

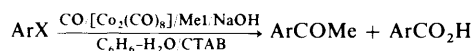
Carbonylation of Aryl Halides and Vinyl Bromides Mediated by Tetracarbonylcobalt Anion

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The reaction of aryl halides (**1a–g**) with octacarbonyldicobalt in the presence of methyl iodide and sodium hydroxide under phase-transfer conditions was found to give a mixture of aryl methyl ketones (**2a–g**) and aromatic carboxylic acids (**3a–h**). From vinyl halides (**9a–c**), however, the corresponding carboxylic acids (**10a–c**) were obtained exclusively.

Not only is the carbonylation of alkyl halides with octacarbonyldicobalt [$\text{Co}_2(\text{CO})_8$] a useful synthetic tool,^{1–4} but recently, its scope has been extended so that less reactive aryl halides may be converted into the corresponding carboxylic acids.^{5–7} Foa and his co-workers have demonstrated that in the presence of appropriate base alkyltetracarbonylcobalt complexes can catalyse carbonylation of aryl halides in aliphatic alcohols, the product composition being a function of the base employed, *e.g.* with an alkoxide, the major product is the corresponding ester whilst with calcium hydroxide it is an α -oxocarboxylic acid.⁷ In direct contrast, we found that (a) the reaction of aryl halides with octacarbonyldicobalt in the presence of methyl iodide and sodium hydroxide under phase-transfer conditions gave a mixture of aryl methyl ketones and aromatic carboxylic acids (Scheme 1).⁸ The reaction also



Scheme 1.

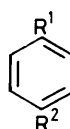
involves the methyltetracarbonylcobalt complex formed by the reaction of the tetracarbonylcobalt anion [$\text{Co}(\text{CO})_4$]⁻ (generated *in situ* from [$\text{Co}_2(\text{CO})_8$] with methyl iodide.^{9,10} (b) Surprisingly, a minor change of the solvent system exerted a marked effect on the course of the reaction.

In the light of these results we have examined: (a) the factors affecting the carbonylation of aryl halides mediated by the tetracarbonylcobalt anion; (b) the carbonylation of vinyl bromides (**9a–c**) under phase-transfer conditions in order to clarify the scope and limitation of this method; and (c) the reaction of benzyl derivatives (**12a–c**) under the same conditions used for aryl halides to obtain an insight into the characteristics of the active cobalt species for the carbonylation reaction of aryl halides.

Results and Discussion

Reaction of Aryl Halides and Vinyl Bromides under Phase-Transfer Conditions.—The reaction of aryl bromides (**1a–d**) with [$\text{Co}_2(\text{CO})_8$] (0.3 equiv.) in the presence of methyl iodide (10 equiv.) and cetyltrimethylammonium bromide (CTAB) (0.2 equiv.) in aqueous NaOH–benzene at 20 °C under a carbon monoxide atmosphere (1 atm), gave the corresponding aryl methyl ketones (**2a–d**) together with the aromatic carboxylic acids (**3a–d**) (Scheme 1 and Table 1). The order of reactivity for the bromide was (**1a**) < (**1b**) < (**1c**) < (**1d**) in agreement with results for the alkylcobalt complex-catalysed alkoxycarbonylation of aryl halides.^{7a}

The reaction of heteroaryl halides (**1e–g**) also gave a mixture of aryl methyl ketones (**2e–g**) and carboxylic acids (**3e–f**). In the case of the nitrogen containing heteroaryl halides (**1h–i**), however, considerable amounts of the methyl-substituted



(1a) $\text{R}^1 = \text{Br}$, $\text{R}^2 = \text{H}$

(1b) $\text{R}^1 = \text{Br}$, $\text{R}^2 = \text{Cl}$

(1c) $\text{R}^1 = \text{Br}$, $\text{R}^2 = \text{Ph}$

(2a) $\text{R}^1 = \text{Ac}$, $\text{R}^2 = \text{H}$

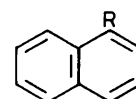
(2b) $\text{R}^1 = \text{Ac}$, $\text{R}^2 = \text{Cl}$

