and the residue was purified chromatographically (TLC preparation). The isolated α-phenylbutyric acid possessed $[\alpha]^{20}$ +0.33° (1 mL, CH_2Cl_2), which indicate *R* configuration for the investigated (+)-1,3-diphenylpropanol-1.

Registry No.—I, 68906-28-5; II, 68906-29-6; III, 68844-59-7; IV, 68844-60-0; V, 68844-61-1; VI, 68844-62-2; XVIIIA, 68844-63-3; XVIIIC, 68844-64-4; *cis*-XIX, 68844-65-5; *trans*-XIX, 68844-66-6; *cis*-XX, 68844-67-7; *trans*-XX, 68844-68-8; (−)-XXIII, 64439-32-3; (+)-XXIII, 68889-69-0; (±)-XXIII, 68889-70-3; XXIV (R = H), 68844-69-9; XXIV (R = Me), 64270-56-0; XXIV (R = Me) ω-camphanic acid ester, 68844-70-2; XXV (R = H), 68844-71-3; XXV (R = Me), 68844-72-4; XXVII (R = H), 68844-73-5; XXVII (R = Me), 68844-74-6; phenyl isocyanate, 103-71-9; (*S*)-(−)-α-phenylethylhydroxylamine, 53933-47-4; benzaldehyde, 100-52-7; trimethylacetaldehyde, 630-19-3; *tert*-butylhydroxylamine, 16649-50-6; L-(−)-menthyl glyoxalate, 26315-61-7; *n*-butyl glyoxalate, 6295-06-3; methyl glyoxalate methyl hemiacetal, 19757-97-2.

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Oxidation of α-Amino Esters. One-Step Synthesis of Sulfenimines

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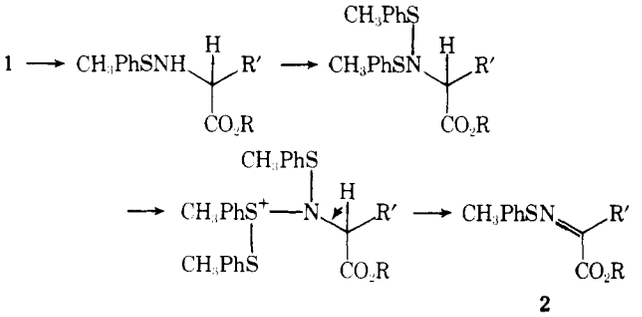
α-Amino esters (1) were oxidized to their corresponding sulfenimine derivatives (2) by mild treatment with *p*-toluenesulfenyl chloride in the presence of acid scavengers. Such amino acid derived sulfenimines are converted to α-keto esters by treatment with triphenylphosphine and silica gel. Oxidation of sulfenimines is discussed, including an example which gives rise to a dehydroamino acid residue.

The chemistry of peptide antibiotics, β-lactam antibiotics, and other peptide derived natural products is tightly interwoven with that of oxidized, dehydro, or "modified" amino acids. Consequently, the synthetic organic chemistry of amino acids (as distinct from "peptide synthesis") is an area which continues to attract increasing attention among organic chemists. Recently we observed facile sulfenyl halide initiated formation of sulfenimine (thiooxime) derivatives from esters of 6-aminopenicillanic and 7-aminocephalosporanic acids.[1] The structural and chemical similarity of such β-lactam nuclei to classical amino acids suggested that our methodology should be applicable to this class of compounds. Amino acid derivatives resulting from such reactions would have oxidation states equivalent to the dehydro amino acid level and, therefore, hold promise as useful synthetic intermediates. We now wish to report that amino acid esters (1) can be oxidized by *p*-toluenesulfenyl chloride (TSC) to sulfenimine derivatives of type **2**.

