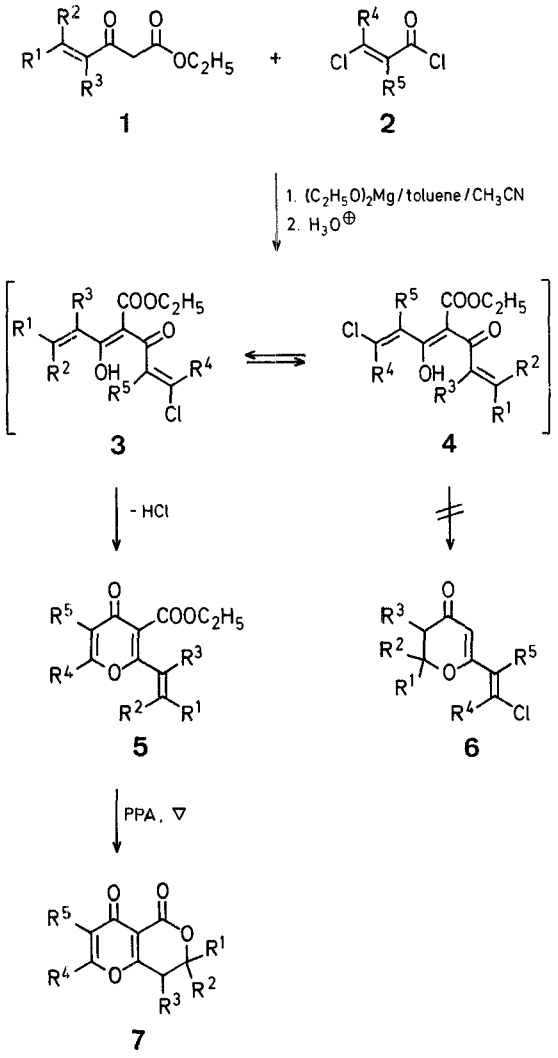
carbon atom bearing the chlorine and subsequent dehydrochlorination. The dihydropyrone derivatives **6**, cyclic tautomers of the intermediate *C*-acylated compounds, are not observed. When compounds **5** are heated with polyphosphoric acid (PPA) at 120 °C for 1 h, the dihydropyranopyrans **7** are obtained in good yields.



Synthesis of 2-Alkenyl-3-ethoxycarbonyl-4-oxo-4*H*-pyrans and 4,5-Dioxo-7,8-dihydro-4*H*,5*H*-pyrano[4,3-*b*]pyrans

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Several years ago, we reported on the preparation of 2,3-dihydro-4-oxo-4*H*-pyran derivatives by condensation of β-keto esters with α,β-unsaturated acid chlorides[1], and of 3-ethoxycarbonyl-2,6-dimethyl-4-oxo-4*H*-pyran from ethyl acetoacetate and 3-chlorocrotonoyl chloride[2]. We now report further work on these acylation reactions which lead to the regiospecific synthesis of new 2-alkenyl-4-oxo-4*H*-pyran derivatives **5** and their conversion into the corresponding 4,5-dioxo-7,8-dihydro-4*H*,5*H*-pyrano[4.3-*b*]pyrans **7**.

Condensation of ethoxymagnesio-enolates of γ,δ-unsaturated β-keto esters **1** with (*E*)-3-chloroacryloyl chlorides **2** results in the exclusive formation of the 4-pyrone derivatives **5** by nucleophilic addition of an enolic hydroxy group to the olefinic

Microanalytical and spectral data support the structure of the compounds **5**. The hypsochromic and hypochromic effects observed in the U.V. spectra of **5c** and **5d**, probably result from a non-planar conformation of these molecules. This fact can be explained by a steric interaction between the methyl substituent R^3 and the ethoxycarbonyl group. The bicyclic structure of products **7** is corroborated by their analytical and spectral data. Moreover, the compound **7a** is identical to the product previously obtained by acylation of 4-hydroxy-6-methyl-5,6-dihydro-2-pyrone with 3-chlorocrotonoyl chloride[3].

