Carbonylation of Vinyl Halides with Carbonylcobalt

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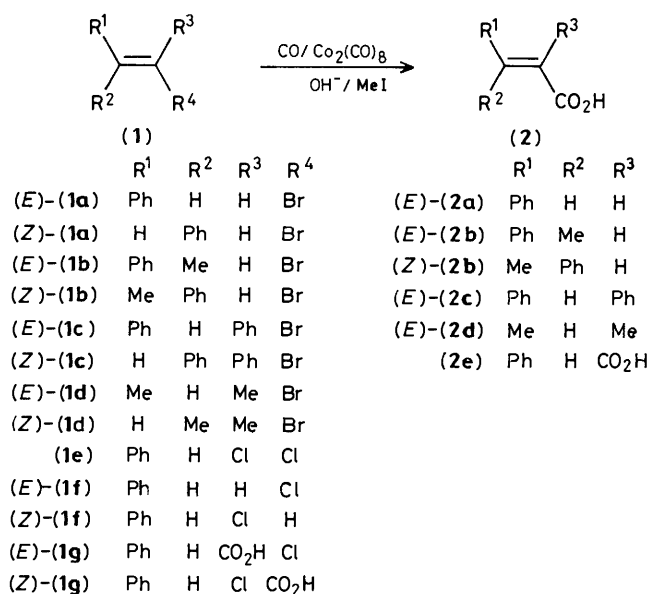
The reactions of both (E)-β-bromostyrene (E)-(**1a**) and its Z-isomer (Z)-(**1a**) with octacarbonyldicobalt in the presence of methyl iodide and calcium hydroxide at 20 °C in dioxane–water under carbon monoxide (1 atm) gave (E)-cinnamic acid (E)-(**2a**) exclusively. In contrast, with (E)-1-bromo-2-phenylpropene (E)-(**1b**), the thermodynamically less stable (Z)-3-phenylbut-2-enoic acid (Z)-(**2b**) was obtained as the major product together with the (E)-isomer (E)-(**2b**). The carbonylation of 3-chloroprop-2-enols (**7a**—**f**) gave the corresponding furan-2(5H)-ones (**8a**—**f**) in good yield.

Recently it has been discovered that, in the presence of base, alkyltetracarbonylcobalt complexes $RCo(CO)_4$ can mediate carbonylation of aryl halides under extremely mild conditions to produce a mixture of alkyl aryl ketones, carboxylic acids, and α-oxo acids, the product composition being remarkably influenced by the base and solvent employed.[1,2] This reaction has also been applied to the carbonylation of vinyl halides to give the corresponding carboxylic acids;[1c,2b] however, the factors affecting the course of the reaction and the product distribution, including the stereochemistry, have not yet been elucidated.

In the light of these results, we carried out the carbonylation of several pairs of (E)- and (Z)-vinyl halides with tetracarbonyl-methyl cobalt generated *in situ* by the reaction of octacarbonyl-dicobalt with methyl iodide in the presence of hydroxide ion under various conditions. The synthesis of furan-2($5H$)-one derivatives, whose skeleton has been found in a large number of biologically important compounds,[3] was also carried out by the carbonylation of 3-chloroprop-2-enols.

