boalkoxy unit appears ca. 0.9 ppm downfield (ca. δ 5.8) relative to the vinyl proton (ca. δ 6.7) arranged trans to a carbomethoxy group.[7] Isomerization of α,β-unsaturated esters through reversible Michael addition of thiols has been noted: R. E. Ireland, M. I. Dawson, C. J. Kowalski, C. A. Lipinski, D. R. Marshall, J. W. Tilley, J. Bordner, and B. L. Trus, *J. Org. Chem.*, **40**, 1 (1975).

(7) Cf. A. Saeffler, R. J. Pratt, H. P. Ruesch, and A. S. Drieding, *Helv. Chim. Acta*, **54**, 383 (1970).
(8) D. A. Evans and G. C. Andrews, *Acc. Chem. Res.*, **7**, 147 (1974).
(9) (a) Personal communication, August, 1975; (b) Abstract ORGN 85, American Chemical Society National Meeting, New Orleans, La., March, 1977; (c) see preceding note in this issue.
(10) This compound is now available commercially, for example, from Aldrich Chemical Co.
(11) Prepared from 3,3-dimethylglutaric anhydride by conventional techniques.
(12) Cf. H. O. House, V. K. Jones, and G. A. Frank, *J. Org. Chem.*, **29**, 3327 (1969).

Allylic Trifluoroacetylation Proceeding via an Additive Pummerer Rearranged Intermediate

Russell R. King*

Research Station, Agriculture Canada, Fredericton, New Brunswick, Canada E3B 4Z7

Roy Greenhalgh and William D. Marshall

Chemistry and Biology Research Institute, Agriculture Canada, Ottawa, Ontario, Canada K1A 0C6

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The rearrangement of sulfoxides to give α-substituted derivatives of the corresponding sulfides is well-known as the Pummerer reaction.[1,2] Recently, several instances of an interesting variation on this reaction, the so-called additive Pummerer rearrangement, have been reported.[3,4,5] In these examples the rearrangement of vinylogous sulfoxides yielded α,β-disubstituted derivatives of the corresponding sulfides. Evidence for a vinylogous Pummerer rearrangement involving an allylic methylene position has also been presented[6] and we have recently demonstrated a transannular-type Pummerer rearrangement with a para-substituted phenol sulfoxide.[7] In both the aforementioned cases the preferential abstraction of a distant hydrogen atom was thought responsible for the substitution pattern. We now report the first example of a reaction sequence involving the functionalization of an allylic methyl group proceeding via an additive Pummerer rearranged intermediate. This novel reaction provides ready access to a number of previously unavailable 2-oxymethyl analogues of the highly active and widely used systemic fungicide carboxin[8] (5,6-dihydro-2-methyl-1,4-oxathiin-3-carboxanilide).

Results and Discussion

Carboxin sulfoxide (**1**, Scheme I) on treatment with trifluoroacetic anhydride in benzene at room temperature rapidly underwent an additive Pummerer rearrangement to yield the spectroscopically homogeneous bis(trifluoroacetoxy)-1,4-oxathiane **2**. The proposed mechanism for the additive Pummerer reaction[4] would predict the possible formation of two diastereomers. However, in the present case, steric considerations appear to favor the trans-substitution pattern only. This would result in production of just the one stereoisomer presently observed. A somewhat analogous result has been reported previously.[5] A related reaction sequence demonstrated that the N–H moiety does not participate in the reaction with trifluoroacetic anhydride; i.e., the *N*-methyl analogue of carboxin sulfoxide yielded the similar bis(trifluoroacetate) **10**. The structure of compound **2** was further elucidated by methanolysis to the dimethoxy analogue **3**.