The general procedure for this transformation is as follows. Amino acid ester hydrochloride salts are converted to their free bases with triethylamine and treated with 3 molar equiv of TSC[2] in dry methylene chloride at 0–5 °C. One or more acid scavengers such as pulverized molecular sieves,[3] propylene oxide, or anhydrous potassium carbonate are employed to trap liberated hydrogen chloride. Sulfenimines (**2**) form rapidly and were obtained in pure form (51 to 95% isolated yield) following silica gel chromatography to remove coproduced *p*-tolyl disulfide. The products were isolated as stable, yellow-orange oils or low melting solids, except for glycine derivative **8** which was obtained as a mobile liquid. Representative examples of this reaction are summarized in Table I. With cysteine ethyl ester (**7**) simultaneous sulfenylation of the sulfhydryl group occurred to afford a mixed disulfide. Free carboxylic acids of type **2** may also be prepared by a modified procedure. Thus silylation [2 equiv of bis(trimethylsilyl)-acetamide, CH_2Cl_2, 1 h] of thienyl glycine, followed by reaction with TSC and subsequent hydrolysis, afforded sulfenimine acid **9**.[4]

We propose that sulfenimines **3–8** arise by the mechanism outlined in Scheme I. Initial *N*-sulfenylation to form a sulfenamide is analogous to the well-known protection of amino acids with *o*-nitrophenylsulfenyl chloride. Further *N*-sulfenylation followed by *S*-sulfenylation, and subsequent elimination, account for the observed products. Support for this pathway comes from another investigation in which we

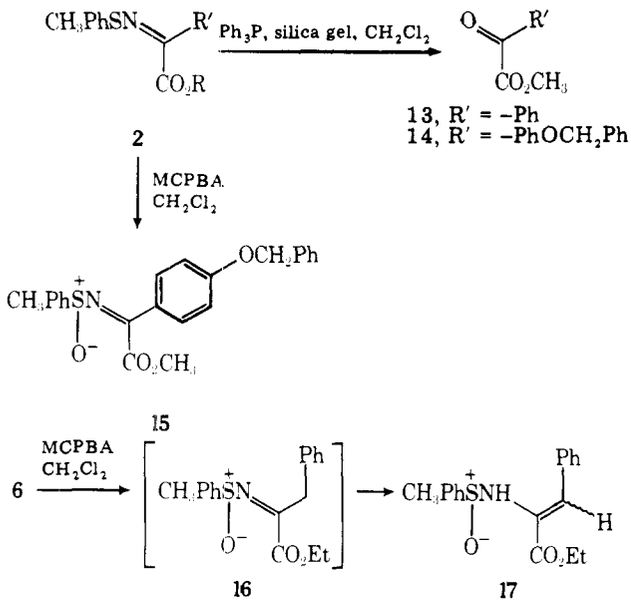
Scheme I



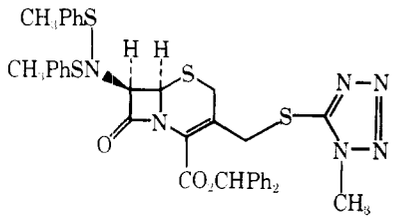
2

0022-3263/79/1944-1218$01.00/0

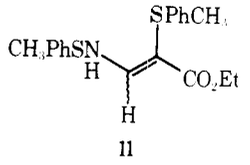
Scheme II



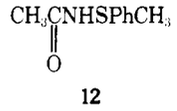
have isolated sulfenimide **10**.[5] This material on contact with TSC ($CDCl_3$, 26 °C) is rapidly converted to the corresponding sulfenimine. As expected, in some cases the α-amino ester derived sulfenimines form as mixtures of syn and anti isomers. Of critical importance to the success of this type of reaction may be the relative acidity of the proton adjacent to nitrogen, which is lost in the final elimination. Thus treatment of cyclohexylamine under the above conditions gave a complex product mixture. Interestingly, similar reaction of β-alanine ethyl ester, although also complex, produced substance **11** which may have a sulfenimine precursor.[6] Atypical α-amino acids also gave results which deviated from the above. Thus proline benzyl ester afforded a mixture comprised mostly of the corresponding sulfenamide and sulfinamide(s), whereas cycloserine led to a multitude of products containing sulfenimide **12**.



10



11

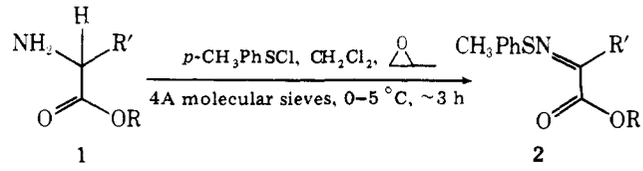


12

We have briefly investigated selected transformations of the aforementioned sulfenimine derivatives. Treatment of these substances with triphenylphosphine and silica gel (CH_2Cl_2, 26 °C)[7] directly produced the corresponding α-keto esters. In this way phenylglycine-derived **4** afforded methyl benzoyl formate (**13**, 45% isolated), and sulfenimine **5** was converted to ester **14** (92% isolated). Thus the sequence **1** → **2** → **13**, **14** represents a mild, neutral, two-step conversion of α-amino esters to α-keto esters.

