Dienediolates from Unsaturated Carboxylic Acids. Reaction with *para*-Substituted Benzaldehydes. Electronic Effects on Regioselectivity

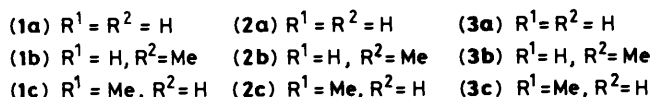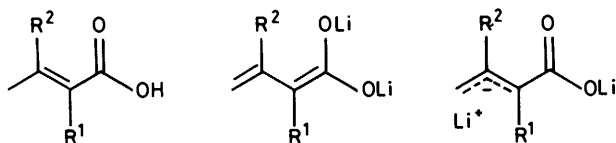**Margarita Parra and Ramon Mestres***
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Regioselectivity α/γ ratios for addition of the lithium dienediolate of crotonic acid to *para*-substituted benzaldehydes are subject to small electronic effects when reactions are carried out at low temperature, but strong influence by substituents is observed on heating for 1 h at 60 °C. A linear correlation is then found between regiochemical ratios and σ_p parameters. Stereoselectivity RR/RS ratios (33:66 to 43:57) for α-adducts obtained in the cold do not depend on the substituents.

Double deprotonation of unsaturated carboxylic acids (1) generates dianions which can be described as dienediolates (2) or as allylic anions (3).[1] It is known that these dianions react

(1a) $R^1 = R^2 = H$ (2a) $R^1 = R^2 = H$ (3a) $R^1 = R^2 = H$
(1b) $R^1 = H, R^2 = Me$ (2b) $R^1 = H, R^2 = Me$ (3b) $R^1 = H, R^2 = Me$
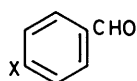(1c) $R^1 = Me, R^2 = H$ (2c) $R^1 = Me, R^2 = H$ (3c) $R^1 = Me, R^2 = H$

reversibly with carbonyl compounds to afford a mixture of α- and γ-adducts, whose composition depends dramatically on temperature and time of the reaction, as well as on the structures of the reagents. Highest yields of α-adducts result at low temperature, whereas γ-adducts can be conveniently obtained after some time at room temperature or on heating.[2–4] These effects have been understood by assuming on the one hand that α-attack is faster than γ-attack, but the latter leads to the more thermodynamically stable product (Scheme 1), and on the
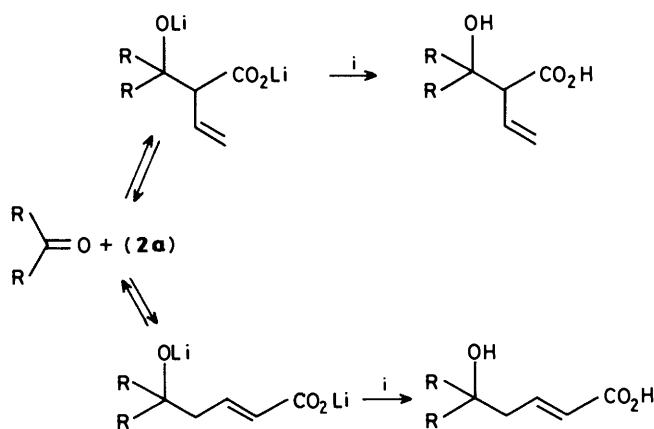
Scheme 1. *Reagent:* i, H_3O^+

other, that equilibration is very slow at $-70\,^{\circ}C$. As for structural effects, it has been observed that steric compression favours γ-addition. Thus, 2-methylbut-2-enoic acid (1c) affords lower α/γ ratios than do crotonic and dimethylacrylic acids (1a) and (1b) under equivalent reaction conditions.[3–4] A similar

