competing. Detection was carried out spectrophotometrically from the enol band at 250 nm, which resembles strongly that of 2-hydroxy-1-cyclohexen-3-one (Figure 1) and by bromometric titration. Assuming similarity of molar absorptivity of the band at 250 nm and that of 2-hydroxy-1-cyclohexen-3-one both methods gave similar results for the enol content, varying from 10% to 30% depending on the sodium hydroxide concentration and time of quenching. At pH 3 the conversion of the monoenol to diketo form takes place during tens of hours, similarly as was observed[3a] for the cyclic monoenols.

Clearly, the combination of polarography and spectrophotometry is a powerful tool in the study of these complex equilibria. We are currently trying to utilize our understanding of these equilibria in attemps to isolate the enol form of biacetyl proved in acidic solutions and to study other 1,2-diketones in this manner.

Experimental Section

Biacetyl (Eastman Organic Chemicals) was used as received. Sodium hydroxide and chemicals used for buffer preparation were reagent grade. Acetonitrile, Me_2SO, and DMF were "Baker Analyzed" reagent grade solvents.

Spectra were recorded at 25 °C on a Unicam SP800A UV–vis spectrophotometer. Polarograms were recorded on a Sargent-Welch Model XVI polarograph in a two-electrode configuration with liquid junction (Kalousek cell), with SCE and a DME with $m = 3.02$ mg s^{-1} and $t_1 = 4.62$ s at $h = 60$ cm. Potentiometric bromometric titrations were carried out with a Pt-electrode.

Stock solutions (0.025 M) of biacetyl in acetonitrile were added to deaerated solutions of a buffer or sodium hydroxide so that the final concentration for spectroscopy or polarography was 5×10^{-4} M and that of acetonitrile 2%. For obtaining the values of pK_{OH} and pK_a measured absorbance or limiting current were extrapolated to $t = 0$. For kinetic studies of carbanion formation, absorbance at 250 nm or polarographic limiting current were measured continuously as a function of time by using cells as reactors. The first measurement was carried out about 30 s after mixing.

To produce the enol form of biacetyl a stock solution of the compound was transferred into 0.01–0.1 M NaOH so that final biacetyl concentration was lower than 1×10^{-3} M. After a time period chosen from kinetic experiments known, an amount of phosphoric acid was added so that the resulting pH was 3.2. An absorption band at 250 nm was used as a measure of enol content of the reaction mixture. Alternatively, an aliquot of this solution was titrated potentiometrically by bromine at 0 °C. As the establishment of the enol–keto equilibrium at pH 3.2 takes several hours, the results of the bromometric titrations were well reproducible even at 25 °C and independent of sampling time within 30 min after acidification. The enol form was not extracted into hexane, carbon tetrachloride, chloroform, or diethyl ether.

Registry No. Biacetyl, 431-03-8; 2-hydroxy-1-cyclohexen-3-one, 10316-66-2.

Cobalt-Catalyzed Normal Pressure Carbonylation of Aryl Halides. Notable Solvent Effects on the Ratio of Mono- to Double-Carbonylation

Masahiro Miura,* Fumiaki Akase, and Masakatsu Nomura

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan

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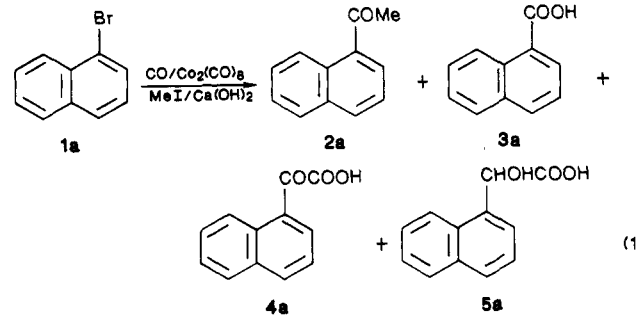
Transition-metal-catalyzed carbonylation of alkyl and aryl halides often gives a mixture of mono- and double-carbonylated products, the composition being influenced by many variables.[1,2] Recently, Foa and his co-workers have demonstrated that in the presence of base alkyltetracarbonylcobalt can catalyze carbonylation of aryl halides in aliphatic alcohols under a normal pressure of carbon monoxide to produce either the corresponding ester or the α-keto acid as the predominant product, depending on the identity of the base employed.[3] In direct contrast, we discovered that the carbonylation of 1-bromonaphthalene (**1a**) catalyzed by methyltetracarbonylcobalt generated in situ in aqueous organic solvents in the presence of sodium hydroxide, gives 1-acetylnaphthalene (**2a**) together with 1-naphthoic acid (**3a**).[4] When the carbonylation is performed in the presence of calcium hydroxide in 3:1 dioxane–water, however, 1-naphthylglyoxylic acid (**4a**) is obtained predominantly.[4b]

In this paper we report our findings that in the cobalt-catalyzed carbonylation of aryl halides using calcium hydroxide as the base in aqueous organic solvents, both the identity of the solvent and the content of water are the drastic factors detertmining the product composition.