Oxidation (1 equiv of *m*-chloroperbenzoic acid/CH_2Cl_2/0 °C) of the sulfenimine derived from *O*-benzyl-*p*-hydroxyphenylglycine (**5**) produced pale yellow sulfinimine[8b] **15** (75% isolated). Similar treatment of phenylalanine derivative **6**, however, gave **16**, which could not be isolated but rapidly isomerized to dehydrophenylalaninesulfinamide **17** (one isomer). Treatment of **6** with 2 molar equiv of oxidant afforded only low yields of *p*-toluenesulfonamide.

Table I



	R'	R	yield, %
3	$-CH_3$	$-CH_3$	74
4	-Ph	$-CH_3$	86
5	$-PhOCH_2Ph$	$-CH_3$	84
6	$-CH_2Ph$	$-CH_2CH_3$	51
7	$-CH_2SH$	$-CH_2CH_3$	75[a]
8	-H	$-CH_2CH_3$	95
9		-H	38

[a] Product isolated as R' = $-CH_2SSPhCH_3$.

The presently reported sulfenimine derivatives may be considered protected α-imino acids and in at least one case (**6** → **17**) have led to a dehydroamino acid derivative. Although a number of reports on the chemistry of sulfenimines have recently appeared, most notably by Davis and co-workers,[8] this area[1,10c,d] is still largely unexplored.[9] Rare use of the sulfenimine functionality in organic synthesis likely reflects a paucity of simple means of preparation.[10,11] Considering the ease with which this functionality may now be introduced into common amino acid derivatives, these products should prove to be useful new synthetic intermediates.

Experimental Section

Melting points were determined on a Thomas-Hoover melting point apparatus and are uncorrected. Proton magnetic resonance spectra were recorded on Varian Associates Models T-60 and XL-100-15 spectrometers. Carbon-13 NMR spectra were measured in deuteriochloroform on a Jeol FX60-Q. Infrared spectra were determined on Perkin-Elmer Models 621 or 257 recording spectrophotometers. Chemical shifts are reported as δ values (ppm) relative to tetramethylsilane as internal standard. Mass spectra were obtained on an AEI-MS-902 mass spectrometer. Ultraviolet spectra were recorded on a Perkin-Elmer 202 spectrophotometer. Analytical and preparative (PLC) thin-layer chromatography were carried out using E. Merck F-254 silica gel plates. Column chromatography was performed with Mallinckrodt Silic*AR* CC-7. Amino acid ester hydrochlorides were either obtained commercially or prepared by the method of Brenner and Huber.[12]

General Procedure for Preparation of Amino Acid Ester Sulfenimines (3–8). The amino acid ester hydrochloride salt (20 mmol) was slurried in dry methylene chloride (100 mL) and propylene oxide (10 mL) and chilled to 0–5 °C under nitrogen. Molecular sieves (4A, 10 g) were added followed in succession by triethylamine (20 mmol) and *p*-toluenesulfenyl chloride (66 mmol). The mixture was stirred at 0–5 °C for 3 h, filtered, and evaporated under reduced pressure, and the residue was redissolved in ethyl acetate. The organic solution was washed with water, dried over sodium sulfate, and concentrated under reduced pressure to a heavy yellow-orange oil. Chromatography on Mallinckrodt Silic*AR* CC-7 (hexane/methylene chloride 1:1) afforded pure amino acid sulfenimines. Crystallization was usually achieved by cooling a hexane solution with dry ice.

Methyl 2-[[(4-Methylphenyl)thio]imino]propanoate (3): yellow oil (74%), one isomer; ^1H NMR ($CDCl_3$) δ 2.25 (s, 3 H), 2.30 (s, 3 H), 3.75 (s, 3 H), 7.15, 7.50 (d of d, 4 H, J = 8 Hz); IR ($CHCl_3$) 1715, 1300, 1280, 1145 cm^{-1}; UV (hexane) 230 nm (ϵ 9300), 323 nm (ϵ 8800); mass spectrum *m/e* 223 (M^+), 123; ^{13}C NMR ($CDCl_3$) δ 19.0, 21.0, 52.6, 125.7, 129.7, 133.8, 137.4, 153.8. Anal. ($C_{11}H_{13}NSO_2$): C, H, N, S.

