Pergamon

Tetrahedron Vol. 50, No. 16, pp. 4651-4666, 1994
Elsevier Science Ltd
Printed in Great Britain
0040-4020/94 $6.00+0.00

0040-4020(94)E0189-Z

Electron Transfer in the Reactions of Aryllithium Compounds with Carbon Monoxide

N. Sbarbati Nudelman* and Fabio Doctorovich

Depto. Química Orgánica, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Pab. II, P. 3,
Ciudad Universitaria, 1428 Buenos Aires, Argentina.

Abstract: the reactions of aryllithium compounds (Ar= phenyl, 1-naphthyl, xylyl, mesityl) with CO have been studied under several reaction conditions. A ^{13}C NMR method developed to determine radicals at preparative concentrations revealed the presence of radical anions in the reaction mixtures in concentrations comparable to those of the reagents. ESR spectroscopic studies, the effect of radical inhibitors, kinetic measurements and isolation of derivatives of some intermediates suggest a mechanism that involves electron transfer as the first and rate determining step of the reaction.

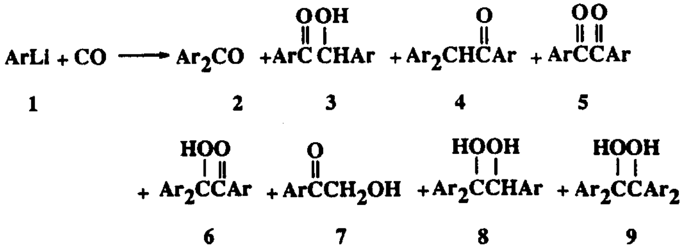
INTRODUCTION

There is a growing recognition of the occurrence of electron transfer in organic chemistry,[1] based on experimental[2-4] and theoretical[5] evidence. Several early studies involved organometallic compounds,[2a-c,3d] but many classical organic reactions, which appear to be simple polar reactions, are being shown to involve several steps in which electron transfer plays a role.[2a,2d,3c,4b] On the other hand, reactions of carbon monoxide with radicals have been recently reported,[6] as well as other studies of reactions involving carbon monoxide and organometallics, in the synthesis of oxygenated fine chemicals[7] or as a model for the elucidation of intermediates in heterogeneous catalysis.[8]

The synthetic usefulness of the reactions of aryllithium compounds,[9] alkyllithium compounds,[10] as well as of lithum amides[11] with carbon monoxide has been recently demonstrated. Nevertheless, no recent research on the mechanisms of these reactions has been carried out. As a matter of fact, these mechanisms were always[9-11] written as conventional polar transformations, as was originally proposed in the first mechanistic study of reactions involving phenyllithium and carbon monoxide.[12] Nevertheless, we have recently reported the observation of paramagnetic intermediates in relatively high concentrations in this reaction.[13a] The present paper describes similar observations for the reactions of other aryllithium compounds with carbon monoxide, as well as additional evidence, which suggests electron transfer to be involved in these reactions. This study also provides understanding as to the routes of formation of some by-products whose origin was uncertain in earlier reports.[12]

RESULTS

Products. GC analysis of the reaction mixture of phenyllithium, **1a**, with CO in ethyl ether led to identification of a number of compounds: benzophenone, **2a**; benzoin, **3a** (originally reported as benzyl, **5a**);[12] and α,α-diphenylacetophenone, **4a** were the main reaction products. Those products formed in minor amounts were: α,α-diphenyl-α-hydroxyacetophenone, **6a**; α-hydroxyacetophenone, **7a**; triphenylglycol, **8a** and benzopinacol, **9a** (eq. 1). (Although aryllithium compounds are known to be aggregated in solution,[9] they will be written as monomers throughout this paper, for the sake of clarity).

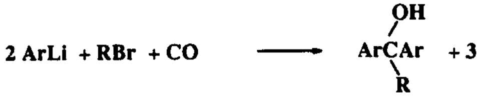


$$\underset{1}{ArLi} + CO \longrightarrow \underset{2}{Ar_2CO} + \underset{3}{Ar\overset{O}{\overset{\|}{C}}\overset{OH}{\overset{|}{C}}HAr} + \underset{4}{Ar_2CH\overset{O}{\overset{\|}{C}}Ar} + \underset{5}{Ar\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}Ar} \qquad (1)$$

$$+ \underset{6}{Ar_2\overset{HO}{\overset{|}{C}}\overset{O}{\overset{\|}{C}}Ar} + \underset{7}{Ar\overset{O}{\overset{\|}{C}}CH_2OH} + \underset{8}{Ar_2\overset{HO}{\overset{|}{C}}\overset{OH}{\overset{|}{C}}HAr} + \underset{9}{Ar_2\overset{HO}{\overset{|}{C}}\overset{OH}{\overset{|}{C}}Ar_2}$$

The reaction is extremely sensitive to variables such as: concentration of the reagent, temperature, solvent, etc. Table 1 shows a few examples of the several reaction conditions examined in the present work. Other reaction conditions that lead to the production of **2a**, **3a** or **4a** in relatively high amounts were previously reported.[14b,c]

When the reaction was carried out in the presence of an alkyl bromide (in THF at -78°C), the corresponding diarylalkylcarbinol, **10**, was the main product, and only **3** was detected as a by-product in variable amounts[15a,b] (eq. 2, Table 1).



$$2\,ArLi + RBr + CO \longrightarrow Ar\underset{R}{\overset{OH}{C}}Ar + 3 \qquad (2)$$

10 (60-80%)

On the other hand, when alkyl chlorides were used instead of alkyl bromides, the product distribution was the same as the one obtained in the **absence** of alkyl chlorides. On the other hand, when the carbonylation was carried out in the presence of alkyl iodides, the aryl-alkyl coupling was the predominant pathway.

The reaction of sterically hindered aryllithium compounds such as 1-naphthyl-, **1b**,[14a] m-xylyl-, **1c**,[14a] and mesityllithium, **1d**, with CO in THF at room temperature produces mainly 1,2-diketones, **5** (which arise from air oxidation of the corresponding "aroins", **3**), and only small amounts, if any, of the diarylketone, **2**. The change to ethyl ether as the solvent in the reaction of naphthyllithium with CO inverted the relative yields of dinaphthylketone, **2b**, and naphthyl, **5b** (Table 1).

Table 1. Reaction of Aryllithium Compounds with CO. Main Products.

ArLi	[ArLi], M	Reaction Conditions	% Conversion							
			4	**2**	**5**	**3**	**8**	**6**	**7**	**10**
PhLi	0.70	ether/-78°C	7	26					40	
	-	solid/110°C	94							
	0.50	THF/25°C	31	18		16	10	17		
	0.50	THF/-78°C				40				
	0.50	hexane/25°C	53	23			14			
	0.50	THF/n-BuBr/-78°C				20				80[a]
	0.50	THF/n-BuI/-78°C[b]								
NpLi[c]	0.40	THF/25°C		27	63					
	0.40	ether/25°C		55	38					
	0.40	THF/s-BuBr/25°C		12	39					29[d]
MesLi[e]	0.70	THF/25°C			93					

[a] R= n-BuBr. [b] PhBu was the only product found (80%). [c] Np= 1-naphthyl. [d] $Ar_2C(OR)R$, R=s-BuBr. [e] Mes= mesityl.