γ,δ-Unsaturated β-Keto Esters 1:
Ethyl (*E*)-3-oxo-4-hexenoate (**1**; $R^1=CH_3$, $R^2=R^3=H$); ethyl 5-methyl-3-oxo-4-hexenoate (**1**; $R^1=R^2=CH_3$, $R^3=H$); ethyl (*E*)-4-methyl-3-oxo-4-hexenoate (**1**; $R^1=R^3=CH_3$, $R^2=H$), and ethyl 4-methyl-3-oxo-4-pentenoate (**1**; $R^1=R^2=H$, $R^3=CH_3$) are prepared by the method previously described[4].

(*E*)-3-Chloroacryloyl Chlorides 2:
These acid chlorides are obtained from the corresponding acids: (*E*)-3-chloroacrylic acid[5] ($R^4=R^5=H$), (*E*)-3-chlorocrotonic acid[6,7] ($R^4=CH_3$, $R^5=H$), (*E*)-2-methyl-3-chlorocrotonic acid[6,7,8] ($R^4=R^5=CH_3$), by reaction with thionyl chloride according to Ref.[9].

0039-7881/82/1232-1107 $ 03.00

2-Alkenyl-3-ethoxycarbonyl-4-oxo-4*H*-pyrans 5; General Procedure:
To a stirred suspension of magnesium ethoxide (11.4 g, 0.1 mol) in dry toluene (150 ml) is added the γ,δ-unsaturated β-keto ester **1** (0.1 mol). The mixture is stirred and heated to reflux for 2 h. After cooling to 0–5 °C with an ice-water bath, the ethoxymagnesio-enolate is diluted with acetonitrile (100 ml) and a solution of the (*E*)-3-chloroacryloyl chloride **2** (0.1 mol) in acetonitrile (50 ml) is added dropwise with efficient stirring. The cooling bath is removed and the mixture is allowed to stand at room temperature for 2 h, then poured on to 10% hydrochloric acid (400 ml). The organic layer is separated and the aqueous layer is extracted with ether (100 ml). The combined extracts are washed with saturated sodium hydrogen carbonate solution (2 × 50 ml), water (2 × 50 ml), dried with sodium sulfate, and evaporated. The residue is distilled in vacuo to give the crude 2-alkenyl-4-pyrones **5**; b.p. 120–160 °C/1 torr. Purified compounds are obtained, in the case of **5a**, **b**, **e**, **f**, and **g**, by recrystallization from ethyl acetate or ethyl acetate/hexane (1/1) and in the case of **5c** and **d**, by chromatography on silica gel with ethyl acetate as eluent (Table 1).

