

^1H NMR (400 MHz) Spectroscopic Studies of some (Z) and (E)
Esters and their Isomeric Derivatives



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Abstract:- The 400 MHz ^1H NMR spectra of the diesters (IIa-c),
their anhydrides (IVa-c) and isomeric hemiesters (Va-c) are
presented. The ratio of (E): (Z) -(IIa-c) is 2:1, 2:1 and
10:1, respectively. (IVa-c) are only (E)-isomers. The
hemiester (Va) is only (E)-isomer, (Vb or c) is a mixture of
(E) and (Z)-isomers with a ratio of 10:1 and 4:1, respectively.

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Recently we described the reaction of furfural or thiophene 2-carbaldehyde with *p*-substituted-3-benzoyl propionic acids (Perkin conditions), to obtain the enol lactones^{1,2}. We also described the reaction of *p*-substituted benzaldehyde or naphthalene-1- or 2-carbaldehyde with succinic esters to afford the (Z/E)-hemiesters and their derivatives^{2,3}. For the first time the ratios of isomers and the structural assignment could be determined by ¹H NMR (400 MHz) spectroscopy. We proved that the chemical evidence is not the crucial element to determine the configuration and the ratios of (Z/E) isomers. Therefore we were interested to study the ¹H NMR spectra of (E/Z)-isomeric compounds (II-V) together with the measurements of their I.R. and MS spectra which have not been previously reported.

Condensation of acetophenone, 4-methyl and 4-chloroacetophenone with dimethyl succinate under Stobbe conditions³⁻⁵ yielded the isomeric hemiesters (Ia-c) which were characterised as their diesters (IIa-c). Analysis of ¹H NMR (400 MHz) spectra showed that (IIa-c) are mixtures of (E/Z) isomers with a ratio of 2:1, 2:1 and 10:1, respectively. (E-Ib) and (Z-Ic) could be separated from the crude hemiesters (Ib) and (Ic) by fractional crystallisation from benzene-light petroleum (60-80°C) and were characterised as their diesters (E-IIb) and (Z-IIc). This is contrary to the publication of El-Wahhab et al.⁵ who assigned (E-Ic) for (Z-Ic)

The most obvious differences between (E-IIa-c) from (Z-IIa-c) are given by the δ -values of -CH₃, -CH₂, -CO₂R¹ and CO₂R². The down field shift of CH₃ protons ($\delta = 2.37-2.40$) and CO₂R² protons (R²=Me) ($\delta = 3.78-3.80$) of the (E)-isomers confirm the cis-position of the methyl group to the carbomethoxy group in comparison to CH₃ protons ($\delta = 2.10-2.20$) and CO₂R²

protons ($R^2 = \text{Me}$) ($\delta = 3.40-3.43$) of the (Z)-isomers. Vice versa the CH_2 protons ($\delta = 3.16-3.30$) and the CO_2R^1 protons ($R^1 = \text{Me}$) ($\delta = 3.65$) of the (E)-isomers are shielded in comparison to CH_2 protons ($\delta = 3.52-3.60$), and CO_2R^1 protons ($\delta = 3.70-3.73$) of the (Z)-isomers (see experimental).

The crude hemiesters (Ia-c) or the pure (E)-Ib) or (Z)-Ic) were hydrolysed to the diacids (IIIa-c) which were directly cyclised to the anhydrides (IVa-c). Analysis of ^1H NMR (400 MHz) spectra proved that the structure of the anhydrides is (E) and there is no any detectable amounts of the (Z)-isomers, most probably isomerisation has occurred to the more stable (E)-isomers during cyclisation. The methyl protons of (E)-IVa-c) ($\delta = 2.24-2.68$) are remarkably deshielded due to the adjacent carbonyl group.

Methanolysis of the anhydrides (E)-IVa-c) gave the isomeric hemiesters (Va-c). The high resolution ^1H NMR spectra showed that (Va) was only (E)-isomer and (Vb) was mainly (E)-isomer and the (Z)-isomer was 10% only. (Vc) showed a mixed of (E/Z)-isomer with a ratio (E):(Z) = 4:1. The difference between the (Z)- and (E)-hemiesters (Va-c) is shown by the δ values of methyl protons. The methyl protons of the (E)-isomers ($\delta = 2.35-2.55$) are deshielded due to the adjacent carboxyl group in comparison to those of (Z)-isomers ((Z)-Vb and c) ($\delta = 2.15$ and 2.05) (see experimental).