Results and Discussion

The carbonylation of 1-bromonaphthalene (**1a**) with 0.3 equiv of $Co_2(CO)_8$ in the presence of methyl iodide (10 equiv) and calcium hydroxide (25 equiv) was undertaken at room temperature under a normal pressure of carbon monoxide for 20 h. When the reaction was performed in dioxane–water (1:1, v/v), 1-naphthoic acid (**3a**) was obtained in 37% yield together with 1-acetylnaphthalene (**2a**, 10%), 1-naphthylglyoxylic acid (**4a**, 15%), and 1-naphthylglycolic acid (**5a**, 3%) (eq 1 and Table I). In



(1)

direct contrast, the reaction in 3:1 dioxane–H_2O gave predominantly **4a** (52%) together with **2a** (1%) and **3a** (8%). In the reaction in 3:1 tetrahydrofuran (THF)–H_2O, **4a** was the major product also. The reaction in 3:1

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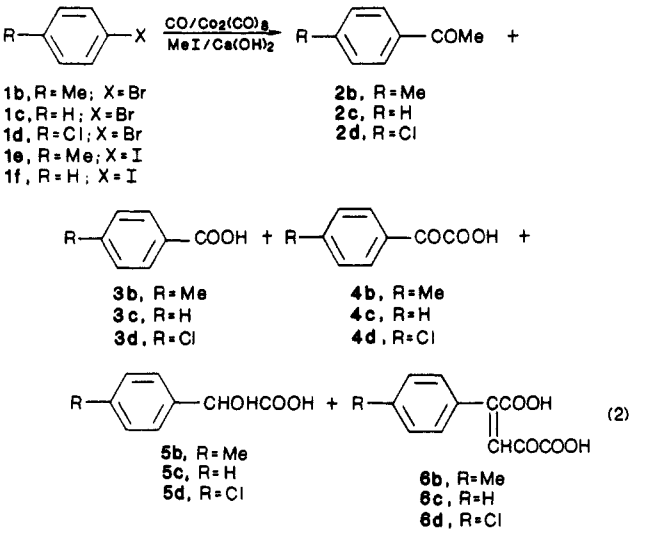
Table I. Carbonylation of 1-Bromonaphthalene (1a)[a]

solvents (ratio, v/v)	products (% yield)[b] 2a	3a	4a	5a	recovery of 1a (%)
dioxane–H_2O (1:1)	10	37	15	3	
dioxane–H_2O (3:1)[c]	1	8	52		8
dioxane–H_2O (15:1)		2	15		62
THF–H_2O (3:1)	4	22	37		3
EtOH–H_2O (3:1)	9	51 (44)[d]	1	2	
EtOH–H_2O (15:1)		26 (22)[d]	19	13	
DMF–H_2O (1:1)	10	44	1	2	
DMF–H_2O (3:1)	29	38	6		
DMF–H_2O (15:1)	46	24	11	2	
DMAc–H_2O (15:1)	33	28	5	1	12
NMP–H_2O (15:1)	28	28	7	2	14

[a] The reaction was carried out with $Co_2(CO)_8$ (0.3 equiv) in the presence of methyl iodide (10 equiv) and calcium hydroxide (25 equiv) at room temperature for 20 h. [b] The yield based on 1a charged was determined by GC analysis. [c] Taken from the data in ref 4b. [d] The product was obtained as a mixture of **3a** and the corresponding ethyl ester. The value in parentheses indicates the yield of the ethyl ester of **3a**.



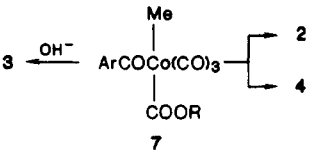
$EtOH–H_2O$ gave mainly a mixture of **3a** (7%) and the corresponding ethyl ester (44%). However, by increasing the $EtOH/H_2O$ ratio to 15:1 the total yield of the double-carbonylation products, **4a** and **5a**, increased to an extent comparable to that of the monocarbonylation products.

A remarkably different trend was observed in the reaction of dimethylformamide (DMF)–H_2O. The carbonylation of **1a** in 1:1 DMF–H_2O gave predominantly the monoacid **3a** (44%), as for the reaction in 1:1 dioxane–H_2O. When the reaction was undertaken in 15:1 DMF–H_2O, however, the ketone **2a** was obtained in a yield of 46% together with **3a** (24%), **4a** (11%), and **5a** (2%). In the reaction in 15:1 dimethylacetamide (DMAc)–H_2O and 15:1 *N*-methylpyrrolidone (NMP)–H_2O, **2a** was also produced in a considerable amount.

