the integrated areas of their vinyl signals in the ^1H NMR spectra (60 MHz).

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Registry No. 1, 82730-02-7; 2, 82730-03-8; 3, 82679-53-6; 4, 82729-99-5; 5, 82679-54-7; 6, 82730-00-5; 7, 82730-01-6; 8, 40420-35-7; naphthalene, 91-20-3; 1,3-cyclohexadiene, 592-57-4; 9,10-dihydro-9,10-ethenoanthracene, 2734-13-6; 2-naphthaldehyde, 66-99-9; xanthone, 90-47-1; acetophenone, 98-86-2; acetone, 67-64-1.

Insertion of Carbon Monoxide into Carbon–Lithium Bonds. A Convenient One-Step Synthesis of 1,2-Diketone Diaryl Derivatives[1]

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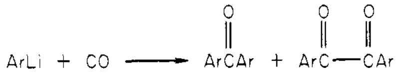
The insertion reaction of carbon monoxide into a two-center, two-electron metal–carbon bond is an extremely important transformation in organometallic chemistry.[2] Attention has recently focused on organometallic complexes of early transition metals[3,4] and actinides.[5,6] We recently reported the convenient insertion reaction of CO into the metal–carbon bond of phenyllithium to obtain α,α-diphenylacetophenone in a high yield (94%)[7] and the usefulness of the insertion reaction for the production of diphenylalkyl carbinols.[8] With the aim of exploring the scope of these interesting reactions, the behavior of 1-naphthyl- (**1a**) and (2,6-dimethylphenyl)lithium (**1b**) under several reaction conditions was examined. Only two products are formed (eq 1), and, in this sense, the reaction



$$\underset{1}{\mathrm{ArLi}} + \mathrm{CO} \longrightarrow \underset{2}{\mathrm{Ar\overset{O}{\overset{\|}{C}}Ar}} + \underset{3}{\mathrm{Ar\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}Ar}} \qquad (1)$$

a, Ar = 1-naphthyl; b, Ar = 2,6-dimethylphenyl

differs considerably from the previously studied reaction of phenyllithium with carbon monoxide in ethyl ether, for which several products were isolated.[9] The reaction of **1a** produces bis(1-naphthyl) ketone (**2a**) and 1,1-binaphthoyl (**3a**), and the reaction of (2,6-dimethylphenyl)lithium affords bis(2,6-dimethylphenyl) ketone (**2b**) and bis(2,6-dimethylphenyl)glyoxal (**3b**).

Table I. Yields from Reaction of 1-Naphthyllithium with Carbon Monoxide[a]

temp, °C	THF 2a	THF 3a	$(C_2H_5)_2O$ 2a	$(C_2H_5)_2O$ 3a	$CH_2(OCH_3)_2$ 2a	$CH_2(OCH_3)_2$ 3a	n-C_6H_{14} 2a	n-C_6H_{14} 3a
−78	22.7	71.2[b]	32.7	58.2	32.9	61.1		
0	17.0	74.9	57.2	34.7	55.0	40.0	<1	<1
25	12.2	82.7	55.3	37.7	47.6	45.3	<1	<1

[a] The reported yields represent percent conversion.
[b] 96.1% in HMPT/THF (20:80, v/v).

Table II. Yields from Reaction of (2,6-Dimethylphenyl)lithium with Carbon Monoxide[a]

temp, °C	THF 2b	THF 3b	$(C_2H_5)_2O$ 2b	$(C_2H_5)_2O$ 3b	$CH_2(OCH_3)_2$ 2b	$CH_2(OCH_3)_2$ 3b
−78	<1	96.4	18.3	75.7	17.1	74.4
0		96.1	31.0	62.8	28.3	64.7
25		97.5	33.2	61.6	30.5	63.8

[a] The reported yields represent percent conversion.

Table I gathers the results obtained from the reaction of **1a** at 1 atm of CO pressure. No CO absorption takes place in hexane solution at −78 °C, and the reaction is practically negligible even at higher temperatures. For the oxygenated solvents, no regular temperature effect is observed. The best result is obtained for the reaction in THF solution at 25 °C, for which a high yield of **3a** is found. The yield is improved to 96.1% when the reaction is run in HMPT/THF (20:80) at −78 °C. In the case of **1b** (Table II) the production of compound **3b** is always higher than of **3a**, and the conversion is almost complete in THF.