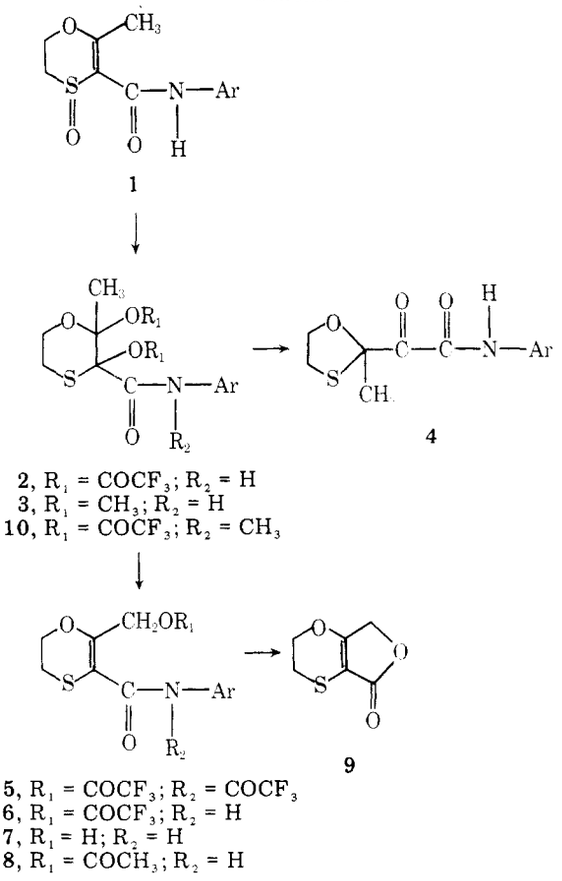
When subjected to mild hydrolytic conditions (i.e., aqueous dimethylformamide), **2** was converted to a 1,3-oxathiolane (**4**). In addition to having the requisite NMR and IR properties, mass spectral data of **4** showed a parent ion of *m/e* 251 and a prominent fragment ion of *m/e* 103, corresponding to the 2-methyl-1,3-oxathiolane moiety. An analogous rearrangement of 2,3-diacetoxy-1,4-dithane has been reported[9] and is similar to the well-known rearrangement of β-halo sulfides.[10]

When a benzene solution of compound **2** (with or without trifluoroacetic anhydride present) was refluxed for 1 h or alternately left to stand at room temperature overnight, it was converted to another compound which was assigned structure **5** on the basis of its spectroscopic properties. Infrared data showed strong absorption at 1795 and 1745 cm^{-1}, indicative of O- and N-trifluoroacetylated groups, respectively, and the NMR spectrum indicated loss of the C-2 methyl signal and the appearance of a two-proton singlet at δ 5.17.

Selective removal of the *N*-trifluoroacetyl group from compound **5** with saturated $NaHCO_3$ solution was shown by loss of the IR absorption band at 1745 cm^{-1} and reappearance of the N–H proton signal at δ 8.02 in the spectral data of the monotrifluoroacetate **6**. Mild treatment of **6** with pyridine hydrolyzed the remaining trifluoroacetyl group. A substantial shift upfield (δ 1.09) in the methylenic proton signal of the resultant alcohol **7** confirmed the postulated site of the trifluoroacetyl group prior to its removal. Acetylation of **7** with acetic anhydride–pyridine afforded the acetate analogue **8**. Prolonged hydrolysis of compounds **5**, **6**, and **7** resulted in quantitative degradation to the α,β-unsaturated-γ-lactone **9**.

Investigations regarding the mode of conversion from compound **2** to **5** suggest a concerted reaction involving participation of the anilide group; i.e., TLC and NMR studies of the reaction mixture failed to detect the presence of any stable intermediates such as the monotrifluoroacetate **6**, and the *N*-methylbis(trifluoroacetyl) analogue **10** once formed did not undergo a similar rearrangement.

Scheme I



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Experimental Section

Melting points are uncorrected and were determined on a Kofler hot stage microscope. NMR spectra were recorded on a Varian T-60 NMR spectrometer with Me_4Si as an internal standard. IR spectra were determined as Nujol mulls using a Beckman IR-20A spectrophotometer. MS were determined by a Finnigan 3100 GC–MS coupled to a D6000 data acquisition system. Thin-layer chromatograms were run on glass plates coated with Silica Gel F-254. Separated components were detected by UV fluorescence and iodine vapor.

2,3-Bis(trifluoroacetoxy)-2-methyl-1,4-oxathian-3-carboxanilide (2). A suspension of carboxin sulfoxide (**1**,[11] 510 mg) in benzene (10 mL) was treated with an excess of trifluoroacetic anhydride (0.5 mL) and stirred for 15 min at room temperature. Removal of the benzene and unreacted trifluoroacetic anhydride with a stream of dry N_2 yielded, after recrystallization from anhydrous diethyl ether, the bis(trifluoroacetate) **2** (793 mg), mp 98–100 °C: IR (Nujol) 3224, 1795, 1700, 1540 cm^{-1}; NMR ($CDCl_3$) δ 7.92 (1 H, s, NH), 7.35 (5 H, m, pH), 2.57–4.17 (4 H, m, ring H), 1.91 (3 H, s, CH_3); MS *m/e* 461 (M^+). Anal. Calcd for $C_{16}H_{13}O_6NSF_6$: F, 24.73. Found: F, 24.41.

