282.0726, found (high-resolution mass spectrometry) (M_r + H) 282.0725. This material was used without further purification to complete the synthesis of **2b**.

Compound 17 was further nitrated by using the procedure reported by Kornblum and co-workers.[12] Thus, **17** (35.0 mg, 0.125 mmol) was added under nitrogen to a rapidly stirred solution which contained sodium hydroxide (19 mg, 0.48 mmol), methanol (0.8 mL), and water (1.0 mL). The resulting mixture was allowed to stir under nitrogen at room temperature for 3 h, at which time a clear yellow solution was obtained. This solution was then added dropwise under nitrogen to a vigorously stirred solution of potassium ferricyanide (670 mg, 2.04 mmol) and sodium nitrite (280 mg, 4.05 mmol) in water (4.1 mL). Diethyl ether (8.2 mL) was then added, and the resulting mixture was stirred for 1 h. The ether layer was separated, and the aqueous layer was extracted twice with ether. The combined organic extracts were dried (anhydrous magnesium sulfate) and filtered, and the filtrate was concentrated in vacuo to afford 4,7,7,11,11-pentanitropentacyclo[6.3.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane (**18**, 30 mg, 65%) as a colorless microcrystalline solid: mp 237-239 °C; IR (KBr) 1565 (s, br), 1375 (m), 1335 (m), 1205 (w), 800 cm^{-1} (s); ^{1}H NMR (DMSO-d_6) δ 3.09-3.81 (m, 8 H), 5.39 (s, 1 H); ^{13}C NMR (DMSO-d_6) δ 42.95 (d), 43.35 (d), 44.20 (d), 44.66 (d), 45.87 (d), 45.95 (d), 46.00 (d), 48.05 (d), 90.92 (d), 129.07 (s), 129.43 (s); exact mass calcd for $C_{11}H_{10}N_5O_{10}$ (M_r + H) 372.0428, found (high-resolution mass spectrometry) (M_r + H) 372.0428. This material was used without further purification to complete the synthesis of **2b**.

Further nitration of **18** was carried out again by using the Kornblum[12] procedure with a somewhat longer reaction time than was employed above. Thus, **18** (15 mg, 10 mmol) was added under nitrogen to a rapidly stirred solution which contained sodium hydroxide (5.0 mg, 0.13 mmol), methanol (0.2 mL), and water (0.2 mL). The resulting mixture was allowed to stir under nitrogen at room temperature for 24 h. The resulting yellow solution was added dropwise under nitrogen to a vigorously stirred solution of potassium ferricyanide (90 mg, 0.27 mmol) and sodium nitrite (40 mg, 0.58 mmol) in water (1.4 mL). Diethyl ether (2.8 mL) was then added, and the resulting mixture was stirred overnight at room temperature. The ether layer was separated, and the aqueous layer was extracted with ethyl acetate. The combined organic extracts were dried (anhydrous magnesium sulfate) and filtered, and the filtrate was concentrated in vacuo. The residue was purified via column chromatography by using silica gel as stationary phase (5% ethyl acetate-ligroin mixed solvent as eluent), thereby affording pure **2b** (10 mg, 62%) as a colorless microcrystalline solid: mp 197-200 °C dec; IR (KBr) 1565 (s), 1365 (w), 1335 (w), 1315 (w) 800 cm^{-1} (m); ^{1}H NMR (DMSO-d_6) δ 3.30-3.38 (bs, 6 H), 3.80 (s, 2 H); ^{13}C NMR (DMSO-d_6) δ 47.55 (d), 47.95 (d), 123.17 (s); mass spectrum (70 eV), m/e (relative intensity) (no molecular ion) 278.0442 ($C_{11}H_8N_3O_6$, 3.2), 139.0539 ($C_{11}H_7$, 25.5), 128.0586 ($C_5H_8N_2O_2$, 83.5), 115.0538 (C_9H_7, 100.0); exact mass calcd for $C_{11}H_8N_6O_{12}$ M_r 417.0278, found (high-resolution chemical ionization mass spectroscopy) M_r 417.0259.

Acknowledgment. We thank Dr. Teh-chang Chou for valuable assistance in performing preliminary experiments and for helpful discussions. Financial support of our study by the United States Army Armament, Munitions, and Chemical Command (Contract DAAA21-86-C-0091), the Air Force Office of Scientific Research (Grant AFOSR-84-0085), the Robert A. Welch Foundation (Grant B-963), and the North Texas State University Faculty Research Committee is gratefully acknowledged.