^{13}C NMR Detection of Radical Intermediates.

The determination of radicals in the dilute solutions used to carry out UV or EPR measurements is not incontrovertible evidence that they are true reaction intermediates.[16,17] We have recently developed a ^{13}C NMR method useful to determine radical anions in concentrations similar to those found under preparative conditions.[13b] The method is based on the interaction between radical anions and THF molecules and the effect of added co-solvents. Screttas and Screttas[18] reported that the α and β carbon ^{13}C NMR signals of THF are shifted to higher fields from the position of resonance of neat solvent when lithium benzophenone ketyl, **11a**, is present. Also, we have found that both THF ^{13}C NMR carbon signals are broadened by the presence of **11a** and other radical anions, the broadening being proportional to the radical concentration in the range 0.2-1.2 M. This broadening may be enhanced by the addition of benzene.[13b] Fig. 1 shows the plot of the bandwidth of the α-carbon signal of THF ($\Delta\nu$) as a function of [**11a**]. A straight line is obtained in pure THF, but it can be observed that, in spite of **dilution** and the fact that the solute is **diamagnetic** in pure benzene,[19] additions of small amounts of benzene to the THF solutions result in important increases in the bandwidth, up to certain [benzene]:[THF] ratio. Measurements of the T_1 and T_2 relaxation times under several conditions proved that the phenomenon is due to a specific interaction (any spurious cause such as impurities, low solubility, field inhomogeneities, etc. were carefully examined and excluded).[13b] This behavior was also observed for other radical anions and it provides a highly reliable method for the determination of radical anion concentrations. Table 2 shows some results obtained in the reactions of phenyllithium, 1-naphthyllithium, and mesityllithium with CO. Since the reaction conditions affect the relative distribution of products, Table 2 shows the ^{13}C NMR results of the reaction mixtures of **1a**, **1b**, and **1e** with CO carried out under different reaction conditions.

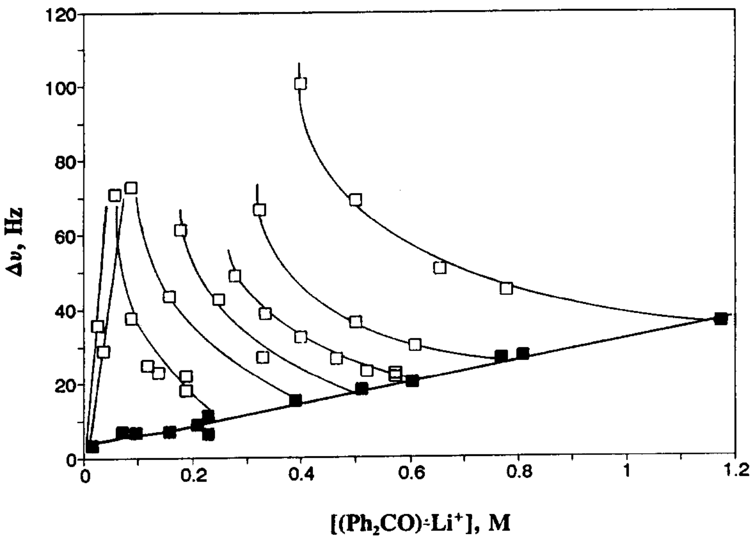


Figure 1. ^{13}C NMR bandwidth of the α-carbon of THF in the presence of lithium benzophenone ketyl, **11**, as a function of [**11**]. ■ pure THF; □ THF-benzene.

Table 2. Reaction of ArLi with CO. ^{13}C-NMR Bandwidth of the α-Carbon of THF.

ArLi	Reaction Conditions	[ArLi][a]	Δυ[b]	$Δυ_m$[c]	["Ar•"][d]
Phenyllithium	ether/-78°C	0.75	7.0	9.4	0.23
	solid/110°C	1.67	9.6	5.8	0.31
	THF/25°C	1.00	23.8	23.8	0.78
		0.67	12.8	19.1	0.42
		0.33	5.1	15.4	0.17
	THF/n-BuBr/-78°C[e]	1.00	2.0	2.0[g]	<0.02
	hexane/25°C	0.66	11.8	17.8	0.39
1-Naphthyllithium	THF/25°C	0.80	12.0	15.0	0.18
	ether/25°C	0.83	8.6	10.4	0.13
	THF/s-BuBr/25°C[f]	0.48	2.0	2.0[g]	<0.02
Mesityllithium	THF/25°C	0.70	3.2	4.6	0.10

[a] Final molarity of the lithium derivative after diluting the reaction mixture with THF, considering THF as the only solvent. [b] Experimental bandwidth. [c] Δυ per mol of ArLi. [d] Estimated overall radical concentration. [e] [PhLi]:[n-BuBr]=1:3. [f] [1-naphthyllithium]:[s-BuBr]=1:2. [g] No bandwidth broadening was observed.

Assuming, in a first approximation, that all the paramagnetic species present in the reaction mixture, have the "response" of the corresponding diarylketyl (30.6 Hz/mol for benzophenone ketyl, **11a**, and 66.6 Hz/mol for the dinaphthoyl ketyl, **12b**) the overall radical anion concentrations present in the reaction mixtures, ["Ar$^{\cdot-}$"], were calculated and they are shown in the last column of Table 2: it can be observed that in most cases ["Ar$^{\cdot-}$"] are in the range of [ArLi]. We must emphasize that this is only a semiquantitative value, as other radicals of different responses could be present in the reaction medium.

Regarding the reaction of **1b**, the results plotted in Figure 2 show a close correspondence between the slope of the line ($\Delta\upsilon$ vs. concentration) due to 1,1'-binaphthoyl-anion, **12b**, and that corresponding to the reaction mixture of **1b** and CO, in spite of the fact that there is probably a $2e^-$ difference between the radical anions present in each solution.

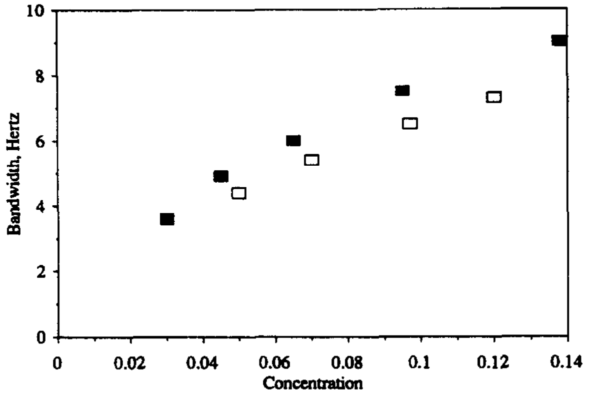


Figure 2. ^{13}C NMR bandwidth of the α-carbon of THF in the presence of: a) lithium naphthoyl, **12b** (■), and of b) the reaction mixture of 1-naphthyllithium, **1b**, with CO (□), as a function of [**12b**], and [**1b**]$_i$, respectively.