Results and Discussion

Carbonylation of Vinyl Halides.—The reaction of (E)-β-bromostyrene (E)-(**1a**) with octacarbonyldicobalt (0.3 equiv.) in the presence of methyl iodide (10 equiv.) and calcium hydroxide (25 equiv.) in dioxane–water (3:1, v/v) at 20 °C under a normal pressure of carbon monoxide for 20 h, gave (E)-cinnamic acid (E)-(**2a**) (94%) exclusively, as did the reaction in a solvent system of benzene–water using sodium hydroxide as a base (Scheme 1 and Table 1).[2b] No evidence for the formation of methyl styryl ketone and styrylglyoxylic acid could be obtained. With (Z)-(**1a**) the acid (E)-(**2a**) was also formed as the sole product, suggesting that the configuration of the bromide is readily inverted during the reaction. The reaction of (E)-1-bromo-2-phenylpropene (E)-(**1b**) gave a mixture of (E)- and (Z)-3-phenylprop-2-enoic acid, (E)-(**2b**) (21%) and (Z)-(**2b**) (71%). From a mixture of (E)- and (Z)-(**1b**) [$(E):(Z) = 3:2$] (Z)-(**2b**) was also obtained as the predominant product. This result contrasts with that observed in the benzene–water system where (E)-(**2b**) was the major product.[2b] It was confirmed that (a) the recovered (**1b**) in the stage of about 50% conversion of the bromide retained its initial configuration; (b) the product $(E)/(Z)$ ratio did not change in dioxane–water in the presence of calcium hydroxide; (c) the Z-acid (Z)-(**2b**) partially isomerized to the E-isomer in benzene–water under the reaction conditions, and (d) treatment of (Z)-(**2b**) with aqueous sodium hydroxide at 100 °C for 20 h afforded a mixture of (E)- and (Z)-(**2b**) in a molar ratio of 81:19. These results indicate that the carbonylation of (**1b**) gives predominantly the thermodynamically less stable Z-acid. The reactions of both (E)- and (Z)-β-bromo-β-phenylstyrene (**1c**) gave the thermodynamically more stable E-

Scheme 1.

	R¹	R²	R³	R⁴		R¹	R²	R³
(E)-(**1a**)	Ph	H	H	Br	(E)-(**2a**)	Ph	H	H
(Z)-(**1a**)	H	Ph	H	Br	(E)-(**2b**)	Ph	Me	H
(E)-(**1b**)	Ph	Me	H	Br	(Z)-(**2b**)	Me	Ph	H
(Z)-(**1b**)	Me	Ph	H	Br	(E)-(**2c**)	Ph	H	Ph
(E)-(**1c**)	Ph	H	Ph	Br	(E)-(**2d**)	Me	H	Me
(Z)-(**1c**)	H	Ph	Ph	Br	(**2e**)	Ph	H	CO_2H
(E)-(**1d**)	Me	H	Me	Br				
(Z)-(**1d**)	H	Me	Me	Br				
(**1e**)	Ph	H	Cl	Cl				
(E)-(**1f**)	Ph	H	H	Cl				
(Z)-(**1f**)	Ph	H	Cl	H				
(E)-(**1g**)	Ph	H	CO_2H	Cl				
(Z)-(**1g**)	Ph	H	Cl	CO_2H				

Table 1. Carbonylation of vinyl bromides[a]

Bromide	Solvent(s)[c]	Base	Yield of (**2**) (%)[b]	
			(E)	(Z)
(E)-(**1a**)	Dioxane–water	$Ca(OH)_2$	94	
(E)-(**1a**)	C_6H_6–water[d,e]	NaOH	85	
(Z)-(**1a**)	Dioxane–water	$Ca(OH)_2$	94	
(Z)-(**1a**)	C_6H_6–water[d]	NaOH	81	
(E)-(**1b**)	Dioxane–water	$Ca(OH)_2$	21	71
(E)-(**1b**)	Dioxane–water	NaOH	40	41
(E)-(**1b**)	C_6H_6–water[d,e]	NaOH	38	30
(E)-(**1b**)	MeOH[f]	NaOH	42	37
(**1b**)[g]	Dioxane–water	$Ca(OH)_2$	24	68
(**1b**)[g]	C_6H_6–water[d]	NaOH	32	25
(E)-(**1c**)	Dioxane–water	$Ca(OH)_2$	92	
(Z)-(**1c**)	Dioxane–water	$Ca(OH)_2$	92	
(E)-(**1d**)	Dioxane–water	$Ca(OH)_2$	88	
(Z)-(**1d**)	Dioxane–water	$Ca(OH)_2$	87	

[a] The reaction was carried out at 20 °C under carbon monoxide (1 atm) for 20 h unless otherwise noted. [Bromide]:[$Co_2(CO)_8$]:[MeI]:[Base] = 1:0.3:10:25. [b] Determined by g.l.c. analysis after trimethyl-silylation with N,O-bis(trimethylsilyl)acetamide. [c] Dioxane–water = 3:1; benzene–water = 1:1 (v/v). [d] The reaction at 60 °C in the presence of cetyltrimethylammonium bromide (CTAB) (0.2 equiv.). [e] Taken from the data from ref. 2b. [f] The product was obtained as a mixture of (**2b**) and the methyl ester. [g] $(E)/(Z) = 3:2$.

isomer (E)((2c) exclusively.[4] Similar results were also obtained in the reactions of (E)- and (Z)-2-bromobut-2-ene (1d).