The reaction of 4-substituted bromo- (**1b–d**) and iodobenzenes (**1e,f**) with 0.06 equiv of $CO_2(CO)_8$ in the presence of methyl iodide (5 equiv) and calcium hydroxide (8 equiv) in 3:1 dioxane–H_2O gave considerable amounts of the products **6b–d**, which may be formed by condensation of arylglyoxylic acids **4b–d** and pyruvic acid, suggesting that pyruvic acid is also produced in the carbonylation (eq 2 and Table II).[3b] The total yield of the double-carbonylation products **4b–d**, **5b-d**, and **6b–d** was 29–49% and the monoacids **3b–d** were formed in 2–16% yield. Aryl halides were also recovered in 6–48%. Consistent with the reaction of **1a** in the same solvent system, 4-substituted acetophenones **2b–d** were negligible products.

In the reaction of **1c–f** in 15:1 DMF–H_2O the ketones **2b–d** were obtained in considerable amounts, as for the reaction of **1a** under the same conditions. The yield of **2b–d** (2–25%) was comparable with both the monoacid **3b–d** (4–23%) and the double-carbonylation products (**4b–d** + **5b–d**) (3–22%).

The key intermediate leading to the major three products **2**, **3**, and **4** in the carbonyation reaction would be an aroylcobalt(III) complex (**7**), which has been proposed previously.[3-5] The nucleophilic attack of hydroxide on **7**

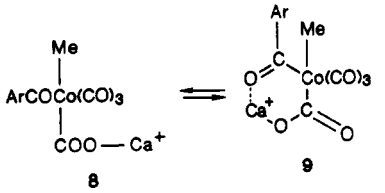


may give **3**: The observation that the increased proportion of water in the mixed solvents results in the increased yield of **3** can be rationalized by considering the fact that the increase in proportion of the water is accompanied by the increase of calcium hydroxide dissolved in the reaction medium. Reductive elimination from **7** would provide either **2** or **4**. The question is the origin of remarkable solvent effects on the mode of reductive eliminations: It would be reaonable to consider that in the reaction medium **7** exists as the open-chain calcium salt **8** (R = Ca) or the chelated form **9**, depending on the nature of the solvent system. In a less polar solvent system, 3:1 dioxane–H_2O, the chelated form **9** would be important, while

Table II. Carbonylation of Halogenated Benzenes[a]

aryl halide	solvents (ratio, v/v)	products (% yield)[b] 2	3	4	5	6[c]	(4 + 5 + 6)/3	recovery of 1 (%)
1b	dioxane–H_2O (3:1)		2	19	2	8	14.5	48
1c	dioxane–H_2O (3:1)		8	13	6	30	6.1	37
1d	dioxane–H_2O (3:1)		16	15	8	13	2.3	6
1e	dioxane–H_2O (3:1)		3	27		12	13.0	27
1f	dioxane–H_2O (3:1)	1	13	12	7	16	2.7	9
1c	DMF–H_2O (15:1)	2	4	3	1		1.0	64
1d	DMF–H_2O (15:1)	19	18	2	1		0.2	39
1e	DMF–H_2O (15:1)	22	17	22			1.3	24
1f	DMF–H_2O (15:1)	25	23	20	1		0.9	15

[a] The reaction was carried out with 0.66 equiv of $Co_2(CO)_8$ in the presence of methyl iodide (5 equiv) and calcium hydroxide (8 equiv) at room temperature for 20 h. [b] The yield based on aryl halide charged was determined by GC analysis unless otherwise noted. [c] Determined by ^1H NMR spectroscopy.



8 9

in the case of more polar 15:1 DMF–H_2O the contribution of the open-chain form 8 would be important. Of these two intermediates, we would like to consider that **9** is the key leading to the formation of **4**.[6] In the open-chain form **8**, the process of reductive elimination providing **2** contributes predominantly in the presence of only small amounts of dissolved calcium hydroxide.

Experimental Section

General Procedures. ^1H NMR spectra were obtained with a JMN-PS-100 spectrometer in $CDCl_3$. GC–MS data were obtained with a Hitachi-RMU-6M. GC analysis was carried out on a Shimazu-GC-4C gas chromatograph.