(2c) $\text{R}^1 = \text{Ac}$, $\text{R}^2 = \text{Ph}$

(3a) $\text{R}^1 = \text{CO}_2\text{H}$, $\text{R}^2 = \text{H}$

(3b) $\text{R}^1 = \text{CO}_2\text{H}$, $\text{R}^2 = \text{Cl}$

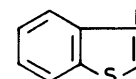
(3c) $\text{R}^1 = \text{CO}_2\text{H}$, $\text{R}^2 = \text{Ph}$



(1d) $\text{R} = \text{Br}$

(2d) $\text{R} = \text{Ac}$

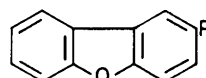
(3d) $\text{R} = \text{CO}_2\text{H}$



(1e) $\text{R} = \text{I}$

(2e) $\text{R} = \text{Ac}$

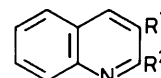
(3e) $\text{R} = \text{CO}_2\text{H}$



(1f) $\text{R} = \text{I}$

(2f) $\text{R} = \text{Ac}$

(3f) $\text{R} = \text{CO}_2\text{H}$



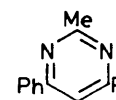
(1g) $\text{R}^1 = \text{Br}$, $\text{R}^2 = \text{H}$

(1h) $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{Cl}$

(2g) $\text{R}^1 = \text{COMe}$, $\text{R}^2 = \text{H}$

(2h) $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{Ac}$

(4a) $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{Me}$



(1i) $\text{R} = \text{Cl}$

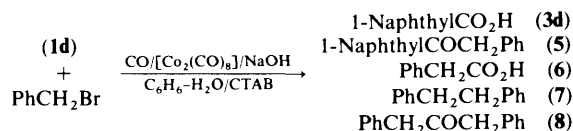
(1j) $\text{R} = \text{I}$

(2i) $\text{R} = \text{Ac}$

(4b) $\text{R} = \text{Me}$

products (**4a, b**) were formed, together with lesser amounts of aryl methyl ketones.

Replacement of methyl iodide with benzyl bromide allowed reaction of (**1d**) with the bromide (10 equiv.) at 20 °C to give benzyl 1-naphthyl ketone (**5**) (15%) and (**3d**) (5%) together with phenylacetic acid (**6**) (18%), 1,2-diphenylethane (**7**) (15%), and dibenzyl ketone (**8**) (1%) (Scheme 2).¹¹ The bromide (**1d**) was also recovered (56%). Ethyl iodide, ethyl bromoacetate, and allyl bromide were ineffective in these reactions.



Scheme 2.

α -Substituted β -bromostyrenes (**9a–c**) appeared less reactive than the aryl halides (**1a–j**), so that with methyl iodide at 20 °C only the starting materials (**9a–c**) were recovered. When the reaction was undertaken at 60 °C, however, the corresponding carboxylic acids (**10a–c**) were obtained in good yield; no evidence for the formation of the corresponding methyl vinyl ketones was obtained (Scheme 3).

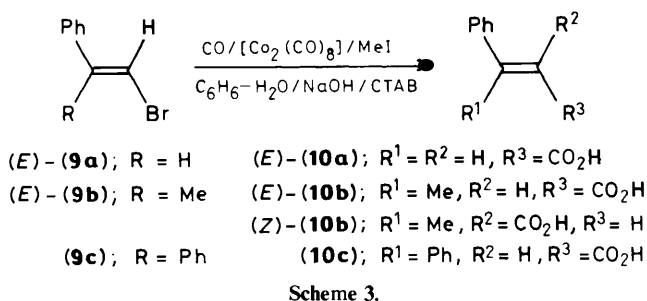


Table 1. Carbonylation of aryl halides and vinyl bromides with [Co₂(CO)₈] in the presence of methyl iodide and sodium hydroxide under phase transfer conditions^a