Two additional criteria were applied for the examination of paramagnetic species present in the reaction mixtures: the nuclear Overhauser (NOE), and the benzene effects. In addition to bandwidth broadening, the presence of radical species produces the disappearance of the NOE that induces changes in the relative intensities of the signals, even at low radical concentrations. On the contrary, when the reactions were carried out in the presence of alkyl halides no broadening was observed and the NOE was normal. Finally, treatment of the reaction mixture solutions in THF with benzene, shows the peculiar behavior depicted in Fig. 1.

EPR Studies

Table 3 shows the hyperfine splitting constants (hfsc) of several experimental EPR spectra and also the calculated hfsc of likely intermediates. It was observed that the EPR spectrum of the reaction mixture of **1a** with CO in THF is very similar in the number of lines, width, and shape compared to the spectrum of benzophenone ketyl (**11a**) in the same solvent.[13a] A similar EPR spectrum was obtained from the reaction mixture of **1a**+ CO, carried out in ethyl ether at -78°C, which does not produce benzoin, **3a**, but does produce benzophenone, **2a**. Simulation of the EPR spectrum with a computer program developed by Joela[20] gave a spectrum almost coincident with that of the reaction mixture (hfsc shown in Table 3). The small differences in the hfsc values could be attributed to coordination of benzophenone ketyl with CO, since it has been observed in the case of phenyllithium that the amount of CO consumed is higher than that expected taking into account the amounts of carbonylated products observed. The gas phase electron densities at each carbon of **11a** and of other likely radical intermediates were calculated and the resulting hfsc given by the McConnell relation are gathered in Table 3. Since calculations do not take into account the solvent effects, there is not exact agreement between experimental and calculated values, but both show the trend $a_p > a_o > a_m$. Although, in principle, the EPR spectrum of the radical anions of **3a** and of **5a** would also be consistent with this hyperfine structure, the experimental EPR of the benzyl radical anion[21] is very different and the calculated hfsc of the radical trianion of **3a** shows an inverted trend, $a_p > a_m > a_o$ (Table 3). In conclusion, the EPR spectra of the reaction mixtures seem to indicate that the lithium benzophenone ketyl, **11a**, is an important reaction intermediate.

Table 3. Carbonylation of Phenyllithium. Hfsc of some Reaction Intermediates.

Compound	hfsc (G)			Source
	o-	*m-*	*p-*	
1a + CO (THF)	2.72	1.02	3.38	Exptl.
11a	2.712	0.938	3.536	Exptl.
11a	1.35	0.19	2.02	Simulated[a]
$[PhC(OLi)=C(OLi)Ph]^{\cdot-}Li^+$	0.77	0.91	3.60	Simulated[a]
$[PhC(O)C(O)Ph]^{\cdot-}Li^+$	0.97	0.39	0.97	Exptl.[b]
$(PhCOLi)^{\cdot-}Li^+$	3.40	<0.05	3.40	Exptl.
$(PhCOLi)^{\cdot-}Li^+$	3.044	0.046	3.226	Simulated[c]

[a]MMX/MMPi (PCMODEL) method. [b]Ref. 21 (c). [c]Huckel method.

1-Naphthyllithium reacts with THF at room temperature.[22] Nevertheless, this reaction is very slow for the time scale of the reaction of 1-naphthyllithium with CO and does not interfere with the measurements if care is taken to avoid long contacts between **1b** and THF prior or after the reaction is carried out. Lithium 1,1'-binaphthoyl radical, **12b**, was independently prepared and its EPR spectrum determined at different concentrations. In all cases poorly resolved spectra were obtained, which is reasonable, taking into account the amount of lines that should be expected and the width of the whole spectrum (10 G). Nevertheless, the observation of EPR signals in the reactions of naphthyllithium, **1b**, with CO, is a good indication of the presence of radicals in these reactions.

Kinetic Measurements

The kinetics of the reaction between **1b** and THF was studied spectrophotometrically using the method of initial rates to estimate the rates of reaction. The complete results will be published elsewhere.[22] The reaction was found to have a kinetic order equal to 0.71 with respect to **1b** and 2.21 with respect to THF. These fractional orders are indicative of aggregates, which are common in organolithium reagents.[9] The relative orders indicate a ratio [**1b**]:[THF]=1:3. The observed rate constant is: $k=1.6\ 10^{-4}\ s^{-1}$, which is at least 10^4 smaller than the rate constant due to the reaction of **1b** with CO.

The rate of reaction of **1b** with CO was found to be of second order; first order in both **1b** and CO; the overall rate constant under these conditions (25°C) is $6.63 \pm 0.35\ M^{-1}s^{-1}$. These results suggest that one molecule of 1-naphthyllithium and one molecule of carbon monoxide are involved in the rate-determining step of the reaction.

Reactions in the presence of Radical Inhibitors

Quinones and hydroquinones can produce stable radicals by one electron uptake or donation. The reaction of naphthyllithium with CO in THF at 25° C was examined in the presence of p-benzoquinone, **15**, hydroquinone, **16**, quinhydrone **17** and tetramethylpiperidine-N-oxyl (TEMPO), **18**, as radical inhibitors. The % of inhibition was calculated as the decrease in CO uptake, taking into account the volume of CO (7.4 mL) consumed under normal conditions (Table 4). It can be observed that quinhydrone (**17**) is a more efficient inhibitor than **15** or **16**, while the mixture of **15**+**16** (1:1) is more effective than any of the separate inhibitors. The % yield of deuterated naphthalene indicates the amount of unreacted 1-naphthyllithium and/or of naphthyl radical recovered after hydrolysis with D_2O.

Although **15** and **16** can react with organolithium compounds, **1**, the addition reactions are slow under the present reaction conditions (It has been found, for instance, that 1,2-addition of **1a** to **15** requires 8 hrs),[25,26] and in all cases they occur in an amount not greater than 15%. In fact, when a mixture of **1b** with **15** in THF was kept at room temperature and then hydrolyzed with D_2O, 86% of naphthalene-d_1 was obtained; the same reaction with **16** or with **17** gave 87% and 84% of naphthalene-d_1, respectively. These results are consistent with those shown in Table 2.

It is shown in Table 4 that the known radical trap TEMPO, **18**, is not so appropriate for this reaction. In fact, 10 % of TEMPO does not produce a noticeable effect; indeed, relatively high amounts are needed to considerably decrease the CO absorption and the concomitant disappearance of the classical brown color of the reaction mixture. Further treatment of the reaction mixture with D_2O results in recovery of almost 90% of undeuterated naphthalene. On the other hand, dibenzalacetone, another radical inhibitor, does not produce an important effect.

DISCUSSION

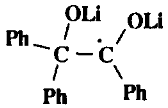
In the previous mechanistic study of the reaction of phenyllithium with CO, the benzophenone dianion, **13a**, was proposed as the possible precursor of **2a** and **4a**.[12] Partial oxidation of **13a** by CO was proposed to occur in dilute solutions producing lithium benzophenone ketyl, **11a**, (detected by UV determinations), which would produce **9a** by coupling. Nevertheless, not even traces of **9a** were found when **11a** or **13a** were treated with CO in ethyl ether.[12] The mechanism of formation of **5a** and **7a** was also unclear.