The fact that in the reaction of (1b) the thermodynamically less favourable isomer (Z)-(2b) was formed as the predominant product accompanied by facile inversion of the configuration of the starting bromide suggests that an equilibrium exists between the two possible vinylcobalt intermediates (5) and (6) (Scheme 2) which is similar to that proposed previously.[1c,2b] The inversion would probably occur via vinyl radical species formed by homolytic cleavage of the cobalt–carbon bond.[5,*] Subsequently, migratory insertion of the ligand carbon monoxide followed by the reaction with hydroxide ion gives (E)-(2) from (5) and (Z)-(2) from (6).† In the case of (1a, c, and d), (5) is more

$$CO_2(CO)_8 \xrightarrow{OH^-} Co(CO)_4^- \xrightarrow{MeI} MeCo(CO)_4 \xrightarrow{OH^-} MeCo(CO)_3CO_2H^-$$
$$(3) \qquad\qquad (4)$$

$$R^1 = Ph, Me$$
$$R^2 = Me, H$$
$$R^3 = Ph, Me, H$$
$$X = Br, Cl$$

Scheme 2.
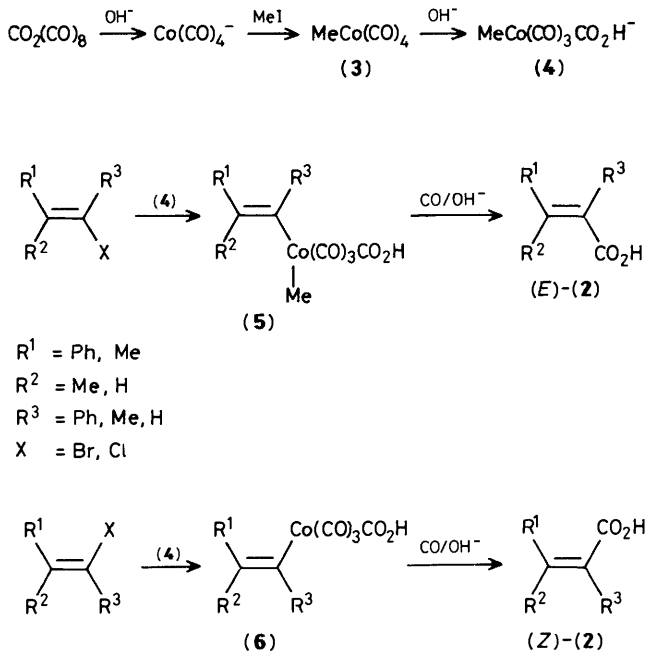
stable than (6) for steric reasons. In contrast, (6) is the favourable intermediate in the case of (1b); the steric repulsion between the methyl group $(R^2 = Me)$ and the relatively large cobalt moiety in (5) is greater than that between the phenyl group $(R^1 = Ph)$ and the cobalt moiety in (6) where the phenyl group is able to rotate to avoid the steric interaction.
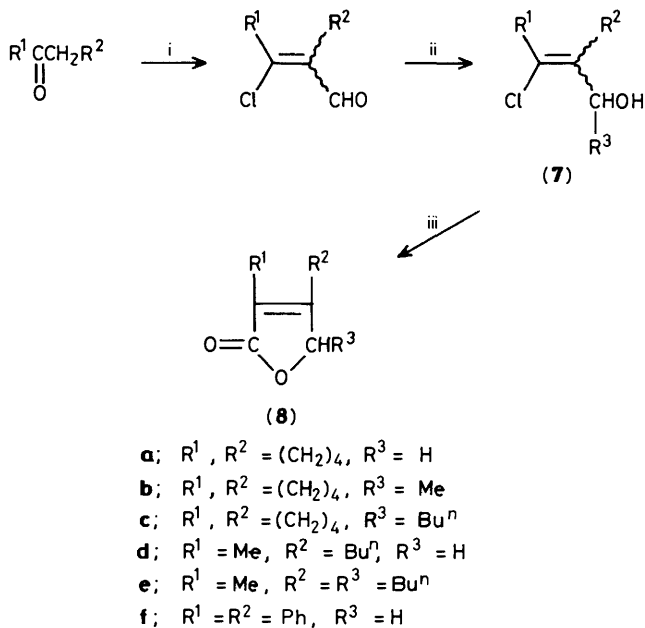
When the reaction of β,β-dichlorostyrene (1e) was performed in methanol–water (15:1, v/v), the corresponding dicarbonylated product (2e) was obtained in 68% yield (Table 2). The reaction of (1e) in dioxane–water gave an equimolar mixture of (E)-(2a) and (Z)-(2a) together with (2e). It was confirmed that (a) the reactions of both (E)- and (Z)-β-chlorostyrene (E)- and (Z)-(1f) gave (E)-(2a) as the sole product, as for the reactions of the bromides (E)- and (Z)-(1a) and (b) from the reactions of both (E)- and (Z)-α-chlorocinnamic acid (E)- and (Z)-(1g) and in dioxane–water the diacid (2e) only was isolated. Therefore, compound (2e) may be formed by the successive introduction of two carbon monoxide molecules to (1e), while a path leading to the monoacid (2a) from (1e) other