In the reaction of these aryllithiums the initial formation of a highly reactive acyllithium intermediate (5, eq 2) can

$$\mathrm{ArLi} + \mathrm{CO} \rightleftharpoons \underset{4}{[\mathrm{ArLi} \leftarrow :\mathrm{CO}]} \rightleftharpoons \underset{5}{[\mathrm{Ar\text{-}C(O)\text{-}Li} \leftrightarrow \mathrm{Ar\text{-}C\text{-}OLi}]} \qquad (2)$$

be postulated as was recently proposed for the reaction of other aryllithiums (Ar = o-anisyl, p-tolil, and o-tolyl).[10] Evidence for the existence of benzoyllithium has been previously reported.[8,11] Alkoxy carbenes are nucleophilic in character,[12] and dimerization to form olefins is a well-characterized phenomenon.[13] Nevertheless, naphtoin is not isolated from the insertion reaction of **1a**, but its oxidation product, **3a**, is. Oxidation could occur in the reaction flask (carbon monoxide is known to be an effective oxidant toward a variety of aromatic radical ions and dianions)[14] or during the hydrolytic workup. Treatment of the reaction mixture of **1a** and carbon monoxide with acetic anhydride produces 1,2-diacetoxy-1,2-bis(1-naphthyl)ethene (**7a**, eq 3). This proves that the intermediate is the corresponding 1,2-dilithiumdiolate **6a** (formed by dimerization of **5a**) and that oxidation occurs

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[1] Presented in part at the 2nd Argentine Meeting on Physical Organic Chemistry, V. Giardino, Córdoba, Argentina, Oct 1981.

[2] (a) Parshall, G. W. "Homogeneous Catalysis"; Wiley: New York, 1980; Chapter 5. (b) Eisenberg, E.; Hendrickson, D. E. *Adv. Catal.* **1979**, *28*, 79.

[3] (a) Wolczanski, P. T.; Bercaw, H. E. *Acc. Chem. Res.* **1980**, *13*, 121 and references therein. (b) Calderazzo, F. *Angew. Chem., Int. Ed. Engl.* **1977**, *12*, 299.

[4] (a) Marsella, J. A.; Caulton, K. G. *J. Am. Chem. Soc.* **1980**, *102*, 1747. (b) Wood, C. D.; Schrock, R. R. *Ibid.* **1979**, *101*, 5421. (c) Barcaw, J. E. *Adv. Chem. Ser.*, **1978**, *No. 167*, 136.

[5] Fagan, P. J.; Manriquez, J. M; Marks, T. J. "Organometallics of the f Elements"; Manriquez, T. J., Fisher, R. D., Eds.; Reidel: Dordrecht, Holland, 1979; Chapter 4.

[6] (a) Fagan, P. J.; Manriquez, J. M.; Vollmer, S. H.; Day, C. S.; Day, V. W.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 2206. (b) Fagan, P. J.; Manriquez, J. M.; Marks, T. J.; Day, V. W.; Vollmer, S. H. *Ibid.* **1980**, *102*, 5393.

[7] Nudelman, N. S.; Vitale, A. A. *Org. Prep. Proced.* **1981**, *13*, 144.

[8] Nudelman, N. S.; Vitale, A. A. *J. Org. Chem.* **1981**, *46*, 4625.

[9] Trzupek, L. S.; Newirth, T. L.; Kelly, E. G.; Nudelman, N. S.; Whitesides, G. M. *J. Am. Chem. Soc.* **1973**, *95*, 8118.

[10] Nudelman, N. S.; Vitale, A. A.; Pérez, D. *F.A.C.E.N.A.*, in press.

[11] Nudelman, N. S.; Vitale, A. A., *J. Organomet. Chem.*, in press.

[12] Wanzlik, H. W. *Angew. Chem., Int. Ed. Engl.* **1962**, *1*, 75.