(Ar$_2$CO$^{\cdot-}$)Li+

11

12

13



14a

TABLE 4. Reaction of 1-Naphthyllithium with CO in THF at 25°C in the Presence of Radical Inhibitors.

Run	Inhibitor	Amount[b] mg	Inhibitor/**11**[c] %	V_{CO}[d] ml	Inhibition[e] %	NafD[f] %
1	-	-	-	7.4	0	
2	**15**	4.0	6.0	5.0	32	
3		7.0	10.5	2.3	66	
4		10.0	15	0.8	88	85
5	**16**	4.0	6.0	4.9	34	
6		10.0	15.0	2.0	73	87
7		7.0[g]	10.5	3.8[h]	62	
8	**17**	2.0	1.5	5.0	32	
9		4.0	3.0	3.7	50	
10		8.5	6.4	1.1	85	82
11	**15**+**16** (1:1 ratio)	3.0	4.5	1.6	78	
12	TEMPO, **18**	9.3	10.0	6.5	12	
13		22.0	23.0	0.7	90	0
14		63.0	65.0	0.8	89	
15		97.0	100	1.0	86	
16	Dibenzalacetone	20.0	14.2	6.9	7	

[a] In all cases 1.5 ml of a solution 0.4 M of 1-naphthyllithium (or PhLi) in THF were used. [b] Weight of trap in 1.5 ml of a 0.4 M solution of 1-naphthyllithium in THF. [c] Moles of trap per 100 moles of 1-naphthyllithium. [d] Volume of CO absorbed in 10 min. [e] Calculated according V_{CO}. [f] % deuterated naphthalene obtained after hydrolysis of the reaction mixture with D_2O. [g] Reaction PhLi\BrPr (1:3) + CO (THF, -78°C). [h] V_{CO} in the absence of trap = 10.0 ml.

When the reaction of phenyllithium with CO is carried out in the presence of alkyl bromides in THF, the results in eq. 2 preclude the direct formation of **13a** as the first intermediate, since it was proved that **13a** does not produce **10a** under the reaction conditions of eq. 2. On the contrary, the present results demonstrate that paramagnetic species are present in the reaction mixtures.

The UV or EPR spectroscopic observation of a radical intermediate does not necessarily mean that an ET is involved in the major reaction pathway leading to products, because both techniques detect intermediates at very low concentrations and the formation of the intermediate could simply be a blind step.[2a,b] Nevertheless, the ^{13}C NMR method applied in the determinations shown in Table 2, allowed the measurement of relatively high radical concentrations. In all cases (except when the reaction was carried out in the presence of RBr) an enhancement of the normal value was observed indicating the presence of radicals that interact with THF molecules. It is shown in Fig. 1 that at a constant [benzene]:[THF] ratio the ^{13}C NMR bandwidth of the α carbon of THF is proportional to the radical anion concentration, and the slope of the line increases with the [benzene]:[THF] ratio.

It can be observed in Table 2 that the Δυ/mol value is not constant indicating the influence of reagent concentration on the relative amounts of radicals present in the reaction mixture. For the reactions of PhLi in THF, the Δυ/mol diminishes on dilution of the reagent from 1.0 M to 0.33 M. If the widening of the bandwidth is mainly due to benzophenone ketyl, then this is consistent with a previous experimental determination showing that when the initial concentration of PhLi increases from 0.2 to 1.0 M the relative yield of benzophenone also increases.[14b] It is also interesting that in the reaction of solid **1a** with CO, only **4a** is obtained as the reaction product (Table 1), and, nevertheless, a considerable broadening is observed at the end of the reaction, indicating that a paramagnetic species, probably **14a** (see previous page) is a likely precursor for **4a**. In other cases (e.g. THF, 25° C, 1.00 M) the broadening is so important (23.8 Hz) that, presumably, other radicals apart from **11a** are present.

The inhibition of CO absorption produced by radical traps such as **15**, **16**, **17**, or the mixture **15+16**, suggests that radicals are involved at the beginning of the reaction. **15** and **16** have been used as radical polymerization inhibitors.[23a] p-Benzoquinone, **15**, is an effective trapping agent for nucleophilic radicals, [23b] and more complex quinone traps have been recently studied.[24] The fact that one-electron acceptors as well as one-electron donors are effective as inhibitors in this reaction suggests that formation of radical cation-radical anion pairs might occur in the first step of the reaction.

The kinetic law found for the reaction of **1b** with CO is consistent with a first step involving the reaction of one molecule of aryllithium with one molecule of CO. This result, together with the effect produced by radical inhibitors, suggests electron transfer from the aryllithium compounds to CO, forming the radical cation-radical anion pair, **19** (eq. 3). (Most of the lithium intermediates shown in the equations are likely in the form of complexes with THF as revealed by ^{13}C NMR measurements).[13b]

Organolithium compounds have been shown to be good one-electron donors[21] to carbonyl compounds, and CO is a known electron deficient compound, and an effective one-electron oxidant toward a variety of aromatic radical ions and dianions.[12,28,29] The electron affinity of CO is 1.8 eV[30] which gives a value of -41.40 kcal/mol for the enthalpy of formation of $(CO)^{\cdot-}$. It has been shown that the enthalpy of formation of the pair $(Ar_2CO)^{\cdot-}(Na)^+$ is 30 kcal/mol smaller than the enthalpy of formation of the radical anion $(Ar_2CO)^{\cdot-}$.[34] Many recent works report ET from Grignard reagents[2a,16,21] or from organolithium compounds[31] as the first step in the addition to carbonyl compounds. Yamataka and col.[31a] reported that the magnitude of the carbonyl carbon kinetic isotope effect (KIE) as well as the absence of substituent effects in the reactions of butyllithium with carbonyl compounds suggest that the initial ET step is **rate determining**.

In the present case, the ET shown in eq. 3 would be a slow step in the overall reaction, since a huge decrease in rate is observed upon addition of lithium complexing donor bases such as DABCO or TMEDA, which suggests that lithium is involved in the activation of CO. The radical pair can then react within the cage affording the acyllithium intermediate, **20**, which is postulated to be in equilibrium with a carbenoid structure (eq. 4). Carbene-like intermediates have been reported in the reactions of actinide-[35] and other metal[7a,7c,8,36a,36b] complexes with CO and coupling of those oxy-carbene intermediates produced enediolates. On the other hand, the structures of diaryl Li-O[37a] and Li-Cl[37b] carbenoids have been recently determined.