Registry No. 1, 110243-21-5; **2a**, 108635-94-5; **2b**, 110270-87-6; **3**, 101312-34-9; **4**, 110311-61-0; **5**, 110243-22-6; **6**, 110243-23-7; **7**, 110243-24-8; **8**, 110243-25-9; **9**, 110243-26-0; **10**, 110243-27-1; **11**, 110243-28-2; **12**, 110243-29-3; **13**, 110243-30-6; **14**, 110243-31-7; **15**, 110243-32-8; **16**, 110243-33-9; **17**, 110243-34-0; **18**, 110243-35-1; propionic acid, 79-09-4.

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A Direct Route for the Synthesis of (*E*)-3-Alkyl-4-oxo-2-butenoic Acid Esters

Sylvain Laugraud, André Guingant,* and Jean d'Angelo

Unité de Chimie Organique associée au CNRS No. 476 ESPCI, 75231 Paris Cedex 05, France

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Esters of (*E*)-3-alkyl-4-oxo-2-butenoic acid (1) are useful intermediates in organic synthesis. Thus, compound **1a** is an important synthon in many retinoic acids syntheses;[1] moreover this ester has recently been used as a dienophile.[2] We required ester **1b** as a diene precursor in order to synthesize aklavinone.[3] Although several syntheses of compound **1a** have already been published[4] none are general methods that can easily be used to prepare ester **1b**. In this paper we report a direct route to *E* esters 1 based on the condensation of aliphatic aldehyde enamines **2** with glyoxylic acid esters.

It has previously been shown that aldol condensation of glyoxylic acid with aliphatic or cyclic ketones led, either in basic or acid medium, to α-hydroxy-γ-oxo carboxylic acids and/or γ-oxo-α,β-unsaturated carboxylic acids in low to moderate yields.[5] However, this process suffers from severe drawbacks (mainly self-aldolization) when aliphatic aldehydes are used instead of ketones, and it is not therefore surprising that so few successful examples of such a condensation have been described in the literature. In 1972, H. H. Inhoffen[6] reported that the aldol condensation of substituted cyclohexylacetaldehydes with glyoxylic acid in acid medium yielded butenolides **3** (Y = OH). Similarly, L. Weiler[7] described in 1979 the condensation of cyclopentylacetaldehyde with glyoxylic acid in basic medium; the crude product yielded 73% of butenolide **3** (R^2 = cyclopentyl, Y = OH) after acid treatment. More recently, C. G. Wermuth[8] reported that condensation of aliphatic aldehydes with glyoxylic acid in the presence of morpholine led, depending on the experimental conditions, to α,γ-dimorpholinobutanolides and/or butenolides **3** (Y = OH).

Somewhat surprisingly, none of the three previous papers mentioned the isolation of 3-formyl 2-enoic acids although the formation of these compounds is highly probable in such condensations. We therefore decided to reinvestigate this reaction in order to obtain the useful target esters 1. For this purpose, we first examined the aldol condensation of butyraldehyde with glyoxylic acid in basic medium (1.15 equiv of KOH in MeOH). After acid treatment, we observed the formation of the desired *E* acid 1 (R^1 = H, R^2 = Et) and butenolide **3b** (Y = OH) isolated with 40% and 10% yields, respectively. Although this acid could be efficiently transformed into *E* ester **1b**, the whole process could not be generally applied, being hampered by the self-condensation of starting aldehydes and/or the formation of large amounts of undesired butenolides **3**.

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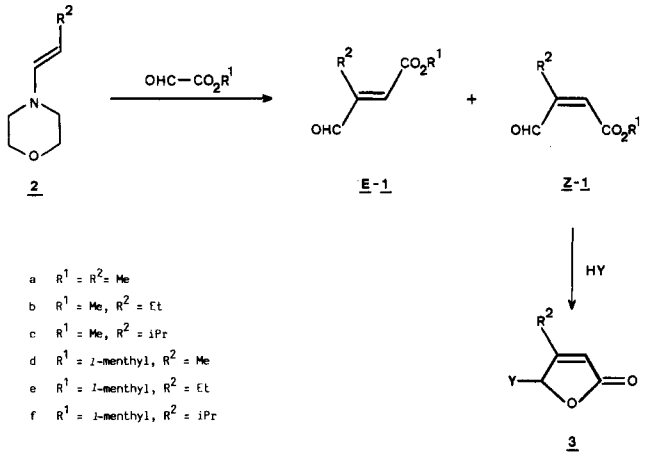
Scheme I