conclusion is drawn on comparison between ketones and aldehydes, or between ketones which differ in the bulk of substituents close to the carbonyl group.[3–5] *I*-Strain has been shown to favour γ-addition as well.[6] Within our study of the reactivity and synthetic applications of the dianions (2), we wanted to know whether or not regioselectivity of their reactions with carbonyl compounds was subject to electronic effects. As a precedent, Hayashi has shown that the α-selectivity for reaction of carbanions of allyl dithiocarbamates with aryl aldehydes increases as the benzene ring becomes more electron-
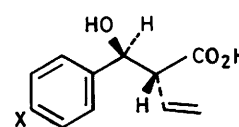
(4a) X = H
(4b) X = Me
(4c) X = OMe   (5b) X = Me
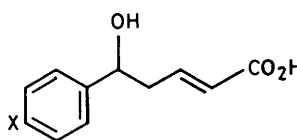(4d) X = Cl   (5c) X = OMe
(4e) X = CO₂Me   (5d) X = Cl
(4f) X = CN
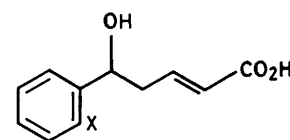(4g) X = NO₂
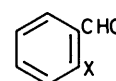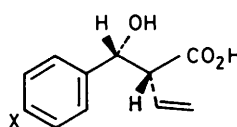
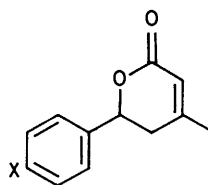(6)   (7)
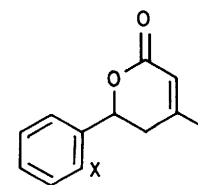
(8)   (9)

(10)   (11)

Table 1. [1]H N.m.r. chemical shifts and spin coupling constants of methyl esters of compounds (6) and (7)

X	Isomer	H_A	H_B	H_C	H_D	H_E	H_F	H_G	OMe	X
H	R,R	5.10	5.25	5.90	3.30	4.95	7.35	7.15	3.60	
	R,S	5.05	5.05	5.60	3.40	4.90	7.35	7.15	3.70	
Me	R,R	5.10	5.20	5.90	3.30	4.95	7.25	7.05	3.55	2.30
	R,S	5.00	5.00	5.65	3.40	4.85	7.25	7.05	3.70	2.30
OMe	R,R	5.15	5.20	5.90	3.30	4.90	6.80	7.20	3.55	3.70
	R,S	5.00	5.00	5.60	3.35	4.85	6.80	7.20	3.70	3.70
Cl	R,R	5.10	5.25	5.90	3.30	4.95	7.35	7.10	3.60	
	R,S	5.00	5.00	5.65	3.35	4.85	7.40	7.10	3.70	
CO_2Me	R,R	5.05	5.20	5.90	3.30	5.10	7.35	7.95	3.60	3.90
	R,S	5.00	5.10	5.65	3.40	4.95	7.35	8.00	3.70	3.90
CN	R,R	5.00	5.20	5.80	3.25	5.10	7.40	7.60	3.60	
	R,S	5.00	5.10	5.55	3.25	4.80	7.35	7.50	3.60	
NO_2	R,R	5.05	5.20	5.90	3.30	5.15	7.50	8.15	3.60	
	R,S	4.95	5.10	5.65	3.35	5.00	7.45	8.15	3.70	

X	Isomer	J_{AB}	J_{AC}	J_{BC}	J_{CD}	J_{DE}	J_{FG}
H	R,R		18.5	10	9	4.5	m
	R,S		16	9.5	8.5	8.5	m
Me	R,R	1.3	17	10.3	9	6	m
	R,S		17	10.3	8.5	8.5	m
OMe	R,R	1.4	18.3	10.4	8.8	6.4	8.7
	R,S		17	10.4	8.5	8.5	8.7
Cl	R,R	1.2	17	10	9	6	m
	R,S		17	10	9	9	m
CO_2Me	R,R		17	10	9	5.5	8
	R,S		17	10	9	8	8
CN	R,R		17	10	10	5.3	8
	R,S		17	9	9	9	8
NO_2	R,R		17	10	9	5	8.5
	R,S		17	10	9	8	9

attractive.[7] In the present work we show that the electron-withdrawing or -donating character of substituents determines the regioselectivity of the reaction of these dianions with *para*-substituted benzaldehydes (4) under equilibrating conditions, but under kinetic conditions both regio- and stereo-selectivity depend only slightly on the substituents.

