A New Facile, and Convenient Synthesis of 2-Oxo-3-alkenoic Acids and Esters

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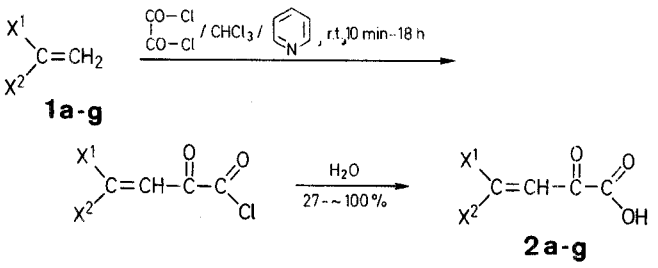
Activated 1-alkenes such as ketene dithioacetals, vinyl sulfides, *N*-vinyl amides, and *N*-vinylcarbazole react with oxalyl chloride or ethoxalyl chloride in the presence of pyridine to give the 2-oxo-3-alkenoic acids or ethyl esters, respectively.

In the course of investigations in this laboratory, 2-oxo-3-alkenoic acids and their esters became necessary. Previously we reported that ketene dithioacetals[1,2], vinyl sulfides[2], vinyl ethers[3], and *N*-vinyl amides[3] react with trifluoroacetic anhydride quite easily at room temperature to give the corresponding *β*-trifluoroacetylated compounds in high yields.

The present work was undertaken as an extension of these electrophilic substitution reactions of olefinic hydrogens and to prepare the title compounds. The substrates are ketene dithioacetals, vinyl sulfides, *N*-vinyl amides, and *N*-vinylcarbazole and the reagents used are oxalyl chloride and ethoxalyl chloride.

As anticipated the oxocarboxylation and oxoethoxycarbonylation did proceed quite easily at room temperature to give the corresponding *β*-acylated products in fair yields (Schemes **A**, **B**). It seems of interest to note here that reactions of oxalyl chloride with 1,1-diphenylethylene and with anthracene are reported to give *β*-phenylcinnamoyl chloride and 9-chlorocarbonylanthracene[4,5,6], respectively.



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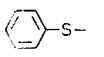
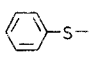
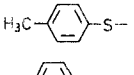
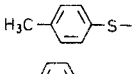
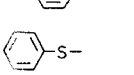
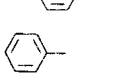
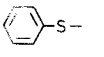
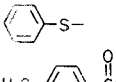
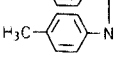
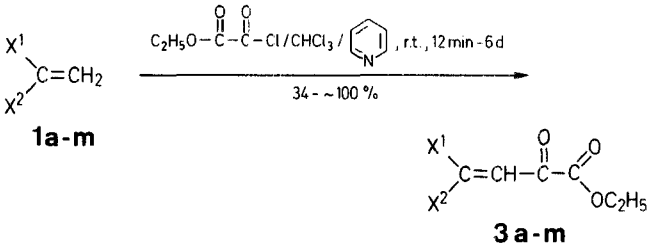
a		
b		
c		
d		
e		H₃C–
f		H
g		H

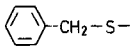
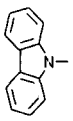
Scheme **A**