2 E-1 Z-1 3

We then examined the possibility of preparing esters 1 in a single operation by condensation of aliphatic aldehyde enamines on glyoxylic ester derivatives. *This route seemed to be general and to provide easy access to the target synthons 1.* Thus, condensation of enamines **2** with methyl 2-hydroxy-2-methoxyacetate (methyl hemiacetal of methyl glyoxylate), followed by acid treatment, led to methyl esters **1a–c** as nonseparable mixtures of $E + Z$ stereoisomers with a yield of 50–70% (Scheme I), without the formation of any butenolides **3** (method A). In contrast, when the hydrolysis was performed under *neutral conditions*, the Z isomers formed were slowly, but quantitatively converted into butenolides **3** (Y = morpholino); *the desired pure, unchanged E isomers could then be easily recovered from the mixtures by flash chromatography on silica gel* (method B). Similar results were obtained by using enamines **2** and *l*-menthyl glyoxylate, as shown by the preparation of esters **1d–f** (method C). To conclude, a simple and practical route for the preparation of stereochemically pure E esters **1** is now available.

Experimental Section

General Methods. Melting points were determined on a Kofler bench. IR spectra were recorded on a 198 Perkin-Elmer infrared spectrophotometer. ^{1}H NMR spectra were recorded on a EM 390 Varian spectrometer by using Me_4Si as internal standard. Optical rotation values were obtained on a Schmidt-Haensch polarimeter. Elemental analyses were performed by the "Service d'Analyse du CNRS, 69390 Vernaison".

(*E*)-Methyl 3-Formyl-2-pentenoate (1b) via (*E*)-3-Ethyl-4-oxobutenoic Acid (R^1 = H, R^2 = Et). To a precooled (0 °C) solution of 5 g (0.054 mol) of glyoxylic acid monohydrate in 30 mL of methanol was added 3.8 g (0.065 mol) of potassium hydroxide under nitrogen followed by 14.35 mL (0.163 mol) of butyraldehyde dropwise. The temperature was slowly raised to 20 °C and the slightly yellow solution kept overnight at this temperature. The solvent and excess butyraldehyde were then removed under reduced pressure. The residue was diluted with 15 mL of water and thoroughly extracted with ether (5 × 50 mL). The organic phase was discarded, and the aqueous phase was carefully acidified below 5 °C with 30% sulfuric acid and extracted with ether (3 × 50 mL). The combined organic layers were dried over anhydrous magnesium sulfate and evaporated under reduced pressure to leave an oil, which was taken up in ether–hexane (1:2) to precipitate undesirable material. Filtration on Celite and evaporation of the solvents gave crude acid **1** (R^1 = H, R^2 = Et) and butenolide **3** (R^2 = Et, Y = OH) in a ratio of 5.6:1 with a combined yield of 50%. Pure acid was obtained through conventional base–acid treatment and recrystallization from ether–petroleum ether: mp 72–73 °C; IR ($CDCl_3$) 3500–2500, 1700, 1640 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.05 (t, 3 H, J = 7.5 Hz), 2.70 (q, 2 H, J = 7.5 Hz), 6.55 (s, 1 H), 9.65 (s, 1 H), 11.25 (s, 1 H). To a solution of 2 g (0.015 mol) of acid **1** (R^1 = H, R^2 = Et) in 25 mL of dry acetone were added, at 0 °C under nitrogen, 2.47 g (0.018 mol) of finely powdered potassium carbonate and 1.46 mL (0.023 mol) of methyl iodide. The resulting mixture was vigorously stirred overnight at 20 °C. Water was added, and the resulting solution was acidified with 1.0 N hydrochloric acid and extracted with ether. The organic layer was dried over magnesium sulfate and evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel (hexane/AcOEt, 4:1) to obtain ester **1b** in 85% yield.