than that by an analogous construction of Scheme 2 should participate. However, the details are not clear.

Synthesis of Furanones.—Furan-2(5H)-ones (8a—f) could be successfully synthesized by the carbonylation of 3-chloroprop-2-enols (7a—f) in methanol–water with calcium hydroxide as base (Scheme 3 and Table 3). The chloro alcohols (7a—f) were

a; $R^1, R^2 = (CH_2)_4, R^3 = H$
b; $R^1, R^2 = (CH_2)_4, R^3 = Me$
c; $R^1, R^2 = (CH_2)_4, R^3 = Bu^n$
d; $R^1 = Me, R^2 = Bu^n, R^3 = H$
e; $R^1 = Me, R^2 = R^3 = Bu^n$
f; $R^1 = R^2 = Ph, R^3 = H$

Scheme 3. *Reagents:* i, DMF–POCl$_3$, CHCl=CCl$_2$; ii, Al(OPr^i)$_3$/PrOH or R^{3}MgX/ether; iii, CO/Co$_2$(CO)$_8$, MeI/Ca(OH)$_2$

conveniently prepared by the reaction of the corresponding ketones with phosphorus oxychloride–N,N-dimethylformamide (DMF) in trichloroethylene[6] followed by treatment with either aluminium isopropoxide in propan-2-ol or alkylmagnesium halides in ether. The reaction of 3-chloro-3-(4-tolyl)-prop-2-enol (7g) did not afford the expected lactone giving instead (E)-4-hydroxy-2-(4-tolyl)but-2-enoic acid (9). This may
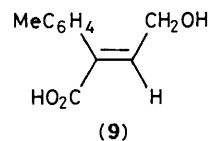
be due to the fact that in the possible two vinylcobalt intermediates (5) and (6) ($R^1 = CH_2OH, R^2 = H, R^3 = 4$-tolyl), (5) may be much more stable than (6) for steric reasons.

While the syntheses of lactones via carbonylation of vinyl halides with palladium[7] and nickel[8] catalysts have been reported, the present method seems to be advantageous in some respects; the relatively less reactive chlorides which are readily available can be used and the reaction can be also carried out under very mild conditions.

It is worth noting that when the carbonylation of chloro alcohol (7a) was carried out in the presence of benzaldehyde using sodium hydroxide as a base, an adduct (10a) was isolated in 70% yield (Scheme 4).[9] In contrast, the reaction of (8a), isolated previously with the aldehyde, gave (10a) in only 13% yield. 4-Methylbenzaldehyde could also be used in place of benzaldehyde, but with propanal the reaction was unsuccessful. The adducts (10a and b) were further converted into γ-

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* Alternatively, the inversion would also occur by the isomerization between the two acyl complexes formed from (5) and (6) by migratory insertion of the ligand carbon monoxide.

† The possibility that the acids are also produced from the intermediates (5) and (6) directly by reductive elimination cannot be excluded.