Methyl α-[[(4-Methylphenyl)thio]imino]benzeneacetate (4):

bright yellow crystals (86%), syn and anti isomers ~3:1; mp 79–81 °C; ^{1}H NMR ($CDCl_3$) δ 2.31 (s, 3 H), 3.91 (s, 3 H), 7.36 (m, 9 H); IR (KBr) 1705, 1490, 1435, 1295, 1230, 1010 cm^{-1}; UV (hexane) 243 nm (ε 12 200), 362 (ε 8600); mass spectrum *m/e* 285 (M^+), 226, 123; ^{13}C NMR ($CDCl_3$) δ 21.0, 52.4, 125.6, 126.1, 127.8, 128.1, 129.6, 138.8, 164.2. Anal. ($C_{16}H_{15}NSO_2$): C, H, N, S.

Methyl α-[[(4-Methylphenyl)thio]imino]-4-(phenylmethoxy)benzeneacetate (5): off white crystals (84%), isomers ~3:1; mp 74–76 °C; ^{1}H NMR ($CDCl_3$) δ 2.36 (s, 3 H), 3.88 (s, ~0.75 H, minor isomer –OCH_3), 3.98 (s, ~2.25 H, major isomer –OCH_3), 5.11 (s, 2 H), 6.88 → 7.80 (m, 13 H); IR (KBr) 1715 (major isomer), 1705 (minor isomer), 1605, 1510, 1215, 1175, 1035 cm^{-1}; UV (hexane) 243 nm (15 100), 365 (12 200); mass spectrum *m/e* 391 (M^+), 369, 332, 300, 285, 123, 91; ^{13}C NMR ($CDCl_3$) δ 21.1, 52.3, 69.9, 114.5, 125.7, 126.1, 128.0, 128.5, 129.4, 129.6, 136.7, 163.2. Anal. ($C_{23}H_{21}NSO_3$): C, H, N, S.

Ethyl α-[[(4-Methylphenyl)thio]imino]benzenepropanoate (6): light orange crystals (51%); mp 42–44 °C; ^{1}H NMR ($CDCl_3$) δ 1.33 (t, 3 H, *J* = 8 Hz), 2.35 (s, 3 H), 4.10 (s, 2 H), 4.25 (q, 2 H, *J* = 8 Hz), 7.28 (m, 9 H); IR (KBr) 1710, 1590, 1195, 1100, 1020 cm^{-1}; UV (hexane) 230 nm (ε 12 100), 337 (ε 8700); mass spectrum *m/e* 313 (M^+), 240, 123, 91. Anal. ($C_{18}H_{19}NSO_2$): C, H, N, S.

Ethyl 3-[[(4-Methylphenyl)dithio]-2-[[4-methylphenyl)thio]imino]propanoate (7): dark orange oil (75%); isomers ~6:5; ^{1}H NMR ($CDCl_3$) δ 1.30 (t, 3 H, *J* = 7 Hz), 2.26 (s, ~1.3 H, minor isomer), 2.33 (s, 4.7 H), 3.86 (s, 1.1 H, major isomer), 3.98 (s, 0.9 H, minor isomer), 7.28 (m, 8 H); IR ($CHCl_3$) 1710 cm^{-1}; UV (hexane) 238 nm (ε 18 300), 355 nm (ε 8600); mass spectrum *m/e* 391 (M^+). Anal. ($C_{19}H_{21}NS_3O_2$): C, H, N, S.

Ethyl [[(4-Methylphenyl)thio]imino]acetate (8): light yellow-orange liquid (95%), isomers ~2:1; ^{1}H NMR ($CDCl_3$) δ 1.33 (t, 3 H, *J* = 6 Hz), 2.38 (s, 3 H), 4.30 (q, 2 H, *J* = 6 Hz), 7.33 (m, 4.7 H), 7.83 (s, ½ H, minor isomer); IR ($CHCl_3$) 1710 cm^{-1}; UV (hexane) 225 nm (ε 9300), 347 (6300); mass spectrum *m/e* 223 (M^+). Anal. ($C_{11}H_{13}NSO_2$): C, H, N, S.