Methyl 3-Alkyl-4-oxo-2-butenoates 1a–c and *l*-Menthyl 3-Alkyl-4-oxo-2-butenoates 1d–f via Methods A–C. To a 100-mL, round-bottom flask fitted with stirrer, reflux condenser, and water trap, were added 40 mL of benzene, a catalytic amount of *p*-toluenesulfonic acid, 0.016 mol of enamine **2**, and 0.016 mol of methyl 2-hydroxy-2-methoxyacetate or *l*-menthyl glyoxylate. The resulting solution was heated under reflux for the following times: **1a**, 1.5 h; **1b**, 1.5 h; **1c**, 2.5 h; **1d**, 1 h; **1e**, 2 h; **1f**, 3 h.

Method A. After the mixture was cooled at 20 °C, 20 mL of ether and 40 mL of 10% sulfuric acid were added, and the mixture was vigorously stirred for 5 min. The organic layer was separated and the aqueous layer extracted with 20 mL ether. The combined organic layer was washed successively with saturated sodium hydrogen carbonate and water and then dried over magnesium sulfate. The solvent was evaporated and the remaining oily product chromatographed on silica gel (eluent, hexane/AcOEt, 4:1) to yield esters **1a,f** as mixtures of E and Z isomers. E/Z (yield, %): **1a**, 13:1 (51); **1b**, 5.5:1 (66); **1c**, 1:1 (70); **1d**, 11.5:1 (53); **1e**, 5.6:1 (56); **1f**, 1:1 (79).

Method B. After the mixture was cooled at 20 °C, 40 mL of ether and 5 mL (**1a,b**) or 20 mL (**1c**) of water were added, and the mixture was vigorously stirred under nitrogen for 1 (**1a**), 1.5 (**1b**), or 20 h (**1c**). The organic layer was extracted, washed successively with 10 mL of 10% sulfuric acid, saturated sodium hydrogen carbonate, and water and then dried over magnesium sulfate. The solvent was evaporated and the remaining oily products (mixture of E esters and butenolides **3**, Y = morpholino) chromatographed on silica gel (eluent, hexane/AcOEt, 4:1) to yield pure E compounds **1a–c** (yield, %): **1a** (43); **1b** (52); **1c** (32).

Method C. To 0.018 mol of $E + Z$ isomers obtained by using method A were added 20 mL of acetone, 3 mL of water, and a few crystals of *p*-toluenesulfonic acid. The resulting solution was heated under reflux for 1 h (**1d**) or 3 h (**1e,f**). After cooling at 20 °C and evaporation of acetone under reduced pressure, the resulting solution was treated with 1 mL of a saturated sodium hydrogen carbonate solution and extracted with ether. The organic layer was dried over magnesium sulfate and evaporated under reduced pressure to yield an oily mixture of E esters **1d–f** and butenolides **3** (Y = OH). From this mixture pure E esters were obtained by flash chromatography on silica gel (eluent, hexane/AcOEt, 4:1) (yield, %): **1d** (39); **1e** (38); **1f** (33).

(*E*)-**1a**: IR (neat) ν 2840, 1725, 1700, 1665, 1645 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.15 (d, 3 H, J = 1.5 Hz), 3.83 (s, 3 H), 6.53 (q, 1 H, J = 1.5 Hz), 9.60 (s, 1 H). Anal. Calcd for $C_6H_8O_3$: C, 56.25; H, 6.29. Found: C, 55.93; H, 6.33.

(*Z*)-**1a**: ^{1}H NMR δ 10.63 (CHO).[9]

(*E*)-**1b**: IR (neat) ν 2880, 2840, 1725, 1695, 1640 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.03 (t, 3 H, J = 7 Hz), 2.69 (q, 2 H, J = 7 Hz), 3.83 (s, 3 H), 6.47 (s, 1 H), 9.58 (s, 1 H). Anal. Calcd for $C_7H_{10}O_3$: C, 59.14; H, 7.09. Found: C, 59.22; H, 7.22.

(*Z*)-**1b**: ^{1}H NMR δ 10.63 (CHO).[9]

(*E*)-**1c**: IR (neat) ν 2875, 1725, 1700, 1635 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.20 (d, 6 H, J = 7 Hz), 3.63 (m, 1 H, J = 7 Hz, J = 2 Hz), 3.80 (s, 3 H), 6.37 (s, 1 H), 9.50 (d, 1 H, J = 2 Hz). Anal. Calcd for $C_8H_{12}O_3$: C, 61.52; H, 7.74. Found: C, 61.36; H, 7.73.