The dianions are generated by two equivalents of lithium diethylamide (LDE), which is prepared from lithium metal, naphthalene, diethylamine, and tetrahydrofuran (THF) in an ultrasonic bath, as formerly described.[8] Experiments have been carried out by slow addition of the benzaldehyde (4) or (5) to the dianions (2a) or (2b) at −70 °C in THF. In a first series of runs the reacting mixtures were heated at 65 °C for ca. 20 h for isolation of γ-adducts (8)—(11). For study of the regio- and stereo-selectivities, a second series of additions was performed. This was restricted to crotonic acid (1a) and to *para*-substituted benzaldehydes (4). These runs were carried out under standard conditions, by use of acid (18 mmol) in THF (80 ml) and aldehyde (18 mmol) in the same solvent (20 ml). An aliquot was withdrawn 40 min after the end of the addition of the aldehyde, and the reaction mixture was heated at 60 °C for 1 h. Longer reaction times led to practical disappearance of α-adducts for some substrates. Individual acid components of the mixtures were isolated as free acids by crystallization, or as esters by column or centrifugal chromatography. Some α-adducts were isolated as mixtures of diastereoisomers (6) and (7). Regio-
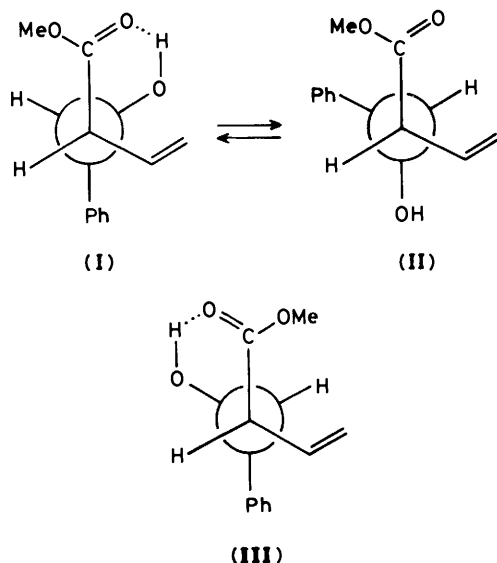
selectivity ratios were estimated through integration curves of 200 MHz [1]H n.m.r. spectra of esterified crude mixtures. Signals of ester methyl groups and/or ethylenic protons allowed determination of both α/γ regioselectivities and RR/RS diastereoselectivities. Configurations of R,R and R,S diastereoisomers (6) and (7) for α-adducts were established through the anisotropic shift effect of the phenyl group on the methyl ester and the vinyl protons.[9,10] Important [1]H n.m.r. data for some α- and γ-adducts are given in Tables 1 and 2. The lower J coupling constants for protons H_D and H_E of the R,R α-adducts (6) (J 5 Hz), when compared with the R,S diastereoisomers (7) (J 9 Hz), are most probably due to the significant population of conformer I, where the above protons attain a dihedral angle of ~60° (Figure 1). On consideration of *gauche* interactions, conformer II, where protons H_D and H_E are *anti* oriented, should be more stable than conformer I, but the latter would be stabilized by hydrogen bonding. For the R,S diastereoisomer (7), just conformer III, with an *anti* orientation for the protons H_D and H_E, would be significant.

As a general observation, the studied additions lead to mixtures of α- and γ-adducts, as expected. However, for aldehydes with electron-withdrawing substituents, the corresponding benzoic acid (12) is found in the reaction mixture, along with the above adducts. This acid derives undoubtedly from a Cannizzaro disproportionation of the aldehyde. Thus,

Table 2. [1]H n.m.r. chemical shifts and spin coupling constants of methyl esters of compounds (8)
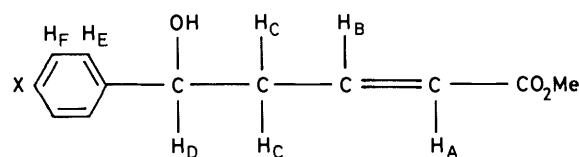
X	H_A	H_B	H_C	H_D	H_E	H_F	OMe
H	5.70	6.90	2.55	4.70	7.35—7.15		3.60
Me	5.85	6.90	2.55	4.70	7.25—7.05		3.65
OMe	5.80	6.90	2.55	4.65	6.80	7.20	3.65
Cl	5.85	6.90	2.60	4.75	7.40—7.10		3.70
CO_2Me	5.85	6.90	2.60	4.85	7.40	8.00	3.70
CN	5.90	6.90	2.60	4.90	7.45	7.65	3.70
NO_2	5.90	6.95	2.60	5.00	7.55	8.20	3.70

| X	J_{AB}	J_{BC}	J_{CD}	J_{AC}
H	16	7.5	6.5	
Me	16	7	7 / 5.7	1.5
OMe	16	7.5	6 / 7	1.5
Cl	16	7	6	2
CO_2Me	16	7 / 6.7	6 / 6.7	
CN	16	7 / 6.5	6.2 / 6.5	1.3
NO_2	16	7.5	6.3 / 7.5	

Figure 1.