[13] Baron, W. J.; Decamp, M. R.; Hendrick, M. E.; Jones, M.; Levin, P. H.; Sohn, M. B. "Carbenes"; Jones, M., Moss, R. A., Eds.; Wiley: New York, 1973; Vol. 1, p 128. Kirmse, W. "Carbene Chemistry"; Academic Press: New York 1971; Chapter 3, Section E.

[14] Buchner, W. *Chem. Ber.* **1966**, *99*, 1485.

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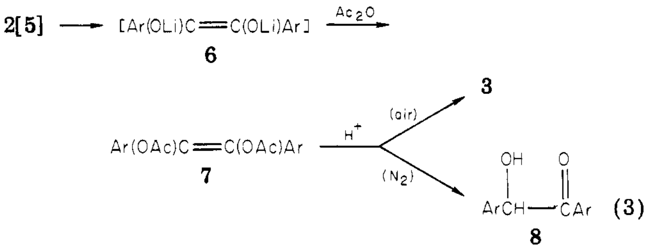

during the hydrolytic procedure. **8a** could only be obtained when special care was taken to avoid any air contamination. Similar properties are exhibited by 2,6-dimethylbenzoin (**8b**) formed in the reaction of **1b**.

Formation of the ketones **2a** and **2b** can be envisaged in the same way proposed for the production of benzophenone in the CO insertion reaction of phenyllithium, i.e., by oxidation of the dilithium dianion produced from the reaction of **5** with another molecule of aryllithium.[11] Again, the oxidation was proved to occur during the hydrolytic workup, with CO–H_2O as the oxidant. When a mixture of **1a** and **1b** in THF at 0 °C is flushed with CO, a mixed benzil derivative [the (1-naphthyl)(2,6-dimethylphenyl)glyoxal] is produced in addition to the expected products **2** and **3**; this provides further support to the intermediation of the acyl **5**.

Experimental Section

Proton NMR spectra were recorded on a Varian XL-100 spectrometer. Mass spectra were determined on a Varian MAT CH7 spectrometer at an ionization potential of 70 eV. IR spectra were recorded with a Perkin-Elmer 137. Melting points are uncorrected. 1-Bromonaphthalene was distilled at 118–120 °C (1 mmHg), and the distillate was passed under pressure through a basic alumina chromatographic column. All the solvents were purified as previously described and distilled from the dark blue solution of benzophenone ketyl under nitrogen immediately before use. Carbon monoxide was generated and purified as previously described.[7] **1a** was prepared by adding 1.1 mL (8 mmol) of 1-bromonaphthalene to a serum-capped test tube containing an hexane solution of butyllithium (8 mmol). The reacting mixture was heated at 70 °C for 20 min. The resulting white crystals were centrifuged and washed three times with hexane, and the remaining solvent was distilled under vacuum until a white dry powder was obtained. **1b** was prepared from 2,6-dimethyliodobenzene and butyllithium in hexane at 0 °C, the resulting white crystals were purified in the same way as **1a**. **1** prepared by these methods can be stored unaltered for several months if kept in a freezer and protected from light.

Reaction of 1a and 1b with Carbon Monoxide. The general procedure described for phenyllithium was followed.[11] In the present case, the absorption of CO was complete within 10 min at 0 °C. The reaction mixture was worked up as previously described and was analyzed by GLC on a 3% SE-30 Chromosorb W column. The reaction products were also isolated by column chromatography and fully characterized by their melting points and spectroscopic characteristics, as compared with those of authentic samples. When the reaction was carried out in the presence of 1.5 equiv of Dabco, no CO absorption occurs, thus confirming the previous finding that CO–lithium coordination is the first activation step for these reactions.[11]

1,1′-Dinaphthoyl- (3a) and Bis(2,6-dimethylphenyl)glyoxal (3b). Compound **3a** can be prepared from the reaction of CO with **1a** in a solution of HMPT/THF (20:80 v/v) at −78 °C and **3b** from the same reaction with **1b** in THF at room temperature. Under these conditions only **3** is formed, which can be easily isolated in 96.1% and 96.5% yields for **3a** and **3b**, respectively. **3a** was crystallized from hexane–ethyl acetate [mp 192–194 °C (lit.[15] mp 190–191 °C)] and of **3b** with hexane, gives yellow plates, mp 151–153 °C (lit.[16] mp 153–154 °C cor).