(*Z*)-**1c**: ^{1}H NMR δ 10.55 (CHO).[9]

(*E*)-**1d**: mp 39 °C; $[\alpha]^{20}_D$ −78° (c 2.95, EtOH); IR ($CDCl_3$) ν 2875, 1725, (shoulder), 1700, 1640 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.8–2.1 (m, 18 H), 2.14 (d, 3 H, J = 1.5 Hz), 4.83 (dt, 1 H, J = 5 Hz, J = 10 Hz), 6.48 (q, 1 H, J = 1.5 Hz), 9.60 (s, 1 H). Anal. Calcd for $C_{15}H_{24}O_3$: C, 71.39; H, 9.59. Found: C, 71.25; H, 9.56.

(*Z*)-**1d**: ^{1}H NMR δ 10.63 (CHO).[9]

(*E*)-**1e**: mp 60–62 °C; $[\alpha]^{20}_D$ −68° (c 2.60, EtOH); IR ($CDCl_3$) ν 2875, 1725 (shoulder), 1700, 1640 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ

(9) As expected, on the basis of previous NMR studies,[4] the E aldehyde proton resonance appears upfield from the Z isomer.

0.7-2.2 (m, 21 H), 2.68 (q, 2 H, J = 7 Hz), 4.83 (dt, 1 H, J = 5 Hz, J = 10 Hz), 6.43 (s, 1 H), 9.56 (s, 1 H). Anal. Calcd for $C_{16}H_{26}O_3$: C, 72.14; H, 9.84. Found: C, 71.85; H, 9.85.

(*Z*)-**1e**: ^{1}H NMR δ 10.62 (CHO).[9]

(*E*)-**1f**: $[\alpha]^{20}_D$ -37° (c 2.77, EtOH); IR (neat) ν 2875, 1725, 1700, 1630 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.7-2.2 (m, 18 H), 1.22 (d, 6 H, J = 7 Hz), 3.57 (m, 1 H, J = 7 Hz, J = 2 Hz), 4.83 (dt, 1 H, J = 5 Hz, J = 10 Hz), 6.33 (s, 1 H), 9.52 (d, 1 H, J = 2 Hz). Anal. Calcd for $C_{17}H_{28}O_3$: C, 72.82; H, 10.06. Found: C, 72.69; H, 10.18.

(*Z*)-**1f**: ^{1}H NMR δ 10.57 (CHO).[9]

Registry No. (*E*)-**1** (R^1 = H, R^2 = Et), 109745-69-9; (*E*)-**1a**, 40835-18-5; (*Z*)-**1a**, 96928-85-7; (*E*)-**1b**, 108044-52-6; (*Z*)-**1b**, 109745-75-7; (*E*)-**1c**, 109745-71-3; (*Z*)-**1c**, 109745-76-8; (*E*)-**1d**, 109745-72-4; (*Z*)-**1d**, 109745-78-0; (*E*)-**1e**, 109745-73-5; (*Z*)-**1e**, 109745-77-9; (*E*)-**1f**, 109745-74-6; (*Z*)-**1f**, 109764-54-7; **2a**, 20521-59-9; **2b**, 15431-03-5; **2c**, 53828-74-3; **3** (R^2 = Et, Y = OH), 109764-53-6; $Me(CH_2)_2CHO$, 123-72-8; (±)-$MeCH(OH)CO_2Me$, 109745-70-2; glyoxylic acid, 298-12-4; L-menthyl glyoxylate, 26315-61-7.

$C_4H_7O_2^+$ Ions. Thermochemistry in Sulfuric Acid Solution and CIMS Relationships

Ana M. Amat, Gregorio Asensio,* Maria J. Castelló, Miguel A. Miranda,* and Antonio Simón-Fuentes

Departamento de Química Orgánica, Facultad de Farmacia, Universidad de Valencia, 46010 Valencia, Spain