α-[[(4-Methylphenyl)thio]imino]-2-thiopheneacetic Acid (9). To a suspended mixture of DL-thienylglycine (10 g, 64 mmol) in dry methylene chloride (400 mL) was added propylene oxide (20 mL), crushed No. 4A molecular sieves (~10 g), and bis(trimethylsilyl)-acetamide (32 mL, 128 mmol). After stirring for 1.5 h, the thienylglycine was almost completely dissolved. After cooling to 0 °C, *p*-tolylsulfenyl chloride (38.8 g, 245 mmol) was added dropwise in methylene chloride (≃75 mL). The reaction mixture was stirred vigorously for 3 h during which time the temperature was allowed to rise to 26 °C.

The resulting mixture was filtered and then extracted with 5% sodium bicarbonate (2 × 200 mL). The combined aqueous extracts were acidified to pH 2.3 with 1 N HCl. The resulting bright yellow precipitate was collected by filtration and washed with 8% NaCl solution. The filter cake was dried under vacuum (without heating) to give the desired product (6.82 g, 38% yield). Crystallization from acetone/hexane afforded an analytical sample: mp 98–99 °C; ^{1}H NMR ($CDCl_3$) δ 2.42 (s, 3 H), 7.2–8.3 (complex multiplet, 7 H), 9.38 (br s, 1 H); IR (KBr) 1680, 1490, 1410, 1270 cm^{-1}; mass spectrum *m/e* 277 (H^+). Anal. ($C_{13}H_{11}NO_2S_2$): C, H, N, S.

Oxidation of β-Alanine Ethyl Ester. The reaction was performed as described in the general procedure. TLC (hexane/CH_2Cl_2, 1:1) indicated at least three major components. Silica gel chromatography afforded the main component of lowest R_f (11) in crystalline form (0.419 g, 12%). Recrystallization from hot hexane provided an analytical sample: white crystals, mp 99–100 °C; ^{1}H NMR ($CDCl_3$) δ 1.18 (t, 3 H, *J* = 7 Hz), 2.23 (s, 3 H), 2.30 (s, 3 H), 4.15 (q, 2 H, *J* = 7 Hz), 6.63 (d, 1 H, *J* = 13 Hz), 7.00 (s, 4 H), 7.06 (s, 4 H), 8.05 (d, 1 H, *J* = 13 Hz); IR (KBr) 3200, 1670, 1580, 1560, 1215 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 14.2, 20.8, 60.6, 96.4, 125.5, 126.8, 129.5, 129.7, 132.0, 135.3, 135.7, 137.3, 159.0, 166.0; UV (hexane) 252 nm (ε 23 300); mass spectrum *m/e* 359 (M^+). Anal. ($C_{19}H_{21}NS_2O_2$): C, H, N, S.

Oxidation of D-Cycloserine. D-Cycloserine (2.96 g, 29 mmol) was slurried at 26 °C in dry methylene chloride (100 mL) and propylene oxide (5 mL). Pulverized molecular sieves (~3 g) were added, followed by bis(trimethylsilyl)acetamide (14.4 mL, 60 mmol). After stirring at 26 °C, under nitrogen, for 1.5 h the mixture was cooled to 0 °C and *p*-toluenesulfenyl chloride (17.46 g, 110 mmol) was added dropwise with efficient stirring. Upon completion of addition the temperature was allowed to rise to 26 °C over 3 h. The resulting mixture was extracted with 5% sodium bicarbonate (3 × 50 mL), and the combined extracts were acidified to pH 3.5 with 1 N HCl. The acidic portion was extracted with ethyl acetate (3 × 100 mL), and the combined extracts were dried over sodium sulfate and concentrated under reduced pressure to a semicrystalline brown solid (1.17 g, 22%). Recrystallization from ethyl acetate/hexane afforded an analytical sample: mp 102.5–104 °C; ^{1}H NMR ($CDCl_3$) δ 2.18 (s, 3 H), 2.33 (s, 3 H), 7.13 (s, 4 H); IR (KBr) 3380, 1690, 1400 cm^{-1}; mass spectrum *m/e* 181 (M^+), 139, 138, 124, 123, 107, 91. Anal. ($C_9H_{11}NOS$): C, H, N, S.