The radical cation in **19** can partially escape the cage and react with CO giving the acyl radical cation **21**, eq. 5. (In this, and the following equations, the radical is assumed to be associated to Li^+ because of the observed Li splitting in the EPR spectra of some of the stable radical intermediates). Nevertheless, we have no way to distinguish, namely, Ar from $(ArLi)^{+\cdot}$. The kinetics of the capture of $CH_3^{\cdot}$ by CO has been recently measured and found to be 2.0 10^6 $M^{-1}s^{-1}$ in aqueous solution at 25° C.[40] The observation that some radical inhibitors have a greater than stoichiometric effect in this reaction implies the possibility of a chain mechanism: $(ArLi)^{+\cdot}$ and $(ArCOLi)^{+\cdot}$ could be the chain carrying species (eq. 5 and 6).

$$\mathrm{ArLi} + \mathrm{CO} \longrightarrow \underset{\mathbf{19}}{(\mathrm{ArLi})^{\dot{+}}(\mathrm{CO})^{\dot{-}}} \qquad (3)$$

$$(\mathrm{ArLi})^{\dot{+}}(\mathrm{CO})^{\dot{-}} \longrightarrow \underset{\mathbf{20}}{\mathrm{Ar}\overset{\overset{\displaystyle O}{\|}}{C}\mathrm{Li}} \rightleftharpoons (\mathrm{Ar}\ddot{\mathrm{C}}\mathrm{OLi}) \qquad (4)$$

$$(\mathrm{ArLi})^{\dot{+}} + \mathrm{CO} \longrightarrow \underset{\mathbf{21}}{(\mathrm{ArCOLi})^{\dot{+}}} \qquad (5)$$

$$(\mathrm{ArCOLi})^{\dot{+}} + \mathrm{ArLi} \longrightarrow \mathrm{ArCOLi} + (\mathrm{ArLi})^{\dot{+}} \qquad (6)$$

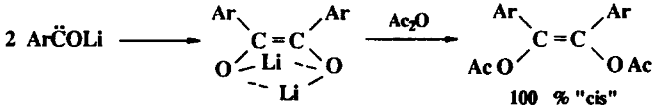
The radical Ar can also dimerize (producing Ar_2) or capture a proton from the solvent (producing the corresponding hydrocarbon). Both by-products have been detected as minor components in the carbonylation reactions: biphenyl was more important in the case of **1a**, and naphthalene in the reaction of **1b**. Although biphenyl can be usually found in old solutions of reagent **1a**, it was not detected in a blank aliquot of the fresh reagent solution that was used for carbonylation. On the other hand, naphthalene was always present as a by-product in 1-naphthyllithium carbonylation mixtures. Walling[38] reported a value of $2x10^9 s^{-1}$ for the rate of dimerization of alkyl radicals, while the rate of proton abstraction from THF by a phenyl radical was found to be 4.9 $10^6 s^{-1}$. Nevertheless, in view of the small amounts of these by-products detected, it is reasonable to assume that the reactions producing carbonylated products are faster.

Formation of Products

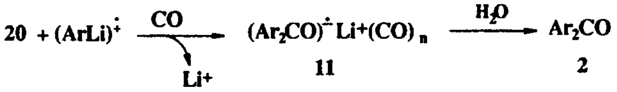
We have previously proposed[14b] that the precursor of **3a** is the cis-dilithium enolate of benzoin, **22a**, since work-up of the reaction mixture with acetic anhydride produces the (100 % *cis*) diacetate of benzoin enolate, **23a**. The high stereoespecificity of this reaction is driven by the likely structure of the intermediate **22a**; a "cisoid" configuration would allow both lithium atoms to be simultaneously coordinated to both oxygen atoms (eq. 7).

The capture of $(ArLi)^{+\cdot}$ by **20** under CO atmosphere (eq. 8), produces the ketyl **11**, which was detected by EPR of the reaction mixtures. **11a** is a highly stable radical and dimerization occurs to a very low extent giving product **9a** (eq. 1). It is proposed that the ketyl is coordinated to CO molecules which produce a one-electron oxidation to **2** during the work-up. Two ortho- substituents in the benzene ring (case of mesityl- and xylyllithium[14a]), slow down this reaction because of steric hindrance, and only compounds **3** are obtained, which rapidly oxidize to **5**.

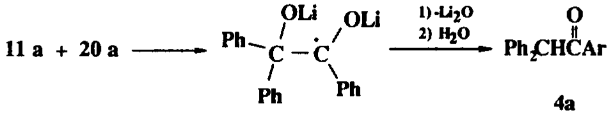
Further reaction of ketyl **11a** with the acyllithium intermediate, **20**, gives the radical intermediate **14a**, precursor of compound **4** (eq. 9). In fact, the EPR spectrum of the reaction mixture of solid **1a** with CO, which only produces **4a**, is consistent with the structure of **14a**. The absence of triarylcarbinol as a reaction product indicates this reaction is faster than the reaction of **11** with $(ArLi)^{+\cdot}$.



22 23 (7)



(8)



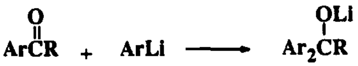
14a (9)

Reactions in the Presence of Alkyl Bromides. When the reaction of **1** was carried out in the presence of an alkyl bromide (eq. 2), no bandwidth broadening was observed in the ^{13}C NMR spectra of the reaction mixtures, (Table 2), which indicates the absence of paramagnetic species at the end of the reaction. Nevertheless, the EPR spectra of the reaction mixture **1a**+CO+RBr in dilute solutions show transient radical signals that closely resembles the EPR spectra obtained in the absence of RBr. The reaction is inhibited by the presence of radical traps (Table 4, run 7). These results are consistent with an initiation of the reaction similar to those shown in the absence of alkyl bromide (eqs. 3-4), and a competing reaction of the acyl intermediate with the alkyl bromide, followed by addition of unreacted aryllithium compound (eq. 10-11).

Electron transfer reactions between organolithium compounds and alkyl bromides are very well known giving aryl $(Ar^\cdot)$ and alkyl $(R^\cdot)$ radicals.[2a] Good yields of **10** were obtained only when RBr was in great excess ([RBr]:[**1**]= 3), and when the reaction **1a**+CO+RBr was carried out at 0°C, only the coupling reaction product PhR was obtained. The reaction of eqs. 5 and 6 has been shown to have a relatively small energy of activation[13b] (see also effect of temperature in Table 1), which is likely smaller than that of metal-halogen exchange; therefore, at 0°C, these reactions cannot compete with metal-halogen exchange.

When the reaction of **1a** was studied in the presence of an alkyl iodide, CO was absorbed, but the only product observed, even at -78° C, was the resulting coupling product. It is known that metal-iodine is faster than metal-bromine exchange; therefore, it is likely that even if the first ET were taking place, the fast decomposition of the $(\mathrm{RI})^{\cdot-}\mathrm{Li}^+$ and further reaction of $\mathrm{R}^{\cdot}+\mathrm{Ph}^{\cdot}$ overcomes the other reactions and no carbonylation products are found.

$$\mathrm{RBr} + \mathrm{Ar}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{Li} \longrightarrow \mathrm{Ar}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{R} + \mathrm{LiBr} \qquad (10)$$



$$\mathrm{Ar}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{R} + \mathrm{ArLi} \longrightarrow \mathrm{Ar_2}\overset{\mathrm{OLi}}{\overset{|}{\mathrm{C}}}\mathrm{R} \qquad (11)$$

Conclusions

The present work affords evidence that seems to indicate the occurrence of electron transfer from the aryllithium compound to carbon monoxide in the carbonylation reactions of aryllithium compounds. Kinetics indicate that the reaction is first order in aryllithium and first order in CO, while the effect of radical inhibitors suggests that a chain mechanism is involved. The first intermediate is an acyllithium that has oxycarbenoid character. Its further parallel reactions afford relatively stable intermediates which are precursors of the main three reaction products; those intermediates have been characterized spectroscopically and by their isolation as diacetates. This is the first report of electron transfer in these reactions.