Halide	Conversion of halide (%)	Products (% yield) ^b
(1a)	31 ^c	(2a) (13), ^c (3a) (48)
(1a)	68 ^{c,e}	(2a) (9), ^c (3a) (85)
(1b)	48 ^c	(2b) (40), (3b) (21)
(1b)	92 ^{c,e}	(2b) (51), (3b) (40)
(1c)	79	(2c) (43), (3c) (29)
(1d)	100	(2d) (54), (3d) (20) ^d
(1d)	100 ^c	(2d) (36), (3d) (49)
(1e)	100	(2e) (13), (3e) (30) ^f
(1f)	96	(2f) (36), (3f) (15)
(1g)	100	(2g) (38) ^g
(1h)	100	(2h) (15), (4a) (30) ^g
(1i)	83	(2i) (5), (4b) (34) ^g
(1j)	100	(2j) (27), (4b) (54) ^g
(<i>E</i>)-(9a)	96 ^e	(<i>E</i>)-(10a) (85)
(<i>E</i>)-(9b)	100 ^e	(<i>E</i>)-(10b) (38), ^h (<i>Z</i>)-(10b) (30) ^h
(9c)	100 ^e	(10c) (80)

^a The reaction was carried out at 20 °C for 20 h under CO (1 atm) unless otherwise noted. ^b Isolated yield based on halide consumed unless otherwise noted. ^c Determined by g.l.c. analysis. ^d Naphthalene-1-carbaldehyde (3%) and di-1-naphthyl ketone (2%) were also formed. ^e The reaction at 60 °C. ^f Benzothiophene was obtained in 45% yield. ^g Products in the aqueous phase were not investigated. ^h Determined by ¹H n.m.r. analysis.

Table 2. Carbonylation of 1-bromonaphthalene (**1d**) with [Co₂(CO)₈] in the presence of methyl iodide and base under various conditions^a

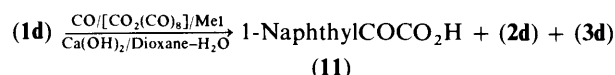
Solvent(s) (ratio)	Proportion of catalyst	Base	Pressure of CO (atm)	Products (% yield) ^b	Recovery of (1d) (%) ^b
THF-H ₂ O (9:1)	0.3	NaOH	1	(2d) (19), (3d) (74)	
Dioxane-H ₂ O (3:1)	0.3	NaOH	1	(2d) (11), (3d) (68)	
Propan-2-ol-H ₂ O (9:1)	0.3	NaOH	1	(2d) (24), (3d) (70)	
MeOH-H ₂ O (3:1)	0.3	NaOH	1	(2d) (19), (3d) (62) ^c	
MeOH	0.3	NaOH	1	(3d) (80) ^c	
THF-H ₂ O (9:1)	0.3	Ca(OH) ₂	1	(2d) (1), (3d) (20), (11) (18)	21
Dioxane-H ₂ O (3:1)	0.3	Ca(OH) ₂	1	(2d) (1), (3d) (8), (11), (52)	8
C ₆ H ₆ -H ₂ O (1:1) ^d	0.2	NaOH	1	(2d) (58), (3d) (23)	
C ₆ H ₆ -H ₂ O (1:1) ^d	0.05	NaOH	1	(2d) (57), (3d) (20)	
C ₆ H ₆ -H ₂ O (1:1) ^d	0.1	NaOH	5	(2d) (60), (3d) (20)	
C ₆ H ₆ -H ₂ O (1:1) ^d	0.1	NaOH	10	(2d) (61), (3d) (13)	5

^a The reaction was carried out in the presence of methyl iodide (10 equiv.) and base (25 equiv.) at 20 °C for 20 h. ^b Determined by g.l.c. analysis. The acidic products were trimethylsilylated by *N,O*-bis(trimethylsilyl)acetamide prior to analysis. ^c The product was obtained as a mixture of (**3d**) and the methyl ester. ^d In the presence of CTAB (0.2 equiv.).