Table 2. Carbonylation of chlorostyrenes[a]

| Chloride | Solvents[c] | Product yield (%)[b] | | | Recovery (%) |
		(E)-(2a)	(Z)-(2a)	(2e)	
(1e)	Dioxane–water	26	23	28	7
(1e)	MeOH–water			68	
(1e)	C_6H_6–water[e]	40	3		45
(E)-(1f)	Dioxane–water	78			6
(Z)-(1f)	Dioxane–water	82			4
(E)-(1g)	Dioxane–water			85	
(E)-(1g)	MeOH–water			62	
(Z)-(1g)	Dioxane–water			71	

[a] The reaction was carried out at 20 °C for 20 h under carbon monoxide unless otherwise noted. [b] Determined by g.l.c. analysis after trimethylsilylation with N,O-bis(trimethylsilyl)acetamide. [c] Dioxane–water = 3:1; methanol–water = 15:1; benzene–water = 1:1 (v/v). [d] The product was obtained as a mixture of (2e) and the dimethyl ester. [e] The reaction at 60 °C in the presence of CTAB (0.2 equiv.).

Table 3. Synthesis of furanones[a]

Propenol	Furanone	Yield (%)[b]	Recovery (%)
(7a)	(8a)	73	
(7a)	(8a)	40[c]	7
(7a)	(8a)	15[d]	32
(7b)	(8b)	73	
(7c)	(8c)	91	
(7d)	(8d)	70	
(7e)	(8e)	85	
(7f)	(8f)	37	35
(7a)	(12a)	70[e]	
(7a)	(12b)	68[e]	

[a] The reaction was performed in methanol–water (5:1, v/v) at 20 °C for 20 h using calcium hydroxide as base unless otherwise noted. [(7)]:[$Co_2(CO)_8$]:[MeI]:[$Ca(OH)_2$] = 2.5:0.5:15:25. [b] Isolated yield. [c] [NaOH] = 25. [d] The reaction in dioxane–water (2:1, v/v). [e] The reaction in the presence of an aryl aldehyde (2 equiv.). [NaOH] = 25.

arylidenebutenolides (11a and b) on treatment with thionyl chloride in pyridine.[9]
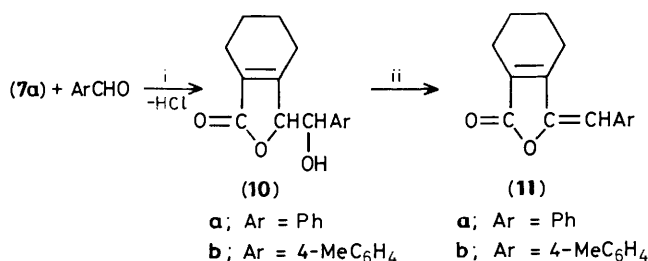
Scheme 4. Reagents: i, CO; ii, $SOCl_2$, C_5H_5N

Experimental

[1]H N.m.r. spectra were obtained with a Nippon Denshi JMN-PS-100 spectrometer for $CDCl_3$ solutions. G.c.m.s. spectra were obtained with a Hitachi RMU-6MG and i.r. spectra with a Shimadzu-400 spectrometer. G.l.c. analysis was carried out on a Shimadzu G.C.-8A gas chromatograph.

Vinyl halides (E)-(1a),[10] (Z)-(1a),[11] (E)-(1b),[12] (1b) [a mixture of E- and Z-isomers],[13] (E)-(1c),[14] (Z)-(1c),[15] (E)-(1d),[16] (Z)-(1d),[17] (1e),[17] (E)-(1f),[10] (Z)-(1f),[10] (E)-(1g),[18] and (Z)-(1g)[19] were prepared by the methods reported. The experimental details given below may be regarded as typical in methodology and scale.

Preparation of the Chloro Alcohols (7a—g).—(a) A mixture of 2-chloro-1-formylcyclohex-1-ene[6a] (9.2 g) and aluminium isopropoxide (13.0 g) in propan-2-ol (80 ml) was heated for 6 h so that the solvent gradually distilled away. The mixture was poured into dilute hydrochloric acid and extracted with ether. The chloro alcohol (7a) (88%) was isolated as an oil by column chromatography on silica gel using hexane–ethyl acetate as eluant; m/z 146 and 148 (M^+); δ_H 1.46—1.98 (4 H, m), 1.98—2.50 (4 H, m), 2.62 (1 H, s), and 4.22 (2 H, s).