Conversion of Sulfenimine 4 to Methyl Benzoylformate (13). To a stirred solution of sulfenimine **4** (1.1 g, 3.85 mmol) in methylene chloride (100 mL) at 26 °C, under nitrogen, was added Mallinkrodt Silic*AR* CC-4 (5.0 g), followed by triphenylphosphine (4.11 g, 15.40 mmol). After stirring for 18 h at 26 °C, the mixture was concentrated under reduced pressure and chromatographed (Silic*AR* CC-7, hexane–methylene chloride 1:1). The product was obtained as a light yellow liquid (0.451 g, 45%): ^{1}H NMR ($CDCl_3$) δ 3.83 (s, 3 H), 7.25–7.70 (m, 5 H); IR ($CHCl_3$) 1735, 1680 cm^{-1}; mass spectrum *m/e* 164 (M^+). Anal. C, H. Identical by NMR, IR, and TLC with a sample of methyl benzoylformate from Aldrich Chemical Co.

Compound 14. In a similar manner sulfenimine **5** was converted to ketone **14**: clear oil (92%); ^{1}H NMR ($CDCl_3$) δ 3.75 (s, 3 H), 5.10 (s, 2 H), 7.00, 8.00 (d of d, 4 H, *J* = 9 Hz), 7.35 (s, 5 H); IR ($CHCl_3$) 1735, 1675, 1600 cm^{-1}; mass spectrum *m/e* 270 (M^+). Anal. ($C_{16}H_{14}O_4$): C, H.

Oxidation of Sulfenimine 5. To a cold (0–5 °C) solution of sulfenimine **5** (0.50 g, 1.27 mmol) in methylene chloride (20 mL) was slowly added a solution of *m*-chloroperbenzoic acid (0.251 g) in the same solvent (5 mL). The reaction mixture was stirred and allowed to react at room temperature over 4.5 h. TLC of the clear solution indicated the absence of **5**. The reactants were poured into ethyl acetate (200 mL) and washed with saturated sodium bicarbonate solution (2 × 100 mL) and brine (1 × 10 mL). The organic layer was dried over sodium sulfate and concentrated under reduced pressure to a yellow oil (0.50 g). Crystallization from methanol afforded pale yellow crystals (0.393 g, 75%): mp 112–114 °C; ^{1}H NMR ($CDCl_3$) δ 2.22 (s, 3 H), 4.03 (s, 3 H), 5.01 (s, 2 H), 6.99, 7.75 (d of d, 4 H, *J* = 9 Hz), 7.40 (s, 5 H); IR (KBr) 1740, 1590, 1560, 1250 cm^{-1}; UV (CH_2Cl_2) 313 nm (ε 23 300). Anal. ($C_{23}H_{21}O_4NS$): C, H, N, S.

Oxidation of Sulfenimine 6. To a cold (0–5 °C) solution of sulfenimine **6** (1.82 g, 5.81 mmol) in methylene chloride (50 mL) was slowly added a solution of *m*-chloroperbenzoic acid (1.169 g, 1 equiv) in the same solvent (20 mL). After addition the reaction mixture was opaque and gradually cleared over 4 h. After stirring 18 h, a negative Starch-Iodide test was obtained. The reaction mixture was washed with aqueous sodium sulfite (2 × 100 mL), aqueous saturated sodium bicarbonate (2 × 100 mL), and brine. The organic layer was dried over sodium sulfate and concentrated under reduced pressure to an orange oil. Column chromatography on Silic*AR* CC-7 (methylene chloride/ethyl acetate) afforded the product (0.602 g, 31%). Crystallization from cold ether/hexane gave white crystals: mp 99–100 °C; ^{1}H NMR ($CDCl_3$) δ 1.36 (t, 3 H, *J* = 7 Hz), 2.43 (s, 3 H), 4.23, 4.48 (d of d, 2 H, *J* = 7 Hz), 6.08 (s, 1 H), 7.4–7.9 (m, 9 H); IR (KBr) 1710, 1630, 1250 cm^{-1}; UV (CH_2Cl_2) 305 nm (ε 15 500). Anal. ($C_{18}H_{19}NO_3S$): C, H, N, S.