Table 1. 2-Alkenyl-3-ethoxycarbonyl-4-oxo-4*H*-pyrans **5**

Product No.	R^1	R^2	R^3	R^4	R^5	Yield [%]	m.p. [°C] (solvent) or b.p. [°C]/torr (n_D^{20})	Molecular Formula[a]	I.R. ($CHCl_3$) $\nu_{C=O}$ [cm^{-1}]	U.V. (C_2H_5OH) λ_{max} [nm] (ε)	^{1}H-N.M.R. ($CDCl_3$) δ [ppm]
5a	CH_3	H	H	CH_3	H	60	120° (C_2H_5OAc)	$C_{12}H_{14}O_4$ (222.2)	1740; 1680	272 (16700); 218 (17200)	1.38 (t, 3H, J=7 Hz); 1.97 (d d, 3H, J=7 Hz, 1 Hz); 2.30 (s, 3H); 4.42 (q, 2H, J=7 Hz); 6.13 (s, 1H); 6.32 (d q, 1H, J=15 Hz, 1 Hz); 6.82 (d q, 1H, J=15 Hz, 7 Hz)
5b	CH_3	CH_3	H	CH_3	H	69	128° (C_2H_5OAc)	$C_{13}H_{16}O_4$ (236.3)	1745; 1680	280 (15400); 224 (16000)	1.37 (t, 3H, J=7 Hz); 1.97 (s, 3H); 2.07 (s, 3H); 2.30 (s, 3H); 4.41 (q, 2H, J=7 Hz); 6.02 (m, 1H); 6.15 (s, 1H)
5c	CH_3	H	CH_3	CH_3	H	63	130–140°/0.1 (1.5225)	$C_{13}H_{16}O_4$ (236.3)	1730; 1660	251 (11100); 222 (9000)	1.28 (t, 3H, J=7 Hz); 1.77 (d[b], 3H, J=7 Hz); 1.92 (s[b], 3H); 2.27 (s, 3H); 4.30 (q, 2H, J=7 Hz); 6.15 (s, 1H); 6.15 (q[b], 1H, J=7 Hz)
5d	H	H	CH_3	CH_3	H	72	120–130°/0.1 (1.5220)	$C_{12}H_{14}O_4$ (222.2)	1735; 1660	252 (10700); 216 (9100)	1.35 (t, 3H, J=7 Hz); 2.11 (s[b], 3H); 2.33 (s, 3H); 4.41 (q, 2H, J=7 Hz); 5.52 (s[b], 1H); 5.70 (s[b], 1H); 6.27 (s, 1H)
5e	CH_3	H	H	CH_3	CH_3	59	85° (1:1 C_2H_5OAc/hexane)	$C_{13}H_{16}O_4$ (236.3)	1740; 1680	274 (17500); 223 (17100)	1.40 (t, 3H, J=7 Hz); 1.97 (s, 3H); 2.02 (d d, 3H, J=7 Hz, 1 Hz); 2.37 (s, 3H); 4.47 (q, 2H, J=7 Hz); 6.42 (d q, 1H, J=15 Hz, 1 Hz); 6.91 (d q, 1H, J=15 Hz, 7 Hz)
5f	CH_3	CH_3	H	CH_3	CH_3	60	92° (1:1 C_2H_5OAc/hexane)	$C_{14}H_{18}O_4$ (250.3)	1730; 1660	278 (16000); 226 (15000)	1.40 (t, 3H, J=7 Hz); 2.00 (s, 6H); 2.12 (s, 3H); 2.38 (s, 3H); 4.45 (q, 2H, J=7 Hz); 6.15 (s[b], 1H)
5g	CH_3	H	H	H	H	60	70° (1:1 C_2H_5OAc/hexane)	$C_{11}H_{12}O_4$ (208.2)	1740; 1680	270 (14400); 215 (13200)	1.42 (t, 3H, J=7 Hz); 2.00 (d d, 3H, J=7 Hz, 1 Hz); 4.50 (q, 2H, J=7 Hz); 6.43 (d q, 1H, J=15 Hz, 1 Hz); 6.45 (d, 1H, J=6 Hz)

[a] The microanalyses were in satisfactory agreement with the calculated values (C, ±0.29; H, ±0.23); exception: **5c** (C, +1.19) and **5d** (C, −1.24).

[b] First order treatment was applied.