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EXPERIMENTAL

All melting points are uncorrected. The ^1H NMR spectra were determined with a Bruker WH-400 instrument (TMS as internal standard). Numbering for proton chemical shift can be found in the structural formula. Mass spectra were recorded with a Varian-MAT 711 spectrometer (70 eV). IR spectra were measured with a specord Model, VEB Carl Zeiss, Jena. Microanalyses were performed by Dr. A. Bernhardt, Microanalytisches Laboratorium, D-5250 Engelskirchen, W.Germany.

Preparation of the hemiesters (Ia-c)^{4,5}. - A mixture of the appropriate acetophenone (0.01 mole), dimethyl succinate (0.012 mole) in tert-butanol (10 ml) and potassium tert-butoxide (from metallic potassium 0.58 g in 15 ml tert-butanol) was treated as usual^{3,5} to give an oily mixture of (E/Z)-isomers (Ia-c) (yield 70-80%).

(Ia; $\text{R}^1=\text{R}^3=\text{H}$, $\text{R}^2=\text{Me}$)- pale viscous oil, failed to solidify.

(Ib; $\text{R}^1=\text{H}$; $\text{R}^2=\text{R}^3=\text{Me}$)- yellow viscous oil from which (E-Ib), m.p. 120°C was separated from the (E/Z) mixture by fractional crystallisation from benzene-light petroleum ($40-60^\circ\text{C}$).

(Ic; $\text{R}^1=\text{H}$; $\text{R}^2=\text{Me}$; $\text{R}^3=\text{Cl}$)- Brown viscous oil of (E/Z)-mixture from which (ZIc), m.p. 150°C was separated by fractional crystallisation from benzene-light petroleum ($60-80^\circ\text{C}$).

The (E/Z) mixture (Ia-c) or the pure (E-Ib) or (Z-Ic) were characterised as their diesters (IIa-c).

Esterification of the hemiesters (Ia-c): - The crude hemiesters (Ia-c) or the pure (E-Ib) or (Z-Ic) (0.01 mole) were refluxed with methyl iodide (0.05 mole) and anhydrous potassium carbonate (0.08 mole) in 20 ml dry acetone. After working up, the product gave a pale yellow oil in nearly quantitative yield.

Dimethyl 4-methyl-4-phenyl-but-3-endioate (IIa $R^1=R^2=Me$; $R^3=H$).--
(E):(Z) = 2:1 (by 1H NMR).-- IR (Nujol):1746,1712 cm^{-1} (CO).-- 1H NMR
($CDCl_3$; data from the mixture) (E-IIa): δ = 3.65 (s, CO_2R^1),
3.30 (s; CH_2), 3.80 (s, CO_2R^2), 2.40 (s, Me), 7.20 (dd; $J = 9$;
1.5 Hz; 1-H), 7.46 (mc; 2, 3-H).-- (Z-IIa): δ = 3.70 (s; CO_2R^1),
3.60 (s; CH_2), 3.40 (s; CO_2R^2), 2.20 (s; Me), 7.25 (dd; $J = 8$;
1.5 Hz; 1-H), 7.46 (mc; 2, 3-H).-- MS= $m/z = 248$ (M^+ , 5%),
238 (40), 166 (27), 165 (100), 164 (20), 115 (13), 111
(10), 83 (38), 82 (46), 81 (24). (Found: C 67.41; H 6.39.
 $C_{14}H_{16}O_4$ (248.3) Calcd. : C 67.72; H 6.45).

Dimethyl 4-methyl-4-(4-methylphenyl)-but-3-endioate (IIb $R^1=R^2=$
 $R^3= Me$).--(E):(Z) = 2:1 (by 1H NMR).-- IR 1735,1715 cm^{-1} (CO).--
 1H NMR ($CDCl_3$; data from the mixture): (E-IIb): δ = 3.65 (s;
 CO_2R^1), 3.21 (s; CH_2), 3.79 (s; CO_2R^2) 2.40 (s; Me), 7.03, 7.16
(AA' BB' system; $J = 8$ Hz; 1, 2-H), 2.35 (s; Ar-Me).-- (Z-IIb):
 δ = 3.71 (s; CO_2R^1), 3.53 (s; CH_2), 3.42 (s; CO_2R^2), 2.12 (s;
Me), 7.04, 7.12 (AA' BB' system; $J = 9$ Hz; 1, 2-H), 2.34 (s;
Ar-Me). -- MS: $m/z = 262$ (M^+ , 30%), 211 (50), 188 (22),
138 (20), 137 (100), 125 (21), 124 (34), 112 (10).
(Found: C 68.45; H 6.71 $C_{15}H_{18}O_4$ (262.3) Calcd. :
C 68.70; H 6.90).