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Registry No.—**3**, 69188-90-5; **4** (isomer 1), 69188-91-6; **4** (isomer 2), 69188-92-7; **5** (isomer 1), 69188-93-8; **5** (isomer 2), 69188-94-9; **6**, 69188-95-0; **7** (isomer 1), 69188-96-1; **7** (isomer 2), 69188-97-2; **8** (isomer 1), 69188-98-3; **8** (isomer 2), 69188-99-4; **9** 69189-00-0; **11**, 69189-01-1; **12**, 69189-02-2; **13**, 15206-55-0; **14**, 69189-03-3; **15**, 69189-04-4; **17**, 69189-05-5; methyl alanate·HCl, 2491-20-5; methyl 2-phenylglycinate·HCl, 13226-98-7; 4-benzyloxy α-aminobenzeneacetate·HCl, 69189-06-6; ethyl phenylalanate·HCl, 3182-93-2; ethyl cysteinate·HCl, 868-59-7; ethyl glycinate·HCl, 623-33-6; DL-thienylglycine, 21124-40-3; β-alanine ethyl ester, 924-73-2; D-cycloserine, 68-41-7; *p*-toluenesulfenyl chloride, 933-00-6.

References and Notes

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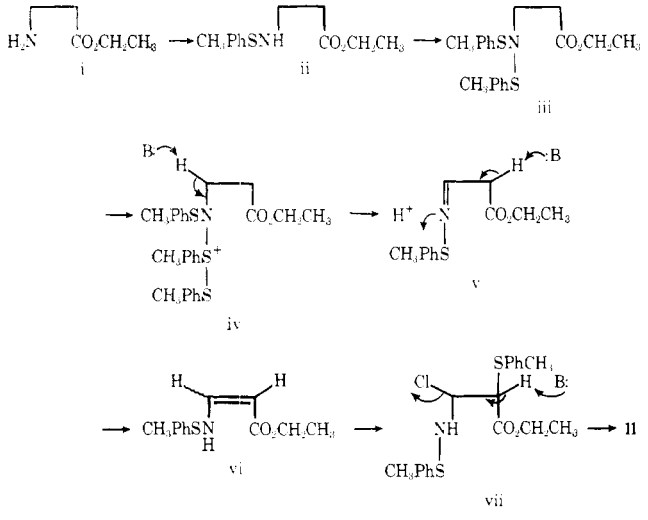
(2) T. L. Cairns, Ed., *Org. Synth.*, **35**, 99 (1955).
(3) L. M. Weinstock, S. Karady, F. E. Roberts, A. M. Hoinowski, G. S. Brenner, T. B. K. Lee, W. C. Lumma, and M. Sletzinger, *Tetrahedron Lett.*, 3979 (1975).
(4) A similar silylation procedure has been found useful with the β-lactam nuclei and will be reported in the near future.
(5) Sulfenimide **10** is derived from the corresponding cephalosporin amine ester by treatment with 2 molar equiv of TSC [propylene oxide, pulverized molecular sieves (4A), CH_2Cl_2, 0 °C] followed by silica gel chromatography.
(6) The formation of **11** may be rationalized as follows.



(7) Previously it was noted[1] that 7-(sulfenimino)cephalosporins and 6-(sulfenimino)penicillins underwent a reaction (triphenylphosphine, silica gel, CH_2Cl_2, 26 °C) to give 7(6)-α-*p*-tolylthioamines which we have termed sulfenyl transfer rearrangement. In contrast, amino acid derived sulfenimines **4** and **5** did not lead to isolable α-tolylthioamines under these conditions.

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(9) The little chemistry known concerning sulfenimines (thiooximes) has been summarized in Davis's review on sulfenamides. F. A. Davis, *Int. J. Sulfur Chem.*, **8**, 71 (1973).

(10) Various methods of preparation, see also ref 9: (a) F. A. Davis, W. A. R. Slegeir, S. Evans, A. Schwartz, D. L. Goff, and R. Palmer, *J. Org. Chem.*, **38**, 2809 (1973); (b) F. A. Davis, A. J. Friedman, E. W. Kluger, E. B. Skibo, E. R. Fretz, A. P. Milicia, W. C. LeMasters, M. D. Bentley, J. A. Lacadie, and I. B. Douglass, *ibid.*, **42**, 967 (1977); (c) T. Saito and T. Hiraoka, *Chem. Pharm. Bull. Jpn.*, **25**, 784, 792 (1977); (d) T. Kobayashi, K. Iino, and T. Hiraoka, *J. Am. Chem. Soc.*, **99**, 5505 (1977).