The reaction of (*E*)-(9b) gave an equimolar mixture of (*E*)-(10b) and (*Z*)-(10b) suggesting that the carbonylation is non-stereospecific. From (*E*)-(9a), however, (*E*)-(10a) was obtained exclusively.

Carbonylation of 1-Bromonaphthalene (1d) under Homogeneous Conditions.—Carbonylation of (**1d**) in the presence of [Co₂(CO)₈] and methyl iodide in aqueous NaOH-THF (THF-H₂O = 9:1), gave the carboxylic acid (**3d**) as the major product (74%) together with the ketone (**2d**) (19%) (Table 2). Similar results were obtained in other homogeneous solvent systems, e.g. dioxane-water (3:1), propan-2-ol-water (9:1), and methanol-water (3:1). This behaviour contrasts with that observed in the benzene-water system where the ketone (**2d**) was the major product. In methanol the acid (**3d**) was the sole product. These results parallel those for the alkyltetracobalt-catalysed carbonylation of aryl halides in methanol in the presence of the methoxide ion where exclusive formation of the corresponding methyl esters were observed.^{7a}

Calcium hydroxide as base in place of sodium hydroxide gave 1-naphthylglyoxylic acid (**11**) in good yield (Scheme 4). In dioxane-water the reaction gave (**11**) (52%), (**2d**) (1%), and (**3d**) (8%) whilst in THF-water it gave (**11**) (18%), (**2d**) (1%), and (**3d**) (20%).



Scheme 4.

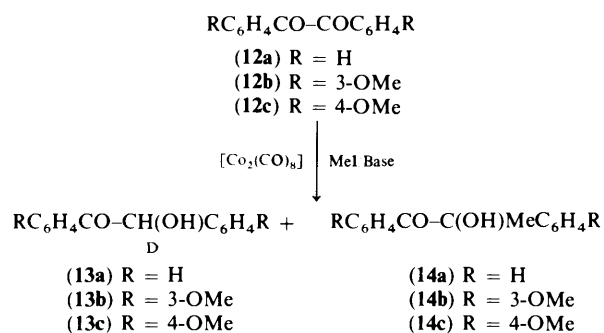
Reaction of Benzil Derivatives.—Treatment of benzil (**12a**) with [Co₂(CO)₈] and methyl iodide in aqueous NaOH-benzene, gave the benzoin (**13a**) (27%) as the only product (Scheme 5 and Table 3).

The reaction using deuterium oxide in place of water gave the monodeuteriated benzoin (**13a–d**), suggesting that the hydrogen source of this reduction is the solvent water. In marked contrast, the reaction of (**13a**) in methanol in the presence of sodium methoxide yielded exclusively the methylated product (**14a**). Since (**14a**) was also the sole product in the reaction in ethanol in the presence of sodium ethoxide, it is evident that the methyl group in (**14a**) came from methyl iodide. The 3,3'- and 4,4'-dimethoxybenzils (**12b,c**) reacted in a similar fashion to (**12a**) to give either (**13b**) or (**13c**) in benzene-water or (**14b,c**) in methanol. In the absence of either methyl iodide or the base benzil (**12a**) was recovered quantitatively.

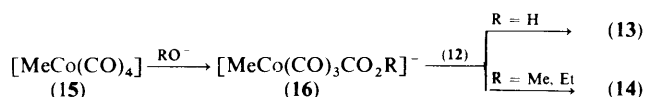
Table 3. Reaction of benzil derivatives with $[\text{Co}_2(\text{CO})_8]$ in the presence of methyl iodide and base^a