(b) A solution of 2-chloro-1-formylcyclohex-1-ene (3.5 g) in ether was added to a solution of methylmagnesium iodide [prepared from magnesium powder (0.7 g) and methyl iodide (4.3 g)] in ether at 0 °C and the resulting mixture was stirred for 10 min. After conventional work up, the chloro alcohol (7b) (60%) was isolated as an oil by column chromatography on silica gel using hexane–benzene–ether as eluant; m/z 160 and 162 (M^+); δ_H 1.26 (3 H, d, J 7.5 Hz), 1.52—1.96 (4 H, m), 2.00—2.60 (4 H, m), 2.96 (1 H, s), and 4.96 (1 H, q, J 7.5 Hz). The chloro alcohol (7c) (79%) was an oil; m/z 202 and 204 (M^+); δ_H 0.86 (3 H, t, J 4.5 Hz), 1.10—1.98 (10 H, m), 1.98—2.60 (4 H, m), 3.02 (1 H, s), and 4.80 (1 H, t, J 7.5 Hz). Compound (7d) (51%) was an oil; m/z 162 and 164 (M^+); δ_H 0.76—1.16 (3 H, m), 1.16—1.80 (4 H, m), 1.80—2.60 (3 H, m), 2.20 (3 H, s), and 4.16 (2 H, s). Compound (7e) (58%) was an oil (an equimolar mixture of E- and Z-isomers); m/z 218 and 220 (M^+); δ_H 0.65—1.05 (6 H, m), 1.14—1.84 (10 H, m), 1.84—2.50 (2 H, m), 2.10 (3 H, s), 2.14 (3 H, s), 2.56 (1 H, s), 4.50 (1 H, t, J 7.5 Hz), and 4.80 (1 H, t, J 7.5 Hz). Compound (7f) (65%) had m.p. 93—96 °C (from ethanol); m/z 244 and 246 (M^+); δ_H 1.55 (1 H, s), 4.34 (2 H, s), and 7.20—7.65 (10 H, m). Compound (7g) (73%) had m.p. 29—31 °C (from hexane); m/z 182 and 184 (M^+); δ_H 1.62 (1 H, s), 2.35 (3 H, s), 4.45 (2 H, d, J 6.0 Hz), 6.30 (1 H, t, J 6.0 Hz), and 7.20—7.65 (4 H, m).

Carbonylation of Vinyl Halides.—The procedure has been described previously.[2b,2c] The following carboxylic acids are known and were compared with authentic specimens: (Z)-(2a),[20] (E)-(2b),[21] (Z)-(2b),[21] (E)-(2c),[4] (E)-(2d),[22] and (2e).[23]

Synthesis of Furanones (8a—f).—Octacarbonyldicobalt (0.5 mmol) was added to a mixture of methanol (20 ml), water (5 ml), and calcium hydroxide (15 mmol) under carbon monoxide and the mixture was stirred at 20 °C for 20 min. A solution of compound (7a) (2 mmol) and methyl iodide (10 mmol) was then added and the resulting mixture was stirred for a further 20 h. After work-up (8a) (73%) was isolated by column chromatography on silica gel using hexane–ethyl acetate as eluant. The furanone (8a) had m.p. 49—52 °C (from hexane) (Found: C, 69.7; H, 10.1. $C_8H_{10}O_2$ requires C, 69.54; H, 10.08); m/z 138 (M^+); $v_{max.}$ 1 720 and 1 670 cm^{-1}; δ_H 1.50—2.00 (4 H, m), 2.00—