Carbonylation of Aryl Halides 1. The carbonylation of **1** (1 or 5 mmol) was carried out with 0.3 mmol of $Co_2(CO)_8$ in the presence of methyl iodide (10 or 25 mmol) and calcium hydroxide (25 or 40 mmol) in an appropriate solvent–water mixture (40 mL) at room temperature for 20 h under carbon monoxide (1 atm). Analysis of the products was performed by GC and GC–MS after addition of an appropriate internal standard. The acidic products were treated with *N,O*-bis(trimethylsilyl)acetamide in acetonitrile or diazomethane in ether before the analysis. The methyl esters of **3–6** were also isolated by column chromatography on silica gel by using ethyl acetate–hexane as eluant. The methyl esters of **3–5** were identified by comparison with those of authentic samples. The methyl ester of **6b** was a solid: mp 152–154 °C (from ethanol); MS, *m/e* 262 (M^+); ^1H NMR δ 2.32 (s, 3 H), 3.76 (s, 3 H), 3.84 (s, 3 H), 6.52 (s, 1 H), 7.12–7.44 (m, 4 H). Anal. Calcd for $C_{14}H_{14}O_5$: C, 64.12; H, 5.38. Found: C, 64.04; H, 5.35. The methyl ester of **6c** was an oil; MS, *m/e* 248 (M^+); ^1H NMR δ 3.76 (s, 3 H), 3.84 (s, 3 H), 6.56 (s, 1 H), 7.20–7.62 (m, 5 H). The methyl ester of **6d** was an oil: MS, *m/e* 282 and 284 (M^+); ^1H NMR δ 3.76 (s, 1 H), 3.82 (s, 3 H), 6.52 (s, 1 H), 7.20–7.62 (m, 4 H). The yield of **6b–d** was, however, determiened by ^1H NMR analysis of the crude products on the basis of the peak intensity of the vinylic proton [**6b**, δ 6.68 (s, 1 H). **6c**, δ 6.68 (s, 1 H). **6d** δ 6.66 (s, 1 H)] because considerable amounts of byproducts were formed by treatment with diazomethane.

(5) Arylgrycolic acid **5** might be produced by the reaction of **4** with an anionic intermediate $[MeCo(CO)_3COOH]^-$ generated in situ.[4b,7]

(6) This is partly supported by the fact that in the reaction of **1a** under phase-transfer conditions using sodium hydroxide, **2a** is obtained predominantly.[4] In this case the corresponding chelated form **9** (R = Na) is improbable.

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A Simple Preparation of a 2-Lithiopropenal Equivalent

Marcus A. Tius,* Donald P. Astrab, and Xue-qin Gu

Department of Chemistry, 2545 The Mall, University of Hawaii, Honolulu, Hawaii 96822

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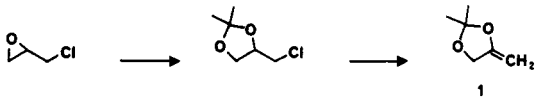
A number of acrolein enolate and acrylate ester enolate equivalents have been developed in recent years.[1] The need for efficient syntheses of α-methylene-γ-butyrolactones provided the impetus for the development of these reagents. All of the acrolein enolate equivalents which have been described to date require the unmasking of the carbonyl group subsequent to the nucleophilic addition step. A more direct approach would be to use the enolate of acrolein itself. Although several studies have described the preparation of 1,2-propadien-1-ol as a transient intermediate,[2] the corresponding alkoxide salt has remained unknown. In connection with our study of alkoxyallenes,[3] we required an efficient synthesis of a 2-lithiopropenal eqivalent (**2**). We report a convenient method for generating this anion.

The starting material for **2** was 2,2-dimethyl-4-methylene-1,3-dioxolane (**1**) which was prepared from epichlorohydrin and acetone according to known procedures[4] (eq 1). Dioxolane **1** was stable to storage at −10



(1)

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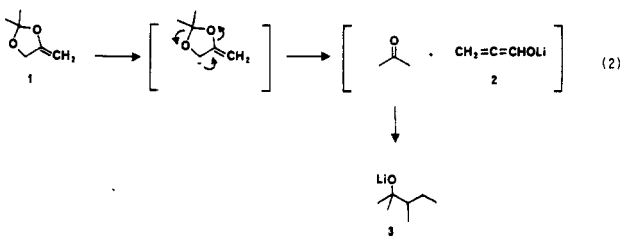
°C for several weeks.[5] Treatment of **1** with ca. 2 equiv of *sec*-butyllithium in tetrahydrofuran at −78 °C for 20–30 min produced a solution of anion **2** (eq 2).[6] Allylic de-



(2)

protonation was followed by fragmentation to **2** and acetone. The addition of the second equivalent of *sec*-butyllithium to acetone took place more rapidly than either proton transfer from acetone to **2** or nucleophilic addition of **2** to acetone. The stable solution of **2** which was obtained in this manner was suitable for addition to electrophiles.

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