Benzil	Solvent(s)	Base	Products (% yield) ^b	Recovery (%) ^b
(12a)	$\text{C}_6\text{H}_6\text{-H}_2\text{O}^c$	NaOH	(13a) (27)	(12a) (50)
(12a)	$\text{C}_6\text{H}_6\text{-D}_2\text{O}^c$	NaOD	(13a-d) (20)	(12a) (65)
(12a)	MeOH	NaOMe	(14a) (36)	(12a) (48)
(12a)	MeOH	NaOH	(13a) (20), (14a) (20)	(12a) (41)
(12a)	EtOH	NaOEt	(14a) (34)	(12a) (35)
(12b)	$\text{C}_6\text{H}_6\text{-H}_2\text{O}^c$	NaOH	(13b) (37)	(12b) (58)
(12b)	MeOH	NaOMe	(14b) (29)	(12b) (68)
(12c)	$\text{C}_6\text{H}_6\text{-H}_2\text{O}^c$	NaOH	(13c) (5)	(12c) (89)
(12c)	MeOH	NaOMe	(14c) (2)	(12c) (95)

^aThe reaction was carried out at 20 °C for 20 h under CO . ^b Isolated yield. ^c In the presence of CTAB (0.2 equiv.).

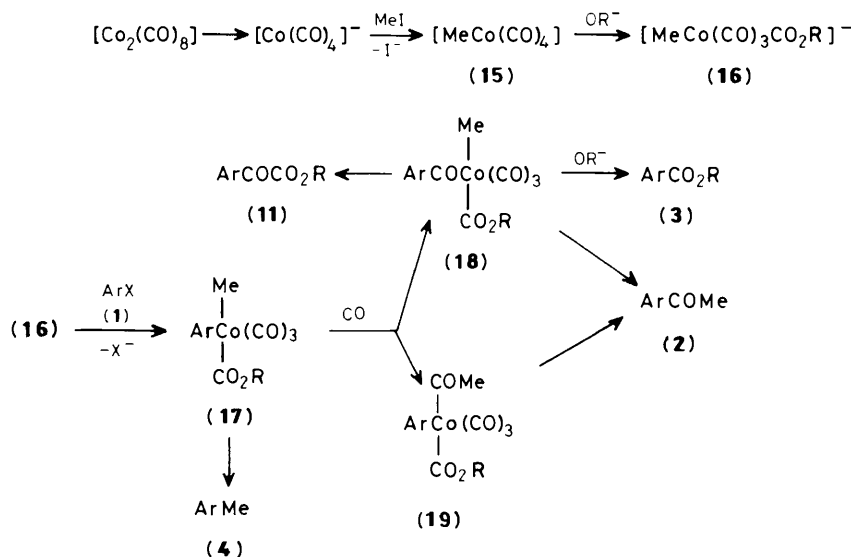
**Scheme 5.**

These results may be taken as evidence that the tetracarbonylmethylcobalt (15) is produced from a mixture of $[\text{Co}_2(\text{CO})_8]$ and methyl iodide and the successive reaction with base gives an anionic complex (16), which acts as the active species in the solvent system benzene-water as well as in alcohols (Schemes 6 and 7).^{7,12} Methyl-transfer from the intermediate (16; R = Me or Et) may give rise to the methylated product (14). When the base is sodium hydroxide, however, hydrogen-transfer from the intermediate (16; R = H) is significantly faster than methyl-transfer and, as a result, the reduced product (13) is obtained exclusively. The detail of the methyl- or hydrogen-transfer is obscure.

**Scheme 6.**

Mechanism for the Carbonylation of Aryl Halides and Vinyl Bromides.—In order to understand the mechanism of the carbonylation of the aryl halides (1) and vinyl bromides (9) mediated by tetracarbonylcobalt anion the following features need to be taken into account. (a) To induce carbonylation the presence of methyl iodide is required; in its absence the aryl halides (1) and vinyl bromides (9) were recovered quantitatively. (b) When the reaction of (1d) under phase-transfer conditions was followed periodically by g.l.c., it was found that only after 30 min did the bromide (1d) consumption commence, with subsequent slow formation of the ketone (2d) (see Figure). (c) The carbonylation is catalytic, the proportion of $[\text{Co}_2(\text{CO})_8]$ (0.05–0.3 equiv.) exerting no meaningful influence on the product ratio (2d):(3d) (Table 2). (d) The carbon monoxide pressure (1–10 atm) failed to affect the (2d):(3d) ratio. (e) Since compound (1d) failed to react with tetracarbonylmethylcobalt (generated from $[\text{Co}_2(\text{CO})_8]$ using solid sodium hydroxide in THF)¹³ an excess of base in the solvent appears necessary for reaction to occur.