Table 2. 4,5-Dioxo-7,8-dihydro-4*H*,5*H*-pyrano[4,3-*b*]pyrans **7**

Product No.	R^1	R^2	R^3	R^4	R^5	Yield [%]	m.p. [°C] (solvent)	Molecular Formula[a]	I.R. ($CHCl_3$) $\nu_{C=O}$ [cm^{-1}]	U.V. (C_2H_5OH) λ_{max} [nm] (ε)	^{1}H-N.M.R.[b] ($CDCl_3$) δ [ppm]
7a	CH_3	H	H	CH_3	H	61	150–152° (C_2H_5OAc)	$C_{10}H_{10}O_4$ (194.2)	1760; 1680	242 (8700); 210 (15500)	1.52 (d, 3H, J=6 Hz); 2.32 (s, 3H); 2.93–3.17 (2H, ABX, system[c,d], J_{AB}=17.5 Hz, J_{AX}=11.2 Hz, J_{BX}=3.8 Hz); 4.70 (m, 1H); 6.22 (s[e], 1H)
7b	CH_3	CH_3	H	CH_3	H	80	160–170° (dec.) (C_2H_5OAc)	$C_{11}H_{12}O_4$ (208.2)	1760; 1675	242 (9900); 212 (19000)	1.55 (s, 6H); 2.32 (s, 3H); 2.98 (s, 2H); 6.23 (s, 1H)
7c	CH_3	H	CH_3	CH_3	H	73	190–200° (dec.) (C_2H_5OAc)	$C_{11}H_{12}O_4$ (208.2)	1740; 1665	242 (8100); 212 (12400)	1.32 (d, 3H, J=8 Hz); 1.41 (d, 3H, J=8 Hz); 2.33 (s, 3H); 2.85 (m, 1H); 4.73 (m, 1H); 6.22 (s[e], 1H)
7d	H	H	CH_3	CH_3	H	53	140° (C_2H_5OAc)	$C_{10}H_{10}O_4$ (194.2)	1755; 1670	242 (8000); 210 (13000)	1.42 (d, 3H, J=7 Hz); 2.32 (s, 3H); 3.15 (m, 1H); 4.16 (2d, 1H) and 4.47 [(2d, 1H), ABX system[c], J_{AB}=11.3 Hz, J_{AX}=6.7 Hz, J_{BX}=4.7 Hz)]; 6.2 (s, 1H)
7e	CH_3	H	H	CH_3	CH_3	75	250° (C_2H_5OH)	$C_{11}H_{12}O_4$ (208.2)	1750; 1670	249 (7300); 214 (14600)	1.50 (d, 3H, J=6 Hz); 1.95 (s, 3H); 2.32 (s, 3H); 2.66–3.14 (2H, ABX system[c,d], J_{AB}=17.5 Hz, J_{AX}=10.5 Hz, J_{BX}=5 Hz); 4.64 (m, 1H)
7f	CH_3	CH_3	H	CH_3	CH_3	79	195° (C_2H_5OH)	$C_{12}H_{14}O_4$ (222.2)	1740; 1665	248 (7300); 215 (13600)	1.52 (s, 6H); 1.97 (s, 3H); 2.35 (s, 3H); 2.93 (s, 2H)
7g	CH_3	H	H	H	H	40	165° (C_2H_5OH)	$C_9H_8O_4$ (180.2)	1745; 1660	240 (7900)	1.52 (d, 3H, J=6 Hz); 2.71–3.17 (2H, ABX system[c,d], J_{AB}=17.5 Hz, J_{AX}=11.8 Hz; J_{BX}=3.2 Hz); 4.69 (m, 1H); 6.40 (d, 1H, J=6 Hz); 7.67 (d, 1H, J=6 Hz)

[a] The microanalyses were in satisfactory agreement with the calculated values (C ±0.22; H ±0.18).
[b] 80-MHz Bruker spectrometer.
[c] The coupling constants are calculated after decoupling experiments
[d] ABX degenerate system.
[e] First order treatment.

4,5-Dioxo-7,8-dihydro-4*H*,5*H*-pyrano[4,3-*b*]pyrans 7; General Procedure:

A mixture of **5** (0.01 mol) and polyphosphoric acid (20 ml) is heated with stirring at 120 °C for 1 h. After cooling, the mixture is poured on to cold water (400 ml) and extracted with chloroform (5 × 50 ml). The combined extracts are washed with water (2 × 30 ml), dried with sodium sulfate, and evaporated under reduced pressure. The residue is triturated with ether (30 ml) and the solid product is isolated by suction and recrystallized from ethyl acetate or ethanol (Table 2).

Received: July 27, 1982

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