Dimethyl (E)-4-methyl-4-(4-methylphenyl)-but-3-endioate (E-IIb
 $R^1=R^2=R^3=Me$).- Yellow viscous oil- IR 1735, 1715 cm^{-1} (CO).-
 1H NMR ($CDCl_3$; data obtained from the diester of the pure (E-Ib)):
 δ = 3.65 (s; CO_2R^1), 3.20 (s; CH_2), 3.76 (s; CO_2R^2), 2.40
(s; Me), 7.0, 7.14 (AA' BB' system; $J = 8$ Hz; 1, 2-H), 2.35 (s;
Ar=Me). (Found : C 68.68; H 6.82. $C_{15}H_{18}O_4$ (262.3) Calcd.:
C 68.70; H 6.90).

Dimethyl 4-methyl-4-(4-chlorophenyl)-but-3-endioate (IIc $R^1=R^2=$
Me; $R^3=Cl$)(E):(Z) = 10:1 (by 1H NMR).- IR (Nujol) 1740, 1720 cm^{-1}
(CO).- 1H NMR ($CDCl_3$; data from the mixture). (E-IIc): δ = 3.65
(CO_2R^1), 3.16 (s; CH_2), 3.78 (s; CO_2R^2), 2.37 (s; Me), 7.03,
7.33 (AA' BB' system, $J = 9$ Hz; 1, 2-H).- (Z-IIc): δ = 3.72 (s;
 CO_2R^1), 3.52 (s; CH_2), 3.43 (s; CO_2R^2), 2.10 (s, Me), 7.06;
7.28 (AA' BB' system; $J = 9$ Hz; 1, 2-H)- MS: $m/z = 268$ ($M^+ - 14$,
8%), 270 (3), 250 (90), 252 (28), 257 (20), 239 (6), 222 (43),
165 (45), 163 (100), 162 (15), 130 (40), 125 (16), 115
(22), 114 (11), 103 (8), 101 (10), 78 (10), 75 (15),
62 (20), 59 (20), 51 (30). (Found: C 59.39; H 5.27;
Cl 12.37. $C_{14}H_{15}O_4$ Cl (282.7) Calcd. : C 59.50; H 5.35;
Cl 12.55).

Dimethyl (Z)-4-methyl-4-(4-chlorophenyl)-but-3-endioate (Z-IIc
 $R^1=R^2=Me$; $R^3=Cl$)- IR (Nujol) 1740, 1720 cm^{-1} (CO).- 1H NMR ($CDCl_3$;
data obtained from the diester of the pur (Z-Ic)): δ = 3.75 (s;
 CO_2R^1), 3.60 (s; CH_2), 3.45 (s; CO_2R^2), 2.10 (s; Me), 7.06,
7.30 (AA' BB' system, $J = 9$ Hz; 1, 2-H).- MS: $m/z = 256$ ($M^+ -$
26, 70%), 258 (25), 231 (12), 229 (32), 180 (15), 179 (100),
171 (23), 173 (70), 139 (31), 138 (47), 137 (38), 116
(20), 105 (11), 78 (10), 73 (9), 68 (9), 57 (15),
55 (20), 53 (9). (Found: C 59.37; H 5.29; Cl 12.41. $C_{14}H_{15}O_4$ Cl
(282.7) Calcd.: C 59.50; H, 5.35; Cl 12.54.

Preparation of the diacids (IIIa-c) :- 0.5 g of the crude hemi-esters (Ia-c) or the pure (E-Ib) or (Z-Ic) were hydrolysed with aqueous alcoholic (15% v/v) potassium hydroxide (2 hrs. reflux) to give the diacids (IIIa-c) as colourless crystals in 85-90% yield. (IIIa), m.p. 140°C, (IIIb), m.p. 180°C and (IIIc) m.p. 183°C. ⁵ The crude acids were converted to their corresponding anhydrides.

Preparation of the anhydrides (E-IVa-c) :- The above crude diacids (IIIa-c) (0.5 g) and 5 ml acetyl chloride (2 hrs reflux). The solid material (80-90% yield) was crystallised from benzene to give the appropriate anhydride.

(E)-4-methyl-4-phenyl-but-3-en-1,3-dicarboxylic anhydride (IVa; R=H) :- Yellow crystals, m.p. 112°C.- IR (Nujol): 1830, 1760 cm⁻¹ (CO).- ¹H NMR (CDCl₃): δ = 3.49 (q; J = 1 Hz; CH₂), 2.68 (t; J = 1 Hz; Me), 7.25 (dd; J = 8; 1.5 Hz; 1-H), 7.44 (mc; 2, 3-H).- MS: m/z = 202 (M⁺, 50%), 174 (24), 129 (100), 128 (44), 127 (16), 114 (13), 89 (9), 78 (10), 77 (21), 65 (15), 64 (26), 63 (23), 51 (45). (Found: C 71.28; H 4.90. C₁₂H₁₀O₃ (202.2) Calcd.: C 71.30; H 4.99).