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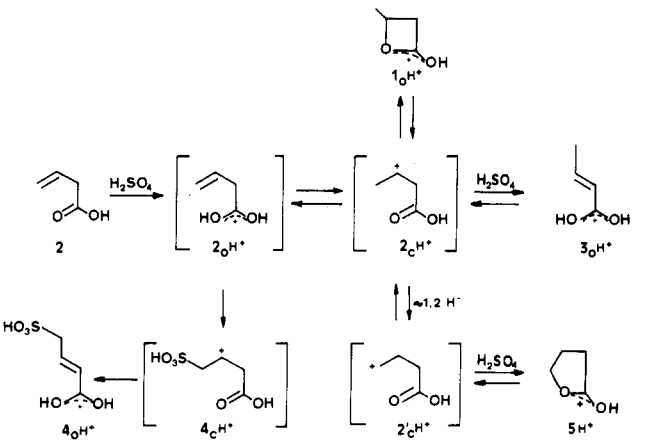
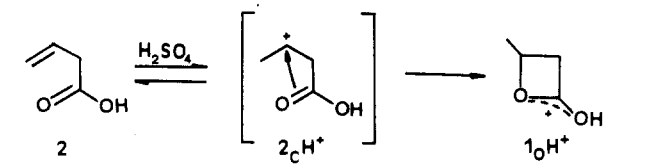
The protonation and cleavage reactions of a series of carbonyl compounds have been studied in strong acid media.[1] Independently, these processes have been also observed to take place, while their chemical ionization mass spectra (CIMS) were recorded.[2] However, no comparison has been made between the results obtained in solution (acid media) and in the gas phase (CIMS) concerning the preferential site of protonation and the further transformations of the resulting cationic species in spite of the relationship found between mass spectrometric and thermolytic reactivity.[3] The correlations between CIMS and thermochemistry in sulfuric acid solution should be meaningful since the most important source of discrepancies between fragmentation in a mass spectrometer and thermochemistry of neutrals, that is, the charge associated with the fragmenting ions, would be absent in this case.

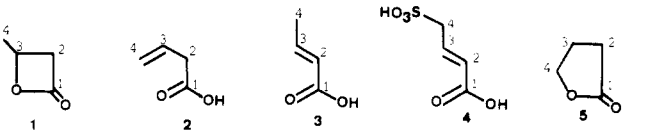
In this context it appeared to us interesting that $C_4H_7O_2^+$ ions $\mathbf{1_OH^+}$,[4] $\mathbf{3_OH^+}$,[5] and $\mathbf{5H^+}$[5] derived from vinylacetic acid (**2**), *trans*-crotonic acid (**3**), and γ-butyrolactone (**5**), respectively, had been described as stable O-protonated species in superacid medium at low temperatures, while the related methyl esters, methyl methacrylate, methyl crotonate, methyl 3-butenoate, and others had been found by CIMS[6] to undergo C-protonation and subsequent fragmentation processes.

Scheme I



Scheme II





This prompted us to study the behavior of the abovementioned $C_4H_7O_2^+$ cations in hot 96% sulfuric acid in order to minimize the difference in energy content of the cations in the acidic solution and in the CIMS experiment.

Protonations at Room Temperature. γ-Butyrolactone **5** was dissolved in 96% sulfuric acid to afford the corresponding O-protonated species $\mathbf{5H^+}$ characterized by its ^{1}H and ^{13}C NMR spectra. The chemical shift values and coupling constants found at room temperature for the ring protons agree well with those reported by Olah and Ku in magic acid at -80 °C.[5] Likewise, *trans*-crotonic acid (**3**) was treated with sulfuric acid to give the O-protonated cation $\mathbf{3_OH^+}$. The ^{1}H NMR spectral data were in concordance with the literature values.[4] The protonation of vinylacetic acid (**2**) had not been reported so far. Under our conditions it afforded O-protonated β-butyrolactone $\mathbf{1_OH^+}$. The ^{1}H NMR parameters were coincident with those reported[5] for the species resulting from direct protonation of commercially available β-butyrolactone (**1**) with Magic Acid at -80 °C. Full characterization including ^{13}C NMR data is given in Table I.

Heat-Promoted Transformations of the Protonated Species. To determine the effect of temperature, the sulfuric acid solutions of O-protonated species $\mathbf{1_OH^+}$, $\mathbf{3_OH^+}$ and $\mathbf{5H^+}$ were heated for several hours at 80, 120, or 140 °C depending on the structure. Protonated γ-butyrolactone $\mathbf{5H^+}$, previously found to be stable up to 65 °C in Magic Acid solution by Olah and Ku,[5] was then heated to 140 °C for several hours in 96% sulfuric acid. Under these conditions the formation of the sulfonated *trans*-crotonic acid derivative $\mathbf{4_OH^+}$ was observed (see Scheme I).

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