the benzyl alcohol (13f) has been isolated in the neutral fractions resulting from additions to the cyanobenzaldehyde (4f). Small amounts of the diethyl amide (14f) and Tischenko's ester (15f) have been isolated as well from the same neutral fractions. The extent of the disproportionation becomes larger on heating, and is accompanied by a corresponding decrease in crude yields. The nitrobenzaldehyde (4g) is especially prone to this and to cause other secondary reactions, namely oligomerization of crotonic acid, as [1]H n.m.r. spectra and the low yields of crude mixtures reveal. The extent of disproportionation is very large again for the methoxycarbonyl-benzaldehyde (4e), but other secondary reactions are not as
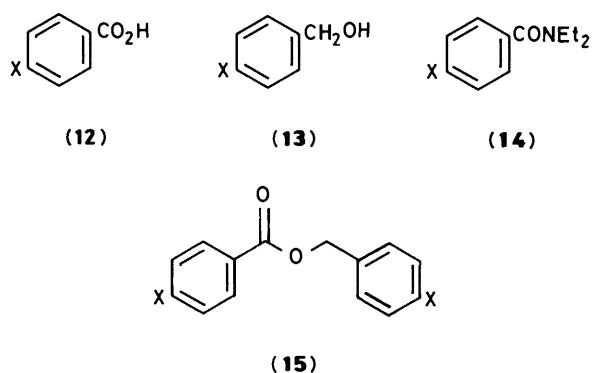
significant for this aldehyde. Oligomerization of crotonic acid under the present reaction conditions has been previously shown to occur through Michael addition of the dienediolate (2a) to the lithium salt of crotonic acid.[3,11] Partial neutralization of the dianion must happen for this secondary reaction to occur. The proton source for this neutralization may be the hydroxy group resulting from the addition of the diethylamine to the carbonyl group. In the first series of runs, heating for 20 h led to mixtures where the E-γ-adducts (8) and (9) for crotonic acid, and the corresponding Z-γ-isomers [isolated as lactones (10) and (11)] for dimethylacrylic acid strongly predominate over their α-regioisomers, which are hardly observed in some of the crude mixtures. When the aldehyde substituents are strongly electron-withdrawing groups, as for aldehydes (4e)—(4g), large amounts of benzoic acids (12) and of oligomeric products are found (Table 3).

For additions at -70 °C, within the second series of runs, regioselectivity ratios were found to depend only slightly on the nature of the para-substituents (between 77:23 and 69:31) (Table 4), although, within experimental error (± 2), differences between substrates are repetitive. A correlation with σ_p or σ_{p+}
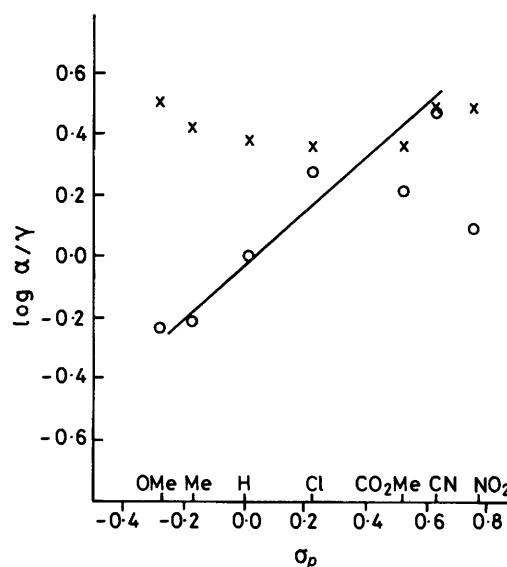
Figure 2. Correlation of log α/γ ratios against σ_p parameters substituents of aldehydes (4). ×, Ratios obtained at -70 °C. ○, Ratios obtained at 60 °C

parameters is obviously not obtained (Figure 2), as highest ratios result for substituents at both ends of the σ scale. On the other hand, the rather poor diastereoselectivity $R,R/R,S$ ratios found (33:64 to 43:57) are similar to those described by Mulzer for reaction of benzaldehyde with lithium enediolates of saturated carboxylic acids.[12] Their trend is in agreement with

Table 4. Reaction of crotonic acid with substituted benzaldehydes

| | | −70 °C; 40 min | | | 60 °C; 1 h | | Yield |
X	α:γ	RR:RS	(12):(6)—(8)	α:γ	RR:RS	(12):(6)—(8)	(%)
H	71:29	35:65	0:100	47:53	37:63	0:100	98
Me	73:27	38:62	0:100	38:62	40:60	0:100	97
OMe	77:23	38:62	0:100	37:63	43:57	0:100	83
Cl	69:31	40:60	0:100	65:35	37:63	0:100	87
CO₂Me	70:20	43:57	20:80	60:40	18:82	33:67	65
CN	75:25	40:60	6:94	74:26	33:67	10:90	77
NO₂	75:25	a	24:76	57:43	a	44:56	60