(E)-4-methyl-4-(4-methylphenyl)-but-3-en-1,3-dicarboxylic anhydride (IVb R=Me) ⁵ :- yellow crystals, m.p. 155°C.- IR (Nujol): 1830, 1770 cm⁻¹ (CO).- ¹H NMR (CDCl₃): δ = 3.66 (q, J = 1 Hz; CH₂), 2.24 (t; J = 1 Hz; Me), 7.18, 7.22 (AA' BB' system, J = 8 Hz; 1, 2-H), 2.38 (s; Ar-Me).- MS: m/z = 216 (M⁺, 66%), 215 (8), 188 (22), 144 (70), 143 (54), 129 (100), 128 (59), 127 (20), 115 (20), 91 (16), 78 (19), 77 (18), 71 (20), 65 (15), 57 (28),

51 (13). (Found : C 72.18; H 5.62. $C_{13}H_{12}O_3$ (216.2) Calcd.:
C 72.22; H 5.60).

(E)-4-methyl-4-(4-chlorophenyl)-but-3-en-1,3-dicarboxylic anhydride (IVc R=Cl) ⁵ .-colourless crystals, m.p. 127°C.- IR (Nujol): 1650, 1770 cm^{-1} (CO).- ¹H NMR (CDCl₃): δ = 5.65 (q; J = 1 Hz, CH₂), 2.24 (t; J = 1 Hz; Me), 7.22, 7.38 (AA' BB' system; J = 8 Hz; 1, 2-H).- MS: m/z = 236 (M⁺, 52%), 238 (16), 208 (25), 166 (16), 164 (48), 163 (26), 149 (16), 129 (100), 128 (57), 127 (28), 77 (15), 64 (35), 63 (30), 58 (24), 57 (19). (Found: C 60.81; H 3.76; Cl 14.88. $C_{12}H_9O_3Cl$ (236.7) Calcd.: C 60.92; H 3.80; Cl 14.99).

Preparation of the isomeric hemiesters (Ia-c):- 0.5 g of the above (E)-anhydrides (IVa-c) were refluxed with 20 ml absolute methanol (2 hrs). The alcohol was distilled to give the appropriate hemiesters (Va-c) after crystallisation from benzene-light petroleum (60-80°C) (70-80% yield).

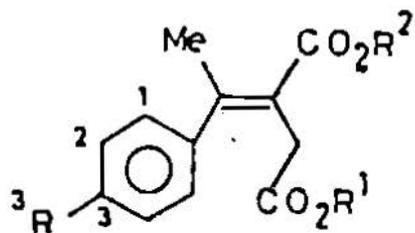
Methyl (E)-3-carboxy-4-methyl-4-phenyl-but-3-enoate (E-Va R¹=CH₃; R²=R³=H), colourless crystals, m.p. 130°C.- IR (Nujol): 1750, 1690 cm^{-1} (CO).- ¹H NMR (CDCl₃): δ = 5.72 (s; CO₂R¹); 3.30 (s; CH₂), 10.56 (s; CO₂R²), 2.55 (s; Me), 7.20 (dd; J = 9; 1.5 Hz; 1-H), 7.45 (mc; 2,3-H).- MS: m/z = 234 (M⁺, 4%), 216 (49), 188 (18), 131 (29), 130 (32), 129 (100), 128 (39), 115 (23), 91 (23), 78 (18), 77 (15), 57 (8), 51 (18). (Found: C 66.64; H 5.97. $C_{13}H_{14}O_4$ (234.2) Calcd.: C 66.64; H 6.04).

Methyl 3-carboxy-4-methyl-4-(4-methylphenyl)-but-3-enoate (Vb
 $R^1=R^3=Me$; $R^2=H$).⁵ - colourless crystals, m.p. $171^{\circ}C$ (E):(Z) = 10:1
(by 1H NMR.- IR (Nujol): $1740, 1690\text{ cm}^{-1}$ (CO).- 1H NMR ($CDCl_3$,
data from the mixture):-(E-Vb): $\delta = 3.67$ (s; CO_2R^1), 3.22 (s;
 CH_2), 11.0 (s; br.; CO_2R^2), 2.45 (s; Me), 7.14, 7.27 (AA' BB'
system, $J = 8\text{ Hz}$; 1, 2-H), 2.36 (s; Ar-Me).- (Z-Vb): $\delta = 3.74$
(s; CO_2R^1), 3.56 (s; CH_2), 11.0 (s; br.; CO_2R^2); 2.15 (s; Me),
7.19, 7.24 (AA' BB' system; $J = 8\text{ Hz}$; 1, 2-H), 2.36 (s; Ar-Me).-
MS: $m/z = 248$ (M^+ , 12%), 230 (52), 202 (22), 145 (29), 142
(100), 130 (14), 129 (35), 128 (52), 115 (18), 105 (13),
91 (16), 77 (9), 53 (7). (Found: C 67.72; H 6.41. $C_{14}H_{16}O_4$
(248.3) Calcd.: C 67.77; H 6.50).