2,3-Bis(methoxy)-2-methyl-1,4-oxathian-3-carboxanilide (3). A solution of **2** (300 mg) in 95% methanol (10 mL) was stirred overnight. After dilution with water (40 mL) the mixture was neutralized by the addition of sodium bicarbonate and then extracted with chloroform (2 × 60 mL). After drying (anhydrous sodium sulfate) the chloroform was removed under vacuum, and the residue was purified by preparative thin-layer chromatography (ethyl acetate–hexane, 1:1). Crystallization of the major component (119 mg) from diethyl ether–hexane gave the dimethoxy analogue **3**, mp 120–122 °C: NMR ($CDCl_3$) δ 8.14 (1 H, s, NH), 7.36 (5 H, m, Ph), 2.24–4.02 (4 H, m, ring H), 3.62 (3 H, s, OMe), 3.38 (3 H, s, OMe), 1.42 (3 H, s, Me); MS *m/e* 297 (M^+).

2-Methyl-1,3-oxathiolan-2-ketocarboxanilide (4). A solution of **2** (200 mg) in dimethylformamide (20 mL) and H_2O (5 mL) was stirred overnight. Removal of the solvents under vacuum yielded, after recrystallization from aqueous ethanol, the 1,3-oxathiolane **4** (78 mg), mp 130–131 °C: IR (Nujol) 3335, 1710, 1690, 1545 cm^{-1}; NMR ($CDCl_3$) δ 9.10 (1 H, s, NH), 7.40 (5 H, m, Ph), 3.01–4.44 (4 H, m, ring H), 2.12 (3 H, s, Me); MS *m/e* 251 (M^+) −103 (M^+ − 148).

***N*-Trifluoroacetyl-5,6-dihydro-2-trifluoroacetoxymethyl-1,4-oxathiin-3-carboxanilide (5).** A solution of **2** in benzene or alternately a solution of **1** in benzene plus an excess of trifluoroacetic anhydride refluxed for approximately 1 h or left to stir overnight afforded (after removal of solvents with a stream of N_2) a near quantitative yield of the 2-trifluoroacetoxymethyl derivative **5**, which did not crystallize but showed one spot on TLC (ethyl acetate–hexane, 3:2): IR (Nujol) 1795, 1745, and 1705 cm^{-1}; NMR ($CDCl_3$) δ 7.36 (5 H, m, Ph), 5.17 (2 H, s, CH_2O), 2.86–4.48 (4 H, m, ring H); MS *m/e* 443 (M^+). Anal. Calcd for $C_{16}H_{11}O_5NSF_6$: F, 25.74. Found: F, 25.84.

5,6-Dihydro-2-trifluoroacetoxymethyl-1,4-oxathiin-3-carboxanilide (6). A solution of **5** (250 mg) in chloroform (40 mL) in a separatory funnel was shaken with saturated sodium bicarbonate solution (25 mL) for several minutes. The chloroform layer was separated and dried over anhydrous sodium sulfate, and the chloroform was removed under vacuum. Recrystallization of the residue from hexane gave the monotrifluoroacetate **6** (174 mg), mp 92–93 °C: IR (Nujol) 3255, 1790, 1650, 1545 cm^{-1}; NMR ($CDCl_3$) δ 8.02 (1 H, s, NH), 7.38 (5 H, m, Ph), 5.36 (2 H, s, CH_2O), 2.98–4.45 (4 H, m, ring H); MS *m/e* 347 (M^+).

5,6-Dihydro-2-hydroxymethyl-1,4-oxathiin-3-carboxanilide (7). A solution of **6** (150 mg) in benzene (10 mL) containing pyridine (5 mL) was stirred for 1 h. The solution was then taken up in chloroform (50 mL) and shaken with water (2 × 30 mL) in a separatory funnel. After separation, drying (anhydrous sodium sulfate), and removal of the chloroform and traces of pyridine under vacuum, washing the crystalline residue with hexane afforded the alcohol **7** (82 mg), mp 87–89 °C: IR (Nujol) 3360, 3295, 1650, 1535 cm^{-1}; NMR ($CDCl_3$) δ 8.22 (1 H, s, NH), 7.42 (5 H, m, Ph), 4.28 (2 H, s, CH_2O), 2.98–4.52 (4 H, m, ring H); MS *m/e* 251 (M^+).

