH_2O$), 7.17-8.11 (m, 6 H, C_6H_5 and NH); mass spectrum, m/e 227 (M^+), 163 ($-SO_2$). Anal. Calcd for $C_{10}D_2H_9NO_3S$: C, 52.85; N, 6.16. Found: C, 52.67; N, 6.08.

5b-d_2: R_f 0.40 (eluent MeOH/CH_2Cl_2, 1/9 v/v); NMR ($CDCl_3$) δ 3.24 and 3.60 (AB part of ABX spectrum, J_{AX} = 3 Hz, J_{BX} = 6.6 Hz, J_{AB} = 14 Hz, 2 H, CH_2S), 4.59 and 4.89 (residual protons CH_2O; 15% by integration), 5.14 (d of t, 1 H, $CHCH_2O$), 6.82 (d, 1 H, NH), 7.16-7.84 (m, 5 H, C_6H_5); mass spectrum, m/e 227 (M^+), 163 ($-SO_2$). Anal. Calcd for $C_{10}D_2H_9NO_3S$: C, 52.85; N, 6.16. Found: C, 53.03; N, 6.28.

3-Benzamidoprop-1-ene (6), 3-Benzamido-(*Z*)-prop-2-ene (7), 3-Benzamido-(*E*)-prop-2-ene (8). The FVT of **5a** or **5b** (0.5 g, 2.2 mmol) was carried out as described above. The products were separated by HPLC (eluent CH_2Cl_2) to give **6**-**8** in yields of 40-50%, 2%, and 7%, respectively.

6: R_f 0.66 (MeOH/CH_2Cl_2, 1/9 v/v); NMR ($CDCl_3$) δ 4.08 (Y_2 part of $ABXY_2$ spectrum, J_{AY} = J_{BY} = 1.6 Hz, J_{XY} = $J_{Y\text{-}NH}$ = 5.6 Hz, 2 H, $NHCH_2$), 5.17 and 5.24 (AB part of $ABXY_2$ spectrum, J_{AB} = 3.2 Hz, J_{AX} = 17.2 Hz, J_{BX} = 10 Hz, 2 H, $C{=}CH_2$), 5.95 (X part of $ABXY_2$, spectrum 1 H, CH_2CH), 6.16-6.76 (br, 1 H, NH), 7.07-7.93 (m, 5 H, C_6H_5); IR ($CHCl_3$) 3460, 3360, 1660, 1520, 995, 930 cm^{-1}; mass spectrum, m/e 161 (M^+).

7: R_f 0.81 (MeOH/CH_2Cl_2, 1/9 v/v); NMR ($CDCl_3$) δ 1.70 (X_3 part of ABX_3 spectrum, d of d, J_{BX} = 6.9 Hz, J_{AX} = 1.7 Hz, 3 H, $CHCH_3$), 4.95 (B part of ABX_3 spectrum, J_{AB} = 8.4 Hz, 1 H, $CHCH_3$), 6.93 (A part of ABX_3 spectrum, J_{AX} = 1.8 Hz, $J_{A\text{-}NH}$ = 10.0 Hz, 1 H, NHCH), 7.30-7.96 (m, 6 H, C_6H_5, NH); mass spectrum, m/e 161 (M^+).

8: R_f 0.73 (MeOH/CH_2Cl_2, 1/9 v/v); NMR ($CDCl_3$) δ 1.74 (X_3 part of ABX_3 spectrum, d of d, J_{BX} = 6.8 Hz, J_{AX} = 11.6 Hz, 3 H, $CHCH_3$), 5.31 (B part of ABX_3 spectrum, J_{AB} = 13.8 Hz, 1 H, $CHCH_3$), 6.97 (A part of ABX_3 spectrum, $J_{A\text{-}NH}$ = 10.0 Hz, 1 H, NHCH), 7.30-8.00 (m, 6 H, C_6H_5, NH); mass spectrum, m/e 161 (M^+).

Acknowledgment. We thank Mr. J. M. J. Verlaak for his assistance in carrying out the FVT experiments, Professor Dr. B. Zwanenburg and Dr. A. J. H. Klunder for making available the FVT apparatus, and H. H. K. Brinkhof for the ^1H NMR spectra and helpful discussions. We are indebted to J. Zwinselman and Professor Dr. N. Nibbering (University of Amsterdam) for the electron-impact and field-ionization mass spectra. Part of the investigations was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research.

Registry No. **4**, 86290-15-5; **4**-d_2, 86290-17-7; **5a**, 86290-16-6; **5a**-d_2, 86290-18-8; **5b**, 86334-10-3; **5b**-d_2, 86334-11-4; **6**, 10283-95-1; **7**, 5500-46-9; **8**, 5202-76-6; *N*-benzoyl-L-cystine methyl ester, 5673-91-6.

Chemistry of Ketene Acetals. 7.† 2-Methoxy-4*H*-pyrans as Strong Hydride Donors in Reactions with Electrophilic Olefins

C. G. Bakker, C. J. J. M. Hazen, J. W. Scheeren,* and R. J. F. Nivard

Department of Organic Chemistry, Catholic University, Toernooiveld, 6525 ED Nijmegen, The Netherlands

Received October 26, 1982

The reactions of 2-methoxy-5,6-dihydropyrans (**2**) and 2-methoxy-4*H*-pyrans (**3**) with a variety of electrophilic olefins $R^4R^5C{=}C(CN)X$ have been studied. Cyclobutanes are formed in an equilibrium reaction from **2** as well as **3**. In general, the compounds **3** give ultimately the thermodynamically stable heptadienoic esters **10**. 2-Methoxy-4*H*-pyrans, substituted at carbon atom 6, yield, however, a pyrone derivative (**11**) when they react with strongly electrophilic olefins substituted with three or four electron-withdrawing groups. Both conversions are supposed to occur via the abstraction of a hydride ion from C(4) in a rate-determining step leading to a pyrylium ion (**14**). The further course of the process is determined by the character of the nucleophile formed in the addition of the hydride ion to the olefin and by the substitution pattern of **3**.

In combination with an investigation of cycloadditions between acyclic ketene acetals, $RR^1C{=}C(OMe)_2$ (**1**), and electrophilic alkenes or dienes[1] we studied the reactivity of two types of *cyclic* ketene acetals, viz., 2-methoxy-5,6-dihydropyrans (**2**) and 2-methoxy-4*H*-pyrans (**3**) toward electrophilic olefins. Apart from a possible effect of the second double bond on the rate and equilibrium constant of the expected cyclobutane formation, the investigation

† Part 6: C. G. Bakker, P. H. M. Ooms, J. W. Scheeren, and R. J. F. Nivard, *Recl. Trav. Chim. Pays-Bas*, **102**, 130 (1983).

(1) H. W. Scheeren, A. J. R. van Rossum, and R. J. F. Nivard, *Tetrahedron*, **39**, 1345 (1983).

0022-3263/83/1948-2736$01.50/0