Methyl 3-carboxy-4-methyl-4-(4-chlorophenyl)-but-3-enoate (Vc
 $R^1=CH_3$; $R^2=H$; $R^3=Cl$)⁵ : colourless crystals, m.p. $155^{\circ}C$.-(E):(Z)-
4:1 by 1H NMR.- IR (Nujol): $1750, 1690\text{ cm}^{-1}$ (CO).- 1H NMR ($CDCl_3$,
data from the mixtures). (E-Vc): $\delta = 3.57$ (s; CO_2R^1), 3.09 (s;
 CH_2), 11.0 (s; br.; CO_2R^2), 2.35 (s; Me), 7.09, 7.25 (AA' BB'
system; $J = 9\text{ Hz}$; 1, 2-H).- (Z-Vc): $\delta = 3.64$ (s; CO_2R^1), 3.45
(s; $-CH_3$), 11.0 (s; br.; CO_2R^2), 2.05 (s; Me), 7.01, 7.20 (AA'
BB' system; $J = 8\text{ Hz}$; 1, 2-H).- MS: $m/z = 268$ (M^+ , 10%), 270
(3), 252 (26), 250 (84), 224 (14), 222 (43), 165 (40), 163
(98), 162 (22), 128 (100), 125 (17), 115 (22), 101 (14),
77 (25), 75 (55), 64 (14), 63 (20), 59 (30), 51 (35).
(Found: C 58.00; H 4.67; Cl 13.00. $C_{13}H_{13}O_4Cl$ (268.7)
Calcd.: C 58.14; H 4.84; Cl 13.20).

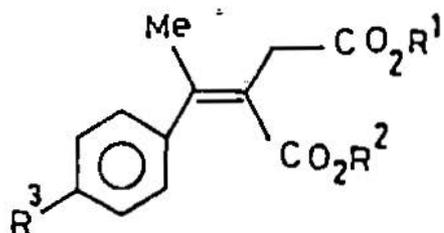
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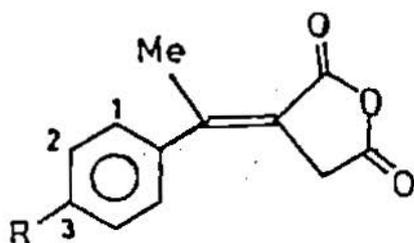
(E)-I-III and V

	R ¹	R ²	R ³
I a	H	CH ₃	H
b	H	CH ₃	CH ₃
c	H	CH ₃	Cl
II a	CH ₃	CH ₃	H
b	CH ₃	CH ₃	CH ₃
c	CH ₃	CH ₃	Cl



(Z)-I-III and V

	R ¹	R ²	R ³
III a	H	H	H
b	H	H	CH ₃
c	H	H	Cl
V a	CH ₃	H	H
b	CH ₃	H	CH ₃
c	CH ₃	H	Cl



(E)-IV

- a; R = H
b; R = Me
c; R = Cl

ملخص عربي

دراسة طيف الرنين النووي المغناطيسي (400 MHz) لبعض الإسترات
(E) ، (Z) و مشتقاتهم

شاذيه رمسيس جرجس - بشرى مسعد عوض - شاذيه محمود عبدالله
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تم دراسة طيف الرنين النووي المغناطيسي (400 MHz)
لشعاع الإستر (II a-c) وأنهايدراتهم (IV a-c) وأنصاف إستراتهم
(V a-c) وقد وجد أن نسبة (E) : (Z) لشعاع الإستر (II a-c)
على التوالي ١:٢ ، ١:٢ ، ١:١٠ . أما أنهايدراتهم (IV a-c) فكانت
(E) فقط . وقد برهنت الدراسة الطيفية أيضا على وجود نصف الإستر
(Va) في (E) فقط . أما أنصاف الإستر (V b أو V c) فوجدت في خليط
من ال (E) و (Z) بنسبة ١:١٠ ، ١:٤ على التوالي .