Table 1. 3-Oxo-2-alkenoic Acids **2a–g** prepared and Data for **2h** and **2i**

Product	Reaction Time	Yield [%]	m.p. [°C]	(*Z*/*E*)-Ratio	Molecular Formula[a]	I.R. (KBr) ν_{OH}	[cm⁻¹] $\nu_{C=O}$	¹H-N.M.R. ($CDCl_3$/TMS) δ [ppm]
2a	40 min	82	159.5°[b]	–	$C_{16}H_{12}O_3S_2$ (316.4)	3500	1764	6.64 (s, 1H); 7.50 (m, 10H); 8.42 (s, 1H)
2b	10 min	92	183–184°[c]	–	$C_{18}H_{16}O_3S_2$ (344.5)	3280	1764	2.27 (s, 3H); 2.41 (s, 3H); 6.59 (s, 1H); 7.25 (s, 1H); 7.42 (q, 8H, *J* = 7.2 Hz)
2c	6.3 h	~100	137°[b]	–	see experimental section			
2d	18 h	11[b]	181°[c]	1	$C_{16}H_{12}O_3S$ (284.3)	3050	1688, 1660	5.40 (s, *E*); 6.09 (s, *Z*); 7.13 (m, *Z*); 7.44 (m, 10H, *E*); 10.70 (br, 1H)
2e	45 min	62	104–106°[c]	0.7	$C_{11}H_{10}O_3S$ (220.2)	3290	1760, 1630	2.06 (s, *Z*); 2.60 (s, *E*); 6.68 (s, *E*); 7.30 (s, *Z*); 7.55 (s, 6H)
2f	6 h	27[b]	113°[d]	1	$C_{10}H_8O_3S$ (208.2)	3420	1720, 1650	6.74 (d, 1H, *J* = 16.2 Hz); 7.39 (d, *J* = 10.8 Hz); 7.56, 7.60 (2s, 6H); 8.10 (d, *J* = 10.8 Hz); 8.59 (d, *J* = 16.2 Hz)
2g	1 h	89	139–140°[b]	*E*	$C_{17}H_{16}NO_5S$ (346.4)	3300	1776, 1668	2.36 (s, 2H); 2.42 (s, 3H); 5.74 (d, 1H, *J* = 13.2 Hz); 6.74–7.77 (m, 9H); 9.03 (d, 1H, *J* = 13.2 Hz)
2h	–	–	103–105°[b] (*n*-C_6H_{14}/C_6H_6)	2	–	3200–2000	1720, 1650	2.08 (s, *Z*); 2.55 (s, *E*); 6.96 (s, *E*); 7.20 (s, *Z*); 7.35 (s, 5H); 9.65 (s, 1H)
2i	–	–	96–97°[b] (*n*-C_6H_{14}/C_6H_6)	0.25	–	3400–3100	1757, 1660	1.49 (t, 3H, *J* = 7.6 Hz); 2.45 (s, *Z*); 2.52 (s, *E*); 2.95 (q, 2H, *J* = 7.6 Hz); 6.91 (s, *E*); 7.14 (s, *Z*); 8.96 (s, 1H)

[a] Satisfactory microanalyses obtained: C ±0.28, H ±0.26, S ±0.30; except **2g** which was not analyzed.
[b] Yield after chromatography.
[c] (*Z*/*E*)-mixture difficultly separable in pure state, value for mixture given.
[d] (*Z*)-Isomer.



1, 3	X^1	X^2
a-g	see Scheme **A**	
h	H_3C-S-	
i	C_2H_5-S-	H_3C-
j	C_2H_5-S-	H–
k		H–
l		H–
m		H–

Scheme **B**

Namely, the carbonyl group is lost during these reactions, while it remains intact in the present reaction. These results are summarized in Table 1 and 2.

The present method is experimentally mild, facile, and useful for 2-oxo-3-alkenoic acids and esters which are not easy to obtain by other methods.

4,4-Bis[4-chlorophenylthio]-2-oxo-3-butenoic Acid (2c); Typical Procedure:

To a stirred mixture of ketene dithioacetal **1c** (0.317 g, 1.01 mmol) and pyridine (0.0934 g, 1.18 mmol) in chloroform (10 ml) is added oxalyl chloride (0.4159 g, 3.28 mmol) and the mixture is allowed to stand for 6.3 h at room temperature. After reaction, the whole mixture is added to an aqueous solution of sodium carbonate (20 ml), washed thoroughly with water (30 ml), and then dried with anhydrous sodium sulfate. The solvent is removed in vacuo to give the product **2c** which is recrystallized from hexane and ethanol; yield: 0.3969 g (100%); m.p. 137°C.