1,2-Diacetoxy-1,2-bis(1-naphthyl)ethene (7a) and 1,2-Diacetoxy-1,2-bis(2,6-dimethylphenyl)ethene (7b). Compound **7** can be isolated from the reaction mixture of **1** with CO quenched by acetic anhydride. Hexane (5 mL) was added, the mixture was washed three times with water and dried, and the solvent was distilled. By successive addition of hexane and evaporation, white crystals of **7** were obtained. Compound **7a** was recrystallized from a hexane-saturated solution of ethyl acetate: mp 249–251 °C; IR (Nujol) 1780 (C=O), 1590 (C=C) cm^{-1}; MS (70 eV), *m/e* (relative intensity 396 (M^+, 13), 354 (M^+ − ketene, 12), 312 (M^+ − 2 ketene, 100), 127 (Ar^+, 23); yield 65.2%. **7b** was recrystallized from hexane: mp 190–195 °C (lit.[16] mp 196–167 °C); yield 42.3%.

Di-1-naphthyl Ketone (2a). A solution of **1a** (3.6 mmol) in THF was added at 0 °C to a THF solution of 1-naphthonitrile (500 mg) prepared by standard methods.[17] The mixture was allowed to warm to room temperature and stirred for 30 min. Concentrated sulfuric acid (10 mmol) in water (5 mL) was added, and the mixture was heated under reflux for 30 min and added dropwise to ice–water. Extraction with ethyl ether and solvent distillation give a noncrystallizable oil that was passed through a silica gel H column by pressurized hexane elution. Distillation of the solvent gives white crystals, mp 100–101 °C (lit.[18] mp 103–104 °C cor).

2,2′,6,6′-Tetramethylbenzophenone (2b). Ethyl formate (0.081 mL, 1 mmol) in hexane (1 mL) was added dropwise to a suspension of **1b** (2.5 mmol in 10 mL of hexane), and the mixture was stirred for 30 min at room temperature. Water (2 mL) was added and the hexane distilled at reduced pressure. A solution of potassium dichromate (0.33 mmol) in acetic acid (10 mL) plus a few drops of sulfuric acid was added to the resulting mass, and the mixture was stirred 10 min at room temperature, added dropwise to ice–water, and extracted with hexane. The Cr^{VI} oxidation procedure was repeated to complete the reaction. After the workup white crystals of compound **2b** [mp 133–134 °C (lit.[19] mp 134 °C)] are obtained.

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Registry No. 1a, 14474-59-0; **1b**, 63509-96-6; **2a**, 605-78-7; **2b**, 14252-21-2; **3a**, 3457-41-8; **3b**, 1225-22-5; **7a**, 82679-07-0; **7b**, 82679-08-1; CO, 630-08-0.

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(15) Mondodoev, G. T.; Przhiyalgouskaya, N. M.; Belov, V. N. *Zh. Org. Khim.* **1965**, *1*, 2008.

(16) Fuson, R. C.; Soctt, S. L.; Horning, E. C.; McKeever, C. H. *J. Am. Chem. Soc.* **1940**, *62*, 2091.

(17) Blicke, F. F. *J. Am. Chem. Soc.* **1927**, *49*, 2848.

(18) Schmidlin, J.; Massini, P. *Ber.* **1909**, *42*, 2388.

(19) Coops, J.; Nauta, W. T.; Ernsting, M. J. E.; Faber, A. C. *Recl. Trav. Chim. Pays-Bas* **1940**, *59*, 1109.

Syntheses of the 5,6-Trimethylene-*exo*- and -*endo*-9-norbornanols

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During our studies of the metabolism of the jet fuel JP-10 [*exo*-5,6-trimethylenenorbornane (**1**)], it was necessary to synthesize *exo*-5,6-trimethylene-*exo*-9-norbornanol (**2**) and exo-5,6-trimethylene-*endo*-9-norbornanol (**3**). Both sodium borohydride ($NaBH_4$) reduction and catalytic hydrogenation (platinum on carbon) of *exo*-5,6-trimethylene-9-norbornanone[1] (**4**) yielded only one product

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(1) Brown, H. C.; Periasamy, M. *J. Org. Chem.* **1981**, *46*, 3166.