^{a} Ratios could not be established.

the Zimmerman–Dubois cyclic transition-state model, where the phenyl and the vinyl groups would be now equatorially oriented, as in **IV** (Figure 3). Axial orientation of any of these
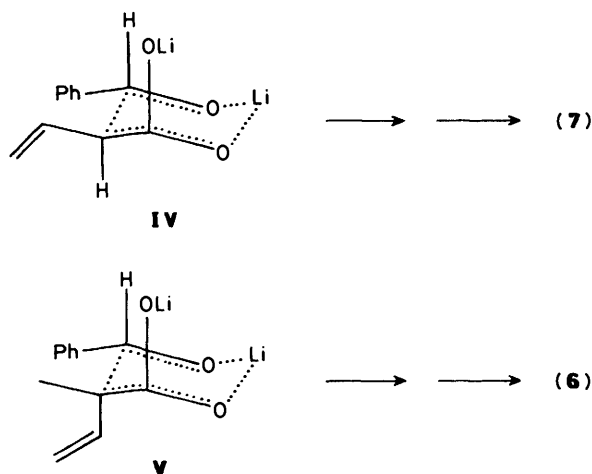
Figure 3.

groups, as in **V**, would lead to the minor *R,R* isomer (**6**). The cycloaddition described by Mulzer[13] would account for the present results as well, but the Noyori's open model[12] would predict the opposite stereochemical trend. On the other hand, the acyclic transition state described by Bassindale and Taylor[14] would account for stereochemical trend currently found, provided the solvated lithium carboxylate was accepted as being smaller than the vinyl group.

The present regioselectivity findings for reactions in the cold were surprising, as either a linear correlation or no influence by the substituents was expected. However, more refined measurements, beyond our present objectives, will be required before we are able to understand the apparently irregular substituent effects now observed.

Within the same series of experiments, heating of the reacting mixtures for 1 h was accompanied by changes in the regio-chemical ratios, whose extent depended strongly on the sub-stituents (Table 4). Low α/γ ratios (37:63, for X = MeO) were obtained for electron-donating groups, whereas high amounts of α-adducts, or, what amounts to the same thing, very little change was observed for electron-withdrawing substituents (76:24, for X = CN). When logarithms of α/γ ratios are plotted against σ_p parameters (Figure 2) a linear correlation was obtained. Strong deviations found for the nitro- and methoxy-carbonyl-benzaldehyde (**4g**) and (**4e**) are not entirely surprising, in view of the side reactions observed for these substrates, namely the Cannizzarro and the oligomerization reactions (see above). This linear correlation could be understood by

Table 3. Reaction of crotonic acid with substituted benzaldehydes at 65 °C for 20 h

X	α:γ	(12):(6)—(8)	Yield (%)
Me	0:100	a	89
OMe	0:100		85
Cl	10:90	35:65	91
CO₂Me	0:100	34:66	68
CN	30:70	33:67	67

^{a} Traces of compound (**12**) were observed.

assuming that the ratios resulting after heating for 1 h are a rough measure of the relative rates of conversion of the kinetically predominant α-adducts into their more stable γ-regioisomers, and that the retro-α-addition is the controlling step in the rearrangement. However, the latter assumption has been shown to be only partly true by a trapping experiment. Addition of crotonic acid to cyanobenzaldehyde (**4f**) was started in the cold as usual. A sample was withdrawn in order to make sure that the α/γ ratio of adducts was the same as for former runs, and p-methylbenzaldehyde (**4b**) (1 mol equiv.) was then added to the reaction mixture, which was then heated for 1 h, as usual. Work-up and ¹H n.m.r. spectroscopy of the mixture revealed that adducts of the methyl aldehyde were present in small amount (16% of the mixture of adducts), though larger than that would be expected from the almost negligible conversion undergone by the mixture of adducts of the cyano aldehyde. This finding shows that the extent of the regio-
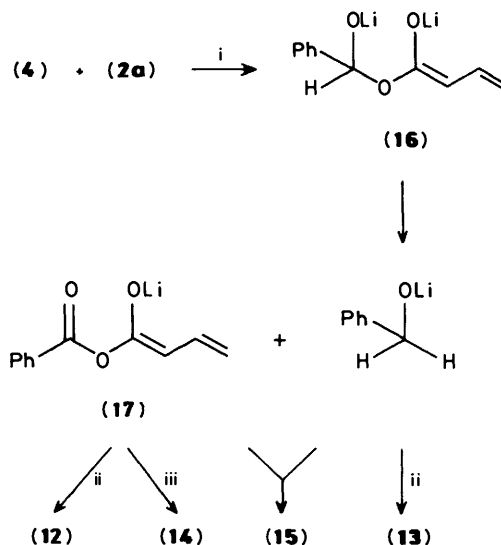
Scheme 2. *Reagents:* i, (**4**); ii, water, iii, Et₂NH