$C_{16}H_{10}Cl_2O_3S_2$	calc.	C 49.88	H 2.62	S 16.64
(385.3)	found	49.27	2.97	16.17

I.R. (KBr): ν = 3325 (OH); 1750 cm^{-1} (C=O).

^{1}H-N.M.R. ($CDCl_3$/TMS): δ = 6.62 (s, 1H); 7.39 (q, 8H, J = 8 Hz); 7.40 ppm (s, 1H).

Ethyl 4,4-Bis[4-chlorophenylthio]-2-oxo-3-butenoate (3c); Typical Procedure:

The reaction mixture from above is added to ethanol (20 ml), instead of aqueous sodium carbonate solution, to give the ester **3c**; yield: ~100%; m.p. 150–151°C.

Table 2. Ethyl 3-Oxo-2-alkenoates **3a–m** prepared

Product	Reaction Time	Yield [%]	m.p. [°C]	(*Z*/*E*)-Ratio	Molecular Formula[a]	I.R. (KBr) $\nu_{C=O}$ [cm^{-1}]	^{1}H-N.M.R. ($CDCl_3$/TMS) δ [ppm]
3a	40 min	59[b]	104–105°	–	$C_{18}H_{16}O_3S_2$ (344.5)	1740, 1639	1.36 (t, 3H, J = 7.2 Hz); 4.36 (q, 2H, J = 7.2 Hz); 6.42 (s, 1H); 7.46 (m, 10H)
3b	12 min	~100	117–118°	–	$C_{20}H_{21}O_3S_2$ (393.5)	1745, 1641	1.39 (t, 3H, J = 7.2 Hz); 2.37 (s, 3H); 2.40 (s, 3H); 4.40 (q, 2H, J = 7.2 Hz); 6.41 (s, 1H); 7.35 (m, 8H)
3c	24 h	~100	150–151°	–	see experimental section		
3d	22 h	34[b]	oil	1	$C_{18}H_{16}O_3S$ (312.4)	1729, 1657	1.34 (t, 3H, J = 7.2 Hz); 4.47 (q, 2H, J = 7.2 Hz); 6.18 (s, *E*); 6.77 (s, *Z*); 6.94–8.17 (m, 10H)
3e	16 h	58[b]	oil	2.6	$C_{13}H_{14}O_3S$ (250.3)	1724, 1665	1.37 (t, 3H, J = 7.2 Hz); 1.99 (s, *Z*); 2.52 (s, *E*); 4.39 (q, 2H, J = 7.2 Hz); 6.48 (s, *E*); 7.14 (s, *Z*); 7.50 (s, br, 5H)
3f	5d	50[b]	83°	*Z*	$C_{12}H_{12}O_3S$ (236.3)	1740, 1640	6.61 (d, J = 15.6 Hz, *E*); 7.09 (d, J = 10.2 Hz, *Z*); 7.41 (s); 7.45 (s); 7.72 (d, J = 10.2 Hz, *Z*); 8.18 (d, J = 15.6 Hz, *E*)
3g	16 h	70[b]	124–124.5°	*E*	$C_{20}H_{21}NO_5S$ (387.5)	1745, 1680	1.31 (t, 3H, J = 6.8 Hz); 2.36 (s, 3H); 2.42 (s, 3H); 4.28 (q, 2H, J = 6.8 Hz); 5.55 (d, 1H, J = 13.8 Hz); 6.74–7.73 (m, 8H); 8.72 (d, 1H, J = 13.8 Hz)
3h	24 h	~100	oil	1	$C_{13}H_{14}O_3S$ (250.3)	1760, 1650	1.33 (t, 3H, J = 7.2 Hz); 1.98 (s); 2.45 (s); 4.28 (q, 2H, J = 7.2 Hz); 6.41 (s); 7.00 (s); 7.29 (s, 5H)
3i	24 h	94	oil	0.3	$C_9H_{14}O_3S$ (202.3)	1708	1.38 (t, 6H, J = 7.8 Hz); 2.40 (s, *Z*); 2.49 (s, *E*); 2.95 (q, 2H, J = 7.8 Hz); 4.29 (q, 2H); 6.66 (s, *E*); 6.90 (s, *Z*)
3j	24 h	48[b]	oil	0.3	$C_8H_{12}O_3S$ (188.2)	1768, 1744	1.34 (t, 6H, J = 7.2 Hz); 2.93 (q, 2H, J = 7.8 Hz); 4.31 (q, 2H, J = 7.2 Hz); 6.67 (d, J = 15.0 Hz); 6.98 (d, J = 9.6 Hz); 7.62 (d, J = 9.6 Hz); 8.06 (d, J = 15.0 Hz)
3k	6d	93	oil	*E*	$C_{13}H_{14}O_3S$ (250.3)	1730, 1655	1.47 (t, 3H, J = 7.0 Hz); 4.18 (s, 2H); 4.30 (q, 2H, J = 7.0 Hz); 6.85 (d, 1H, J = 15.0 Hz); 7.40 (m, 5H); 8.20 (d, 1H, J = 15.0 Hz)
3l	23 h	90	58–59°	*E*	see experimental section		
3m	2.5 h	~100	108–109°	*E*	$C_{18}H_{15}NO_3$ (293.3)	1723, 1686	1.45 (t, 3H, J = 6.6 Hz); 4.45 (q, 2H, J = 6.6 Hz); 7.32 (d, 1H, J = 14.4 Hz); 7.20–8.10 (m, 8H); 8.74 (d, 1H, J = 14.4 Hz)