The mechanism illustrated in Scheme 7 seems to rationalize

**Scheme 7.**

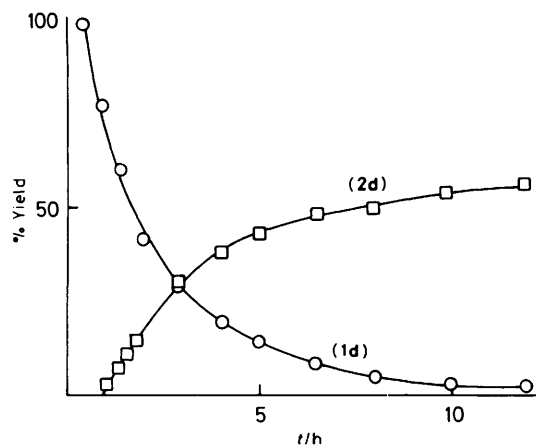


Figure. Reaction of (1d) with $[\text{Co}_2(\text{CO})_8]$ in the presence of methyl iodide and sodium hydroxide under phase-transfer conditions

the results most satisfactorily. Octacarbonyldicobalt is well known to produce the tetracarbonylcobalt anion $[\text{Co}(\text{CO})_4]^-$ under the conditions employed. Since the presence of methyl iodide is required to induce the carbonylation of aryl halide and vinyl bromide and, moreover, there exists a significant induction period, it is reasonable to consider that the first step of the reaction involves attack of the relatively more reactive methyl iodide on the $[\text{Co}(\text{CO})_4]^-$ anion to give the tetracarbonylmethylcobalt (15); this then reacts with hydroxide to yield an active anionic cobalt complex (16). Subsequently, the reaction with aryl halide may occur to give a Co^{III} -complex (17),* followed by migratory insertion of the ligand carbon monoxide to afford an aroyl-(18) or acetyl-complex (19). Reductive elimination of the aryl methyl ketone (2) may then occur *via* the intermediate (18) or (19). Alternatively, nucleophilic attack of the hydroxide on the intermediate (18) would provide the aromatic carboxylic acid (3).† The solvent dependent ratio of (2) to (3) may be interpreted as follows. Under phase-transfer conditions the effective concentration of hydroxide is very low and, consequently, reductive elimination of aryl methyl ketone from (18) or (19) is more favoured than the nucleophilic attack of (18) by the hydroxide. In homogeneous systems, the reverse trend in the contribution of the two competing processes would be observed. Exclusive formation of the carboxylic acid (10) from vinyl bromide (9) would, however, imply that the rate of reductive elimination of methyl ketone from the intermediates (18) or (19) is substrate-dependent; in the case of vinyl bromide (9) this step is extremely slow. A possible explanation for the formation of the α -oxoacid (11) may be *via* reductive elimination from the intermediate (18). It is unclear, however, why compound (11) is produced only in the presence of calcium hydroxide. The methyl-substituted product (4) may be formed from the complex (17) by reductive elimination.‡

Experimental

¹H N.m.r. spectra were obtained with a JMN-PS-100 spectrometer for CDCl_3 solutions. G.c.-m.s. spectra were obtained with a Hitachi RMU-6M spectrometer and i.r. spectra

* It seems most likely that this step involves initial single electron transfer.⁷

† The possibility that the carboxylic acid (3) is also produced from the intermediates (17) and (19) by reductive elimination cannot be excluded.