Experimental

Materials. Tetrahydrofuran (THF) was purified as previously described.[11a] Benzene was distilled over sodium wire and then refluxed over lithium benzophenone ketyl and distilled immediately prior to use. Hexane was purified by refluxing with sulfuric acid (c) for 2 hrs., then distilled and stored over sodium hydroxide lentils; it was distilled over lithium benzophenone ketyl immediately prior to use. Ethyl ether was passed through a column with alumina, then refluxed over sodium benzophenone ketyl and distilled; it was stored over sodium/benzophenone and distilled immediately prior to use. Carbon monoxide was generated from the reaction of sulfuric acid with 98% formic acid and treated as previously described.[14b] Benzophenone (Fluka) was 99% pure and was used after recrystallization from ethanol. Lithium benzophenone ketyl was prepared by treatment of benzophenone in THF solution with a slight excess over the stoichiometric amount of lithium wire, as previously described.[13b] Dilithium benzophenone anion was prepared in a similar way, but using lithium wire in large excess. The concentration of the aryllithium compounds and independently prepared radicals were determined by double titration technique using ethylene 1,2-dibromide. Solid phenyllithium was prepared as described previously[14c]. ^{13}C- NMR in THF (C_6D_6 as lock solvent) (ppm) relative to the THF α-carbon signal (δ=68.2 ppm) 186.5; 143.0; 124.0; 122.2. 1-Naphthyllithium was prepared following a similar procedure, using 0.56mL (4mmol) of 1-bromonaphthalene and 4.7 mL (4 mmol) of a 0.85 N solution of n-butyllithium in hexane, at 40-50° C for 45 min. ^{13}C NMR (THF/C_6D_6)(ppm) 188.3; 140.4; 138.5; 133.7;

128.4; 128.3; 126.2; 124.0; 122.8; 121.7. Mesityllithium was prepared from the reaction of bromomesitylene with n-BuLi at room temperature for 24 hs, following the same procedure than **1b**. ^{13}C NMR (THF/C_6D_6) (ppm) 176.3; 150.3; 133.0; 123.6; 28.5; 21.7. 1,1-dinaphthoyl and di-1-naphthylketone were identified spectroscopically and by their mp 192-194 C (lit. 190-191 C) [43] and 101-102 C (lit. 103-104 °C)[44], respectively. All glassware, syringes and needles were dried in a vacuum oven and cooled in a dessicator.

Reactions with Carbon Monoxide. The reactions of aryllithium compounds with carbon monoxide were carried out according to the general procedure reported previously for **1a**.[14b] The products of the reactions of **1a**[12] and of **1b**[14a] were isolated and characterized as previously reported. The reaction of **1c** was carried out using a 0.5 N THF solution. The colorless solution turns to bright green at the beginning of the reaction changing to red after 10 min; the CO absorption was complete in 30 minutes. The reaction mixture was treated with a satd. solution of NH_4Cl. The solvent of the dried ($MgSO_4$) organic layer was removed at reduced pressure, and the yellow residue was crystallized from methanol. A 93% conversion to dimesityl-diketone, m.p. 116-117° C was obtained by GC, isolated yield 74%. Because of the difference with the reported mp (lit. 122°C)[45] **5c** was fully characterized by spectroscopic and elemental analysis. UV (THF) λ_{max} 237, 262, 286 nm. IR (nujol) cm^{-1} 1690; 1600; 1195; 1130; 835; 800. ^{1}H NMR (C_6D_6) (ppm) 6.65 (s, 2H), 2.15 (s, 6H), 2.05 (s, 3H). ^{13}C NMR (C_6D_6) (ppm) 197.9; 139.5; 135.4; 134.5; 128.8; 20.9; 20.1. C: 81.93% (calcd. 81.60%), H: 7.58% (Calcd. 7.53%)

Reactions in the Presence of Radical Inhibitors. The reactions of aryllythium compounds were carried out similarly to the general procedure already described, in a reaction flask containing a weighed amount of the inhibitor. The % inhibition was calculated as the decrease in the CO uptake taking into account the volume of CO consumed in the absence of radical inhibitors (7.4 mL). The effects of these inhibitors were also evident through a change in the brown color observed at the beginning of the reaction, to an orange-colored mixture at the end of the reaction. The % yield of deuterated naphthalene indicates the amount of unreacted 1-naphthyllithium and/or naphthyl radical recovered after hydrolysis with D_2O.The % inhibition was also checked against the GC analysis of the reaction mixture: a good agreement was found between the global product yields and the % inhibition, the ratio [**2b**]:[**4b**] obtained in the presence of 15, 16 or 17 does not change with respect to the reaction carried out in the absence of these compounds.

NMR Measurements. A Varian XL-100 NMR spectrometer was used for recording the ^{13}C NMR spectra. C_6D_6 in a concentric cell was used as external lock for measurements in pure THF. A septum-capped NMR tube was evacuated and flushed with pure N_2; several vacuum-N_2 cycles ensured the complete removal of air and its replacement by N_2. The radical anion solutions or the reaction mixtures after appropriate treatment (see below) were then syringed into the NMR tube.

The bandwidth vs. concentration relationships in each case were determined as previously described.[13b]. The spin-lattice relaxation times (T_1) were measured by the sequence 180°-t-90°-T, where t ranges between 0.5 and 2 T_1 and T is the data acquisition time. The T_1 and T_2 values were calculated following the method proposed by Sass and Ziessow.[46] It was found that application of the equation for transverse nuclear relaxation, T_{2N},[47b] shows that T_{2N}^{-1} correlates with the squares of the observed chemical shifts, $(\Delta\delta)^2$.

As stated previously, the broadening of the α-carbon signal bandwidth of THF is also solvent dependent; very little if any broadening is observed for ether or hexane. Therefore, when the reaction was carried out in a solvent different from THF, treatment of the sample was required previous to the ^{13}C NMR measurement. In those cases, THF was added to the mixture after the reaction was complete. [ArLi] in Table 2 refers to the molarity of the lithium derivative considering only THF as the solvent. The other solvent (ether or hexane) is not considered in the calculation of $\Delta\upsilon_m$ ($\Delta\upsilon$ per mol of ArLi) due to the fact that the bandwidth is a function of the THF/radical ratio, and other solvents as ether or hexane (but not benzene) do not have any measurable effect.