chemical conversion occurring at 60 °C is in fact determined not only by the rate of the retro-α-addition, but also by the relative rates of α and γ attack, as consideration of simple kinetic equations would lead us to expect. The increase in Cannizzaro product (12f) (from 5 to 14%) on heating the reaction mixture of the dienediolate (2a) and the cyano aldehyde (4f) is in agreement with this view, as it shows that an amount of aldehyde has become free, in spite of the negligible progress of the α to γ rearrangement.

The mechanism of the observed disproportionation has not been established. *O*-Attack of the dianion (2) to the aldehyde (Scheme 2) would lead to adduct (16), which on hydride transfer to a second molecule of aldehyde would afford the lithium alkoxide of the benzylic alcohol (13) and the anhydride dienolate (17). The latter could give amide (14) and ester (15) on reaction with the amine and the above alkoxide, but we have not found any direct evidence for anhydride (17).

Experimental

I.r. spectral data were obtained for liquid films or KBr discs, unless otherwise stated, with a Perkin-Elmer 281 spectrophotometer. 60 and 200 MHz n.m.r. spectra were recorded for $CDCl_3$ solutions, with Perkin-Elmer R24B and Bruker AC-200 spectrometers, respectively. M.p.s were determined with a Kofler hot-plate apparatus, and are uncorrected. Elemental analyses were determined with a Perkin Elmer CHN 240C Elemental Analyzer or by Servicio de Semimicroanálisis del Instituto de Química Orgánica de Barcelona. Kieselgel 60 was used for column chromatography. Centrifugal chromatography was performed with a Chromatotron model 7924 on Kieselgel 60 PF_{254} (Merck) plates. Esterifications were performed by treatment of acids with diazomethane. Aldehydes were commercially available and purified by crystallization or distillation before use. THF was distilled from sodium diphenylketyl immediately before use. Diethylamine was dried over CaH_2 and distilled before use. Generation and reactions of the dienediolates were carried out in nitrogen or argon, under standard conditions for exclusion of moisture.

The generation of the dilithium dienediolate of crotonic and dimethylacrylic acids with LDE) (2 mol equiv.), as well as addition conditions and general work-up procedures have been described[3,8] The reaction temperatures, -70 and 65 °C, were achieved with solid CO_2–Me_2CO-bath, and THF reflux, respectively, whereas 60 °C was the internal reaction temperature.

The following hydroxy acids were obtained (200 MHz ^1H n.m.r. data are given in Tables 1 and 2).

(*E*)-5-*Hydroxy*-5-(4-*methylphenyl*)*pent*-2-*enoic Acid* (8b).— White prisms, m.p. 122—123 °C (Found: C, 69.85; H, 6.65. $C_{12}H_{14}O_3$ requires C, 69.9; H, 6.8%); $v_{max.}$ 3 400 (OH) and 1 700 cm^{-1} (C=O).

(*R,R*)- *and* (*R,S*)-2-(α-*Hydroxy*-4-*methoxybenzyl*)*but*-3-*enoic Acid* (6c) + (7c).—White prisms (from hexane), m.p. 119 °C (Found: C, 64.55; H, 6.4. $C_{12}H_{14}O_4$ requires C, 64.85; H, 6.3%).

(*E*)-5-*Hydroxy*-5-(4-*methoxyphenyl*)*pent*-2-*enoic Acid* (8c).— White prisms (from hexane), m.p. 116 °C (Found: C, 64.75; H, 6.2. $C_{12}H_{14}O_4$ requires C, 64.85; H, 6.3%); $v_{max.}(CCl_4)$ 3 500— 3 400 (OH) and 1 720 and 1 700 cm^{-1} (C=O).

(*R,R*)- *and* (*R,S*)-2-(4-*Chloro*-α-*hydroxybenzyl*)*but*-3-*enoic Acid* (6d) + (7d).—White prisms (from dichloromethane), m.p. 129 °C (Found: C, 58.25; H, 4.9. $C_{11}H_{11}ClO_3$ requires C, 58.3; H, 4.9%).