[a] Satisfactory microanalyses obtained: C ±0.30, H ±0.27, S ±0.19, Cl ±0.23, N ±0.06; the identities of **3d** and **3e** were confirmed by comparison with authentic samples derived from the acids **2d** and **2e**.

[b] Yield after chromatography.

$C_{18}H_{14}Cl_2O_3S_2$	calc.	C 52.60	H 3.54	S 15.41	Cl 17.38
(413.3)	found	52.31	3.41	15.51	17.15

I.R. (KBr): $\nu = 1724, 1637\ cm^{-1}$ (C=O).

^{1}H-N.M.R. ($CDCl_3$/TMS): $\delta = 1.25$ (t, 3H, $J = 7.8$ Hz); 4.20 (q, 2H, $J = 7.8$ Hz); 6.44 (s, 1H); 7.20–7.69 ppm (m, 8H).

***trans*-*N*-β-Ethoxalylvinylpyrrolidone (31); Typical Procedure:**
To a stirred mixture of *N*-vinylpyrrolidone (**11**; 0.8514 g, 7.66 mmol) and pyridine (0.6042 g, 7.64 mmol) in chloroform (2 ml) is added ethoxalyl chloride[7] (3.1061 g, 22.7 mmol) in chloroform (3 ml) with cooling and the mixture is allowed to stand for 23 h at room temperature. After reaction, the mixture is added to an aqueous solution of sodium carbonate (20 ml). After washing with water (2 × 30 ml) the solution is dried with sodium sulfate. The crude product **31** is obtained by the evaporation of the solvent and is recrystallized from hexane and benzene; yield: 1.4584 g (90%); m.p. 58–9°C.

$C_{10}H_{13}NO_4$	calc.	C 56.87	H 6.20	N 6.63
(211.2)	found	56.59	6.11	6.69

I.R. (KBr): $\nu = 1741, 1720\ cm^{-1}$ (C=O).

^{1}H-N.M.R. ($CDCl_3$/TMS): $\delta = 1.36$ (t, 3H, $J = 6.8$ Hz); 2.10–2.77 (m, 4H); 3.66 (t, 2H, $J = 6.6$ Hz); 4.30 (g, 2H, $J = 6.8$ Hz); 6.04 (d, 1H, $J = 13.2$ Hz); 8.22 ppm (d, 1H, $\tau = 13.2$ Hz).

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