EPR Spectra. A Brucker ER 200t (X band) TE102 cavity was used for recording the EPR. Those were determined at room temperature using the same tubes and procedure described for the NMR measurements. The reaction mixtures in preparative concentrations (0.2-1.5 M) and in different media (solid, ethyl ether, THF) were diluted up to nearly 10^{-5} M with THF. Optimization of the final concentration was adjusted in each case. The electron densities at each carbon of **11a** were calculated by mean of the PCMODEL program that uses the MMX force field;[47a] calculation of the pi system was carried out with the MMP1.[47b] Lithium 1,1-binaphthoyl radical, **12b**, was independently prepared and its EPR spectrum run at different concentrations. The usual techniques for the manipulation of air sensitive compounds were used.[48]

Kinetic Measurements. The initial rates of reaction for different [**1b**] were measured spectrophotometrically by means of a diode array spectrophotometer. The initial concentracion of CO was equal to its solubility in the solvent used and was determined to be 8.6 10^{-3} M. The initial concentration of **1b** in these experiments was in the range 1.8 10^{-2} M to 3.0 10^{-2} M. The absorbances were recorded at 500 nm between intervals of 0.4 to 0.6 seconds. The initial rates were given by the slope of the lines obtained by plotting absorbance vs. time. Different kinetic orders of behavior were considered for **1b** and CO, but an adequate fitting between the experimental data and the kinetic equation was only found in the case where both orders and both stoichiometric coefficients were the unity.

Acknowledgments. F. D. is a grateful recipient of a fellowship from the National Research Council (CONICET). The courtesy of the Dept. of Physical Chemistry of the Universidad de Mar del Plata were the ESR measurements were carried out, is acknowledged. We also want to thank Dr. E.C. Ashby for proofreading this work. The authors are indebted to the CONICET and the University of Buenos Aires for financial support.

REFERENCES

1.- (a) Fox, M-A. *Chem. Rev.* **1992**, *92*, 365. (b) Eberson, L. *New J. Chem.* **1992**, *16*, 151. (c) "Electron Transfer in Inorganic, Organic, and Biological Systems": Bolton, J. R.; Mataga, N.; McLendon, G. Eds.; Adv. Chem. Series 228, ACS; Washington, D. C., **1991**. (c) Eberson, L. "Electron Transfer Reactions in Organic Chemistry", Springer, Berlin and Heidelberg, **1987**. (d) "Photoinduced Electron Transfer"; Fox, M. A.; Chanon, M. eds. Elsevier: Amsterdam, **1988**.

2.- (a) Ashby, E. C *Acc. Chem. Res.* **1988**, *21*, 414; (b) Newcomb, M.; Curran, D. P. *Acc. Chem. Res.* **1988**, *21*, 206 (c) Ashby, E. C.; Pham, T. *J. Org. Chem.* **1987**, *52*, 1292. (d) Ashby, E.C.; Coleman, D.; Gamasa, M. *J. Org. Chem.* **1987**, *52*, 4079. (e) Sato, T.; Wakahara, Y.; Otera, J.; Noyaki H. *J. Am. Chem. Soc.* **1991**, *113*, 4028.

3.- (a) Beckwith, A. L. J.; Bowry, V. W.; Ingold, K. U. J. *Am. Chem. Soc.* **1992**, *114*, 4983. (b) Bowry, V. W.; Ingold, K. U. *J. Am. Chem. Soc.***1992**, *114*, 4992. (c) Bockman, T. M.; Karpinski, Z. J.; Sankararaman, S.; Kochi, J. K. *J. Am. Chem. Soc.* **1992**, *114*, 1970. *J. Am. Chem. Soc.* **1991**, *113*, 4962. (d) Bordwell, F. G.; Wilson, C. A. *J. Am. Chem. Soc.* **1987**, *109*, 5465.

4.- (a) Saveant, J. M. *New J. Chem.* **1992**, *16*, 131. (b) Poli, R.; Owens, B. E.; Linck, R. G. *J. Am. Chem. Soc.* **1992**, *114*, 1302. (c) Andrieux, C. P.; Hapiot, P.; Saveant, J. M. *Chem Rev.* **1990**, *90*, 113; (d) Evans, D. H. *Chem. Rev.* **1990**, *90*, 739. (e) Chanon, M. Tobe, M. L. *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 1.

5.- (a) Cho, J. K.; Shaik, S. S. *J. Am. Chem. Soc.* **1991**, *113*, 9890. ; (b) Shaik, S. S. *Acta Chem. Scand.* **1990**, *44*, 205. (c) Newton, M. D. *Chem. Rev.* **1991**, *91*, 767. (d)Eberson, L.; Shaik, S. S. *J. Am. Chem. Soc.* **1990**, *112*, 4489 (e) Purcell, K.F.; Blaive, B. "Theory of Electron Transfer Reactions" in "Photoinduced Electron Transfer"; Fox, M. A.; Chanon, M. eds., Elsevier: Amsterdam, **1988**, Part A. (f) Shaik, S. S. *Prog. Phys. Org. Chem.* **1985**, *15*, 197. (g) Pross, A. *Acc. Chem. Res.* **1985**, *18*, 212; (h) Pross, A. *Adv. Phys. Org. Chem.* **1985**, *21*,99.

6.- (a) Nishiyama, Y.; Katsuura, A.; Negoro, A.; Hamanaka, S.; Miyoshi, N.; Yamana, Y.; Ogawa, A.; Sonoda, N. *J. Org. Chem.* **1991**, *56*, 3776. (b) Ryu, I.; Kusano, K.; Yamazaki, H.; Sonoda, N. *J. Org. Chem.* **1991**, *56*, 5003. (c) Ryu, I.; Kusano, K.; Ogawa, A.; Kambe, N.; Sonoda, N. *J. Am. Chem. Soc.***1990**, *112*, 1295.

7.- (a) Protasiewicz, J. D.; Lippard, S. J. *J. Am. Chem. Soc.* **1991**, *113*, 6564. (b) Dufaud, V.; Thivolle-Cazat, Basset, J.-M.; Mathieu, R.; Jaud, J.; Waissermann, J. *Organometallics*, **1991**, *10*, 4005. (c) Chen, J.-T.; Tzeng, W.-H.; Tsai F.-Y.; Cheng, M.-C.; Wang, Y. *Organometallics*, **1991**, *10*, 3954.

8.- (a) Moloy, K. G.; Fagan, P. J.; Manriquez, J. M.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 56. (b) Marks, T. J.; Day, V. W. in "Fundamental and Technological Aspects of Organo-f-Element Chemistry";Marks, T. J.; Fragala, I. L., Eds.; Reidel: Dordrecht, **1985**, pp. 115-157.

9.- Nudelman, N. S. "Carbonylation of Main-Group Organometallic Compounds" in "The Chemistry of Double Bonded Functional Groups" Patai, S. and Rappoport, Z. eds. ch. 13, Wiley, Chichester **1989**.

10.- Seyferth, D. ; Hui, R. C.; Weinstein, R. M.; Wang W.-L *Nova Acta Leopoldina* **1985**, *9*, 335 and refs. therein.

11.- (a) Nudelman, N. S.; Lewkowicz, E. S.; Perez, D. G. Synthesis 1990, 917. (b) Nudelman, N. S.; Lewkowicz, E. S.; Furlong, J. P. J.; in press; (c) Perez, D. G.; Nudelman, N. S. *J. Org. Chem.* **1988**, *53*, 408.