(*E*)-5-(4-*Chlorophenyl*)-5-*hydroxypent*-2-*enoic Acid* (8d).— White prisms (from benzene), m.p. 145—146 °C, of white

needles (from acetone–chloroform), m.p. 148—150 °C (Found: C, 58.5; H, 4.8. $C_{11}H_{11}ClO_3$ requires C, 58.3; H, 4.9%); $v_{max.}$ 3 100 (OH), 1 680 (C=O), 1 625 (C=C), and 975 cm^{-1} (*E*-CH=CH).

(*R,R*)-*Methyl* 2-(α-*Hydroxy*-4-*methoxycarbonylbenzyl*)*but*-3-*enoate* (6e; *Methyl Ester*).—This was obtained as an oil (Found: C, 63.9; H, 6.4. $C_{14}H_{16}O_5$ requires C, 63.6; H, 6.1%); $v_{max.}$ 3 480 (OH), 1 720 (C=O), 1 640 and 1 615 (C=C), and 970 and 930 cm^{-1} ($CH=CH_2$).

(*R,S*)-*Methyl* 2-(α-*Hydroxy*-4-*methoxycarbonylbenzyl*)*but*-3-*enoate* (7e; *Methyl Ester*).—White prisms (from hexane–diethyl ether), m.p. 102—105 °C (Found: C, 63.65; H, 6.1%); $v_{max.}$ 3 410 (OH), 1 715 (C=O), 1 635 and 1 605 (C=C), and 995 and 930 cm^{-1} ($CH=CH_2$).

(*E*)-*Methyl* 5-*Hydroxy*-5-(4-*methoxycarbonylphenyl*)*pent*-2-*enoate* (8e; *Methyl Ester*).—This was obtained as an oil; $v_{max.}$ 3 460 (OH), 1 770 (C=O), 1 660 and 1 610 (C=C), and 980 cm^{-1} (*E*-CH=CH).

(*R,R*)-*Methyl* 2-(4-*Cyano*-α-*hydroxybenzyl*)*but*-3-*enoate* (6f; *Methyl Ester*).—White needles (from hexane–diethyl ether), m.p. 88—90 °C (Found: C, 67.45; H, 5.8; N, 5.8. $C_{13}H_{13}NO_3$ requires C, 67.5; H, 5.66; N, 6.0%); $v_{max.}$ 3 500 (OH), 2 210 (CN), 1 710 (C=O), 1 625 (C=C), and 990 and 930 cm^{-1} ($CH=CH_2$).

(*R,S*)-*Methyl* 2-(4-*Cyano*-α-*hydroxybenzyl*)*but*-3-*enoate* (7f; *Methyl Ester*).—White needles (from ethyl acetate), m.p. 92— 94 °C (Found: C, 67.5; H, 5.95; N, 6.35%); $v_{max.}$ 3 440 (OH), 2 210 (CN), 1 710 (C=O), 1 630 (C=C), and 995 and 925 cm^{-1} ($CH=CH_2$).

(*E*)-(4-*Cyanophenyl*)-5-*hydroxypent*-2-*enoic Acid* (8f).— White prisms, m.p. 122—126 °C; $v_{max.}$ 3 490 (OH), 2 210 (CN), 1 680 (C=O), 1 640 and 1 630 (C=C), and 980 cm^{-1} (*E*-CH=CH).

(*R,R*)-*Methyl* 2-(α-*Hydroxy*-4-*nitrobenzyl*)*but*-3-*enoate* (6g; *Methyl Ester*).—Yellow oil, obtained as a spectroscopically (^1H n.m.r.) and chromatographically (t.l.c.) pure sample; $v_{max.}$ 3 450 (OH), 1 720 (C=O), 1 640 (C=C), 1 430 and 1 345 cm^{-1} (NO_2).

(*R,S*)-*Methyl* 2-(α-*Hydroxy*-4-*nitrobenzyl*)*but*-3-*enoate* (7g; *Methyl Ester*).—Yellow oil (Found: C, 57.5; H, 5.5; N, 5.75. $C_{12}H_{13}NO_5$ requires C, 57.35; H, 5.2; N, 5.6%); $v_{max.}$ 3 440 (OH), 1 710 (C=O), 1 630 (C=C), and 1 430 and 1 340 cm^{-1} (NO_2).

(*E*)-*Methyl* 5-*Hydroxy*-5-(4-*nitrophenyl*)*pent*-2-*enoate* (8g; *Methyl Ester*).—Yellow prisms (from hexane–dichloromethane), m.p. 85—86 °C (Found: C, 57.35; H, 5.45; N, 5.55. $C_{12}H_{13}NO_5$ requires C, 57.35; H, 5.2; N, 5.6%); $v_{max.}$ 3 400 (OH), 1 705 (C=O), 1 655 (C=C), and 1 425 and 1 350 cm^{-1} (NO_2).