2-Acetoxymethyl-5,6-dihydro-1,4-oxathiin-3-carboxanilide (8). A solution of **7** (140 mg) in acetic anhydride (5 mL) and pyridine (3 mL) was stirred for 3 h at room temperature and then neutralized by decantation into a cold saturated solution of sodium bicarbonate. After extraction of the neutral solution with chloroform (2 × 50 mL), the chloroform extracts were dryed and concentrated under vacuum. Any residual pyridine was removed with a stream of N_2, and the residue was crystallized from hexane to yield the acetate **8** (113 mg), mp 90–91 °C: IR (Nujol) 3255, 1730, 1650, 1545 cm^{-1}; NMR ($CDCl_3$) δ 8.98 (1 H, s, NH) 7.40 (5 H, m, Ph), 4.97 (2 H, s, CH_2O), 3.00–4.37 (4 H, m, ring H), 2.92 (3 H, s, OAc); MS *m/e* 337 (M^+).

5,6-Dihydro-2-(hydroxymethyl)-1,4-oxathiin-3-carboxylic Acid γ-Lactone (9). **5**, **6**, or **7** in benzene and pyridine stirred overnight after workup inevitably yielded the α,β-unsaturated-γ-lactone **9**, which after crystallization from hexane had mp 117–118 °C: IR (Nujol) 1750 cm^{-1}; NMR ($CDCl_3$) δ 4.74 (2 H, s, CH_2O), 3.04–4.65 (4 H, m, ring H); MS *m/e* 158 (M^+). Anal. Calcd for $C_6H_6O_3S$: C, 45.56; H, 3.82. Found: C, 45.75; H, 3.73.

***N*-Methyl-2,3-bis(trifluoroacetoxy)-2-methyl-1,4-oxathian-3-carboxanilide (10).** A suspension of *N*-methylcarboxin sulfoxide[11] (200 mg) in benzene (5 mL) was treated with an excess of trifluoroacetic anhydride and stirred for 15 min. Benzene and unreacted trifluoroacetic anhydride were removed with a stream of N_2. Recrystallization of the residue from anhydrous diethyl ether furnished the *N*-methylbis(trifluoroacetoxy) compound **10**, mp 190 °C dec: IR (Nujol) 1795, 1645 cm^{-1}; NMR ($CDCl_3$) δ 7.34 (5 H, m, Ph), 2.18–5.14 (4 H, m, ring H), 4.38 (3 H, s, N–Me), 1.88 (3 H, s, Me).

A solution of **10** in benzene with or without trifluoroacetic anhydride on refluxing for several hours or after stirring at room temperature for up to 3 days did not produce any change in the compound.

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Registry No.—**1** (Ar = Ph), 17757-70-9; **2** (Ar = pH), 64754-69-4; **3** (Ar = Ph), 64754-70-7; **4** (Ar = Ph), 64754-74-1; **5** (Ar = Ph), 64754-72-9; **6** (Ar = Ph), 64754-73-0; **7** (Ar = Ph), 64754-75-2; **8** (Ar = Ph), 42825-80-9; **9**, 64754-76-3; **10** (Ar = Ph), 64754-71-8; trifluoroacetic anhydride, 407-25-0; acetic anhydride, 108-24-7; *N*-methylcarboxins sulfoxide, 17757-81-2.

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(11) Uniroyal Research Laboratory Ltd., Guelph, Ont., Can.

Transition Metal Catalyzed Reactions of Lithium Aluminum Hydride with Alkyl and Aryl Halides

Eugene C. Ashby* and J. J. Lin

School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332

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The reduction of organic halides to the corresponding hydrocarbons is an important transformation in organic synthesis. Recently, $2LiAlH(OCH_3)_3$–CuI[1] and LiCuHR[2] compounds (where R = alkyl and alkynyl) were evaluated as reagents for removal of halo and mesoloxy groups. $TiCl_3$–Mg[3] and $(\pi\text{-Cp})_2TiCl_2$–Mg[4] have been used for the same purpose at almost the same time by different research groups. More recently, we have been able to synthesize complex metal hydrides of copper and have demonstrated their ability to remove the halo and tosylate group from alkyl and aryl halides and tosylates.[5] We wish to report here that $LiAlH_4$ in the presence of first row transition-metal halides is a powerful and convenient reagent for the removal of halo and tosylate groups.

$LiAlH_4$ is not as effective a reagent for the removal of halo

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