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

13.- (a) Nudelman, N. S.; Doctorovich, F.; Amorin, G. *Tetrahedron Lett.*, **1990**, *31*, 2553. (b) Doctorovich, F.; Nudelman, N. S. *Magn. Res. Chem.* **1990**, *28*, 576.

14.- (a) Nudelman, N. S.; Outumuro, P. *J.Org. Chem.*, **1982**, *47*, 4347. (b) Nudelman, N. S.; Vitale, A. A. *J. Organometal. Chem.* **1983**, *241*, 143. (c) Nudelman, N. S.; Vitale, A. A. *Org. Prep. Proced.* **1981**, *13*, 144.

15.- (a) Vitale, A. A.; Doctorovich, F.; Nudelman, N. S. *J. Organometal. Chem.*, **1987**, *332*, 9. (b) Nudelman, N. S.; Vitale, A. A. *J.Org. Chem.*, **1981**, *46*, 4625.

16.- (a) Ashby, E. C.; Argyropoulos, J. N. *J.Org. Chem.*, **1986**, *51*, 472. (b) Ashby, R. N.; De Priest, R. N.; Su, W.-Y. *Organometallics* **1984**, 1718.

17.- (a) Newcomb, M.; Sanchez, R. M.; Kaplan, J. *J. Am. Chem. Soc.* **1987**, *109*, 1195. (b) Newcomb, M.; Burchill, M. *J. Am. Chem. Soc.* **1984**, *106*, 8276.

18.- Screttas C. G.; Micha-Screttas, M. *J. Phys. Chem.* **1983**, *87*, 3844.

19.- Doesher, R. N.; Wheland, G. W. *J. Am. Chem. Soc.* **1934**, *56*, 2011.

20.- Joela, H. *Comp. Chem.* **1987**, *12*, 189.

21.- (a) Maruyama, K.; Katagiri, T. J. *Phys. Org. Chem.* **1989**, 2, 205; (b) Maruyama, K.; Katagiri, T. J. *Phys. Org. Chem.* **1988**, *1*, 21; (c) Maruyama, K.; Katagiri, T. *J. Am. Chem. Soc.* **1986**, *108*, 6263.

22.- Nudelman, N. S.; Doctorovich, Fabio; in preparation.

23.- (a) Capek, I.; Barton, *J. Makromol. Chem.* **1985**, *186*, 1297. (b) Arnoldi, C.; Citterio, A.; Minisci, F. *J. Chem. Soc., Perkin Trans. 2*, **1983**, 531.

24.- Rak, S. F.; Miller, L. L. *J. Am. Chem. Soc.* **1992**, *114*, 1388.

25.- Hanhela, P. J.; Paul, D. B. *Aust. J. Chem.* **1970**, *34*, 1701.

26.- Moore, H. W.; Sing, Y. L.; Sidhu, R. S. *J. Org. Chem.* **1977**, *42*, 3320.

27.- (a) Yamataka, H.; Fujimura, N.; Kawafuji Y.; Hanafusa, T. *J. Am. Chem. Soc.* **1987**, *109*, 4305. (b) Yamataka, H.; Matsuyama, T.; Hanafusa, T. *Chem. Lett.* **1987**, 647. (c) Matsuyama, T.; Yamataka, H.; Hanafusa, T. *Chem. Lett.* **1988**, 1367.

28.- Buchner, W. *Chem. Ber.* **1966**, *99*, 1485.

29.- (a) Rizkallc, N.; Goliaszewski, A. *ACS Symposium Ser.* **1987**, *328*, 136. (b) Prent, E. *ACS Symposium Ser.* **1987**, *328*, 154.

30.- Rempt, R. D. *Phys. Rev. Lett.* **1969**, *22*, 1034.

31.- (a) Yamataka, H.; Matsuyama, T.; Hanafusa, T *J. Am. Chem. Soc.* **1989**, *111*, 4912; (b) Yamataka, H.; Kawafuji Y.; Nagareda, K.; Miyano, N.; Hanafusa, T. *J. Org. Chem.* **1989**, *54*, 4706;

32.- Okubo, M.; Matsuo, K. *J. Synth. Org. Chem.* **1992**, *50*, 682.

33.- Stevenson, G. R.; Hashim, R. T. *J. Am. Chem. Soc.* **1985**, *107*, 5794.

34.- Hiiro, T.; Morita, Y.; Inoue, T.; Kambe, N.; Ogawa, A.; Ryu, I.; Sonoda, N. *J. Am. Chem. Soc.* **1990**, *112*, 455.

35.- (a) Moloy, K. G.; Marks, T. J.; Day, V. W. *J. Am. Chem. Soc.* **1983**, *105*, 5696. (b) Sonnenberger, D. C.; Mintz, E. A.; Marks, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 3484.

36.- (a) Berg, F. J.; Petersen, J. L. *Organometallics* **1991**, *10*, 1599. (b) Hoffmann, R.; Wilker, C. N.; Lippard, S. J.; Templeton, J. L.; Brower, D. *J. Am. Chem. Soc.* **1983**, *105*, 146.

37.- (a) Boche, G.; Opel, A.; Marsch, M.; Harms, K.; Haller, F.; Lohrenz, J. C. W.; Thummler, C.; Koch, W. *Chem. Ber.* **1992**, *125*, 2265. (b) Boche, G.; Marsch, M.; Muller, A.; Harms, K. *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1032.

38.- Walling, C. *J. Am. Chem. Soc.* **1988**, *110*, 6845.

39.- Scaiano, J. C.; Stewart, L. C. *J. Am. Chem. Soc.* **1983**, *105*, 3609.

40.- Bakac, A.; Espenson, J. H. *J. Chem. Soc., Chem. Comm.***1991** , 1497.

41.- Garst, J. F.; Smith, C. D. *J. Am. Chem. Soc.* **1976**, *98*, 1520.

42.- Carloni, P.; Greci, L.; Stipa, P.; Eberson, L. *J. Org. Chem.* **1991**, *56*, 4733.

43.- Mondodoev, G. T.; Przhiyalgouskaya, N. M.; Belov, V. *Zh. Org. Khim.* **1965**, *1*, 2008.

44.- Schmidlin, J.; Massini, P. *Ber.* , **1909**, *42*, 2388.

45.- Kohler, E. P.; Baltzly, R. *J. Am. Chem. Soc.* **1932**, *54*, 4015.

46.- (a) Sass, M; Ziessow, D. *J. Magn. Res.* **1977**, *25*, 263. (b) Swift, T. J. in "NMR of Paramagnetic Molecules", La Mar, G. N., Harrocks, W. D.; Holm, R. H. eds., Academic Press, New York, **1973**, pp. 53-83.

47.- (a) Allinger, N. L.; Yuh, Y. H. *QCPE* **1980**, *12*, 395. (b) Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127. (c) Propheta, Jr., S. *QCPE Bull.* **1981**, *1*, 57.

48.- Shriver, D. F. "The Manipulation of Air Sensitive Compounds", Wiley, N. Y. **1989**.

(*Received in USA* 27 *December* 1993; *accepted* 17 *February* 1994)