(*E*)-5-*Hydroxy*-5-(2-*methylphenyl*)*pent*-2-*enoic Acid* (9b).— White prisms, m.p. 86—87 °C (Found: C, 69.75; H, 6.75. $C_{12}H_{14}O_3$ requires C, 69.9; H, 6.8%); δ_H(60 MHz) 7.1—6.2 (5 H, m, C_6H_4 and C*H*=CCO$_2$H), 5.3 (1 H, d, *J* 16 Hz, C=C*H*CO$_2$H), 4.5 (1 H, t, *J* 7 Hz, ArC*H*OH), 4.3 (1 H, s, OH), 2.2 (2 H, t, *J* 7 Hz, CH$_2$C=C), and 1.9 (3 H, s, ArMe).

(*E*)-5-*Hydroxy*-5-(2-*methoxyphenyl*)*pent*-2-*enoic Acid* (9c).— White prisms, m.p. 112 °C (Found: C, 65.0; H, 6.25. $C_{12}H_{14}O_4$ requires C, 64.9; H, 6.3%); $v_{max.}$ 3 450 (OH) and 1 700 cm^{-1} (C=O); δ_H (60 MHz) 7.3—6.5 (5 H, m, C_6H_4 and C*H*=CCO$_2$H), 5.6 (1 H, d, *J* 15 Hz, C=C*H*CO$_2$H), 5.3 (1 H, br, OH), 4.9 (1 H, t,

J 6 Hz, ArCHOH), 3.8 (3 H, s, OMe), and 2.4 (2 H, t, J 6.5 Hz, CH$_2$C=C).

(E)-5-(2-*Chlorophenyl*)-5-*hydroxypent*-2-*enoic Acid* (**9d**).—White prisms, m.p. 135—135 °C (Found: C, 58.1; H, 4.8. C$_{11}$H$_{11}$ClO$_3$ requires C, 58.3; H, 4.9%); $\nu_{max.}$ 3 500 (OH) and 1 720 cm^{-1} (C=O); δ_H(60 MHz) 7.5—6.6 (6 H, m, C$_6$H$_4$, CH=CCO$_2$H, OH) 5.5 (1 H, d, J 15 Hz, C=CHCO$_2$H), 4.7 (1 H, t, J 6 Hz, ArCHOH), and 2.2 (2 H, t, J 6 Hz, CH$_2$C=C).

6-(4-*Methoxyphenyl*)-4-*methyl*-5,6-*dihydro*-2H-*pyran*-2-*one* (**10c**).—White prisms, m.p. 56 °C (Found: C, 71.65; H, 6.3. C$_{13}$H$_{14}$O$_3$ requires C, 71.56; H, 6.4%); $\nu_{max.}$ 1 710 cm^{-1} (C=O); δ_H (60 MH$_3$) 6.8 (4 H, m, C$_6$H$_4$), 5.7 (1 H, s, CH=C), 5.2 (1 H, m, ArCH), 3.7 (3 H, s, OMe), 2.4 (2 H, d, J 7 Hz, CH$_2$), and 2.0 (3 H, s, Me).

4-*Methyl*-6-(2-*methylphenyl*)-5,6-*dihydro*-2H-*pyran*-2-*one* (**11b**).—White prisms, m.p. 81 °C (Found: C, 77.3; H, 6.3. C$_{13}$H$_{14}$O$_2$ requires C 77.6; H, 6.5%); $\nu_{max.}$ 1 720 cm^{-1} (C=O); δ_H(60 MHz) 7.3 (4 H, m, C$_6$H$_4$), 5.9—5.5 (2 H, m, ArCH and C=CH), 2.6 (2 H, m, CH$_2$), 2.4 (3 H, s, Me), and 2.1 (3 H, s, Me).

6-(2-*Methoxyphenyl*)-4-*methyl*-5,6-*dihydro*-2H-*pyran*-2-*one* (**11c**).—White prisms, m.p. 74 °C (Found: C, 71.45; H, 6.5. C$_{13}$H$_{14}$O$_3$ requires C, 71.56; H, 6.4%); $\nu_{max.}$ 1 730 cm^{-1} (C=O); δ_H 7.3—6.5 (4 H, C$_6$H$_4$), 5.6—5.4 (2 H, m, ArCH and CH=C), 3.7 (3 H, s, OMe), 2.4 (2 H, d, J 7 Hz, CH$_2$), and 1.9 (3 H, s, Me).

Acknowledgements

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