(11) This point was first made by Davis.[9,10a]

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A New, Convenient, and Stereospecific Method for the Dehydration of Alcohols. The Thermal Decomposition of Magnesium, Zinc, and Aluminum Alkoxides. A Mechanistic Study

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Alkoxides of magnesium, zinc, and aluminum thermally decompose at 195–340 °C to give a hydrocarbon, an olefin, and a metal oxide. Kinetic and stereochemical studies indicate that a cyclic, unimolecular six-center transition state is involved. This reaction represents the conversion of an alcohol to an olefin in a stereochemical syn manner and compares favorably as an alternative to the Chugaev and acetate pyrolysis reactions.

Several methods are known for the dehydration of alcohols to olefins.[1] These methods include the pyrolysis of esters of carboxylic acids[2,3] and the pyrolysis of xanthates (Chugaev reaction).[4-6] Both reactions involve a syn elimination to produce an olefin. The pyrolysis of esters occurs at 300–600 °C, usually in the vapor phase. The yields are reasonable, but carbon skeleton rearrangements can occur due to the high temperature involved. The Chugaev reaction occurs at 100–250 °C, but preparation of the xanthate may proceed in low yield. The pyrolysis product is often contaminated with sulfur-containing impurities which are usually removed by distillation from sodium metal with an accompanying decrease in yield.

This report concerns a new type of thermal decomposition reaction that compares favorably with the above mentioned reactions and offers an alternative method for the dehydration of alcohols to olefins. The alkoxides of magnesium, zinc, and aluminum have been well characterized[7] and have been evaluated as stereoselective alkylating agents.[8] We now wish to report our study concerning their thermal decomposition.

Results

Magnesium, zinc, and aluminum alkoxides are prepared quantitatively by the reaction of a suitable alkyl or aryl metal compound with an alcohol. This general reaction is

$$(CH_3)_2Mg + Ph_2C(CH_3)OH \rightarrow CH_3MgOC(CH_3)Ph_2 + CH_4 \quad (1)$$

$$Ph_2Zn + i\text{-}PrOH \rightarrow PhZnO\text{-}i\text{-}Pr + PhH \quad (2)$$

$$Ph_3Al + C_6H_{11}OH \rightarrow Ph_2AlOC_6H_{11} + PhH \quad (3)$$

Details of the preparation are given in the Experimental Section and are summarized in Tables I–III. Then, in a second step, the alkoxide is thermally decomposed as illustrated

$$CH_3MgOC(CH_3)Ph_2 \xrightarrow{\Delta} CH_4 + Ph_2C{=}CH_2 + MgO \quad (4)$$

$$PhZnO\text{-}i\text{-}Pr \xrightarrow{\Delta} PhH + CH_3CH{=}CH_2 + ZnO \quad (5)$$

$$Ph_2AlOC_6H_{11} \xrightarrow{\Delta} PhH + \text{cyclohexene} + [PhAlO]_x \quad (6)$$

The products are hydrocarbon, olefin, and metal oxide.

DTA–TGA Data. The decomposition reaction was studied by DTA–TGA (differential thermal analysis–thermogravimetric analysis).[9] These data are summarized in Tables IV–VI. Samples of alkoxides were decomposed under vacuum at 4 °C/min from 25 to 450 °C. Typical DTA–TGA curves are shown in Figures 1–3. The DTA–TGA curves have several common characteristics, i.e., the decomposition is endothermic, coordinated solvent is lost first, and then the main decomposition occurs in one step with no apparent intermediate formed. Both condensable and noncondensable evolved gases are detected and analysis of the product after decomposition indicates that the residue is the corresponding metal oxide.

Some of the compounds studied were volatile. Sublimation of the alkoxides was especially predominant for the dimethylaluminum alkoxides and some of the alkoxides of magnesium and zinc (mainly the isopropoxides and *tert*-butoxides). An additional problem encountered was the disproportionation of methylzinc alkoxides during preparation and removal of solvent (30% disproportionation for methylzinc cyclohexyl oxide, eq 7).

$$2CH_3ZnOC_6H_{11} \rightarrow CH_3ZnCH_3\uparrow + Zn(OC_6H_{11})_2 \quad (7)$$

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