2.50 (4 H, m), and 4.65 (2 H, br s); δ_C 19.9, 21.4, 21.6, 23.6, 72.1, 126.2, 161.3, and 174.3. Compound (**8b**) was an oil; m/z 152 (M^+); $\nu_{max.}$ 1 720 and 1 670 cm^{-1}; δ_H 1.42 (3 H, d, J 7.5 Hz), 1.56—1.96 (4 H, m), 1.96—2.40 (4 H, m), and 4.82 (1 H, q, J 7.5 Hz). Compound (**8c**) was an oil; m/z 194 (M^+); $\nu_{max.}$ 1 720 and 1 660 cm^{-1}; δ_H 0.90 (3 H, t, J 6.0 Hz), 1.16—2.05 (10 H, m), 2.05—2.50 (4 H, m), and 4.82 (1 H, br s). Compound (**8d**) was an oil; m/z 154 (M^+); $\nu_{max.}$ 1 745 and 1 670 cm^{-1}; δ_H 0.95 (3 H, t, J 7.5 Hz), 1.12—1.78 (4 H, m), 1.86 (3 H, s), 2.42 (2 H, t, J 6.0 Hz), and 4.66 (2 H, br s). Compound (**8e**) was an oil; m/z 210 (M^+); $\nu_{max.}$ 1 740 and 1 670 cm^{-1}; δ_H 0.88 (3 H, t, J 6.0 Hz), 0.92 (3 H, t, J 6.0 Hz), 1.05—1.74 (10 H, m), 1.84 (3 H, s), 2.04—2.64 (2 H, m), and 4.80 (1 H, br s). Compound (**8f**) had m.p. 114—116 °C (from methanol) (lit.,[24] 115—116 °C); m/z 236 (M^+); $\nu_{max.}$ 1 750 and 1 640 cm^{-1}; δ_H 5.14 (2 H, s) and 7.00—7.60 (10 H, m). The methyl ester of (**9**) was an oil; m/z 206 (M^+); $\nu_{max.}$ 3 230 and 1 700 cm^{-1}; δ_H 2.35 (3 H, s), 2.80 (1 H, br s), 3.72 (3 H, s), 4.12 (2 H, d, J 6.0 Hz), and 6.82—7.40 (4 H, m).

Synthesis of the Butenolides (**11a**—**b**).—The reaction of (**8a**) (2 mmol) with octacarbonyldicobalt (0.5 mmol), methyl iodide (15 mmol), and sodium hydroxide (25 mmol) in the presence of benzaldehyde (4 mmol) gave the adduct (**10a**) (70%), which was isolated as an oil by column chromatography on silica gel using hexane–ethyl acetate as eluant; $\nu_{max.}$ 3 350, 1 740, and 1 650 cm^{-1}; δ_H 1.30—1.84 (4 H, m), 1.84—2.50 (4 H, m), 3.56 (1 H, br s), 4.70—5.20 (2 H, m), and 7.10—7.60 (5 H, m). Treatment of (**10a**) (1 mmol) with thionyl chloride (0.5 ml) in pyridine (3 ml) at 25 °C for 20 h gave the butenolide (**11a**) (33%) which was isolated by column chromatography on silica gel using hexane–ethyl acetate as eluant; m.p. 123—125 °C (from methanol) (Found: C, 79.5; H, 6.9. $C_{15}H_{14}O_2$ requires C, 79.62; H, 6.71); $\nu_{max.}$ 1 745, 1 660, and 1 635 cm^{-1}; δ_H 1.50—2.05 (4 H, m), 2.05—2.80 (4 H, m), 5.86 (1 H, s), 7.10—7.60 (3 H, m), and 7.60—8.00 (2 H, m). The alcohol (**12b**) had m.p. 172—174 °C (from methanol); $\nu_{max.}$ 3 350, 1 740, and 1 650 cm^{-1}; δ_H 1.40—1.96 (4 H, m), 1.96—2.50 (4 H, m), 2.36 (s, 3 H), 4.96—5.20 (2 H, m), and 7.12—7.42 (4 H, m). The butenolide (**13b**) (78%) had m.p. 145—148 °C (from methanol) (Found: C, 80.05; H, 6.9. $C_{16}H_{16}O_2$ requires C, 79.97; H, 6.71); $\nu_{max.}$ 1 740, 1 660, and 1 635 cm^{-1}; δ_H 1.68—2.04 (4 H, m), 2.08—2.80 (4 H, m), 2.36 (3 H, s), 5.84 (1 H, s), 7.02—7.36 (2 H, m), and 7.60—7.80 (2 H, m).

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