‡ Alternatively, the direct reaction of (1h-j) with (16) would give the methyl-substituted product (4) without the formation of (17).

with a Shimadzu-400 spectrometer. G.l.c. analysis was carried out on a Shimadzu G.C.-4C gas chromatograph.

Aryl halides (1e),¹⁴ (1f),¹⁵ (1i),¹⁶ (1j),¹⁷ and vinyl bromides (*E*)-(9a),¹⁸ (*E*)-(9b),¹⁹ and (9c),²⁰ were prepared by the methods reported. Substituted benzils (12b) and (12c) were prepared by benzoin condensation and successive oxidation with copper(II) sulphate in aqueous pyridine.²¹ Other starting materials were commercially available. The experimental details given below may be regarded as typical in methodology and scale.

Carbonylation of (1d) Under Phase-Transfer Conditions.—To a solution of $[\text{Co}_2(\text{CO})_8]$ (0.3 mmol) in benzene (15 ml) was added a solution of cetyltrimethylammonium bromide (0.2 mmol) and sodium hydroxide (25 mmol) in water (25 ml) under carbon monoxide (1 atm) and the mixture was stirred at 20 °C for 2 h. A solution of 1-bromonaphthalene (1d) (1 mmol) and methyl iodide (10 mmol) in benzene (10 ml) was then added and the resulting mixture was stirred for a further 20 h. After conventional work-up, the neutral products were isolated by column chromatography on silica gel using benzene-hexane as eluant. The first fraction was a mixture of naphthalene-1-carbaldehyde (3%) and di-1-naphthyl ketone (2%) which was confirmed by g.c.-m.s. analysis. From the second fraction, 1-acetylnaphthalene (2d) (54%) was obtained. Acidification of the aqueous phase afforded 1-naphthoic acid (20%).

Carbonylation of (1d) in Aqueous Dioxane with Calcium Hydroxide.—To a mixture of dioxane (10 ml), water (10 ml), and calcium hydroxide (25 mmol) was added a solution of $[\text{Co}_2(\text{CO})_8]$ (0.3 mmol) in dioxane (10 ml) under carbon monoxide (1 atm) and the mixture was stirred at 20 °C for 30 min. A solution of (1d) (1 mmol) and methyl iodide (10 mmol) in dioxane (10 ml) was then added and the resulting mixture was stirred for a further 20 h, when the reaction mixture was poured into dilute hydrochloric acid and extracted with ether. The acidic products were extracted with aqueous sodium hydroxide. After acidification and re-extraction with ether the products were trimethylsilylated with *N,O*-bis(trimethylsilyl)acetamide in dichloromethane.²² Analysis by g.c.-m.s. confirmed the formation of the α -oxoacid (11) (52%) and (3d) (8%). The oxoacid was also isolated by trituration of the product mixture with benzene-hexane in 45% yield. The neutral phase was found to contain (2d) (1%) and (1d) (8%) by g.l.c. analysis.

Reaction of Benzil (12a) with Sodium Hydroxide in Methanol.—A solution of $[\text{Co}_2(\text{CO})_8]$ (0.3 mmol) in methanol (5 ml) was added to a solution of sodium hydroxide (25 mmol) in methanol (25 ml). After 10 min a mixture of (12a) (1 mmol) and methyl iodide (10 mmol) in methanol (10 ml) was added and the resulting mixture was stirred at 20 °C under carbon monoxide for 20 h. After conventional work-up, the product mixture was separated by column chromatography on silica gel using hexane-ethyl acetate as eluant to afford the following products; (12a) (41%), (14a) (20%), and (13a) (20%) in order of elution.

Products.—All the products obtained are known and were compared with authentic specimens: (2e),²³ (2f),²⁴ (2g),²⁵ (2h),²⁶ (2i),²⁷ (3e),¹⁴ (3f),¹⁵ (4b),²⁸ (7),²⁹ (*E*)-(10b),³⁰ (*Z*)-(10b),³¹ (10c),²⁰ (11),³² and di-1-naphthylketone.³³

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