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SPECTROSCOPIC DETERMINATION OF RADICAL ANIONS IN THE REACTION OF PHENYLLITHIUM WITH CARBON MONOXIDE

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Summary: A ^{13}C NMR method was developed for quantitative determination of radical anions in relatively high concentration and applied to the reaction of phenyllithium with carbon monoxide where those species were detected.

The usefulness of the reactions of phenyllithium,[1,2] and of other aryl-[3] and alkyllithiums,[4] and of lithium amides[5] with carbon monoxide in organic synthesis has been recently shown. A polar mechanism for the reaction of phenyllithium with CO had been previously postulated[6] and the reactions were always written as conventional polar transformations.[1-5] Nevertheless, recent observations indicate the presence of radicals in relatively high concentrations in these reactions. Since methods usually employed to study the role of radicals as real intermediates in the reaction pathways, e.g. UV or EPR detection of radical species[7-9] or identification of products indicative of radical intermediates [10-12] may have inherent limitations,[13] an NMR method was developed and applied at concentrations similar to those of reactions in *preparative conditions*.

The method is based on the interaction between radical anions and THF molecules. It was found that the α and β carbon ^{13}C NMR signals of THF are widened by the presence of radical anions: the effect is larger on the α signal and the broadening is proportional to the radical concentration in the range 0.2-1.2 M.[14] 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 inhomogenities, etc. were examined and excluded) and allowed proposal of the mechanism for the spin density transfer from the radical to the THF molecules.[14]

The method was applied to the study of the reaction between phenyllithium and CO. The formation of radical anions in *low concentrations* (*ca.* 10^{-5}M) was first detected by UV (λ_{max} 610 nm, reaction mixture in THF) and EPR measurements under several conditions. Fig. 1 shows the spectrum of the reaction mixture carried out in THF at r.t. Simulation of the spectrum of lithium benzophenone ketyl, 3, closely resembles that of Fig. 1. The reaction was then carried out at concentrations similar to those of preparative conditions. Solid phenyllithium was prepared as described,[15] and the reaction with CO has been carried out under several reaction conditions. When the reaction is carried out in solution the main products are: benzophenone, benzoin and α,α-diphenylacetophenone[2] (the relative yields are highly dependent on the reaction conditions) while the reaction in the absence of solvent quantitatively renders

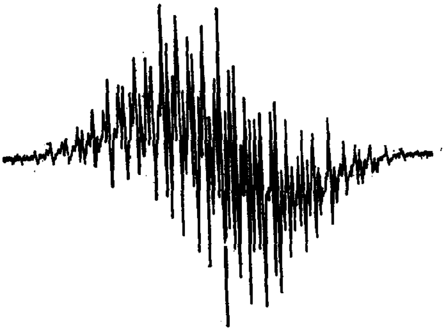


Figure 1. e.s.r. spectrum of the reaction mixture of PhLi + CO in THF at r.t.

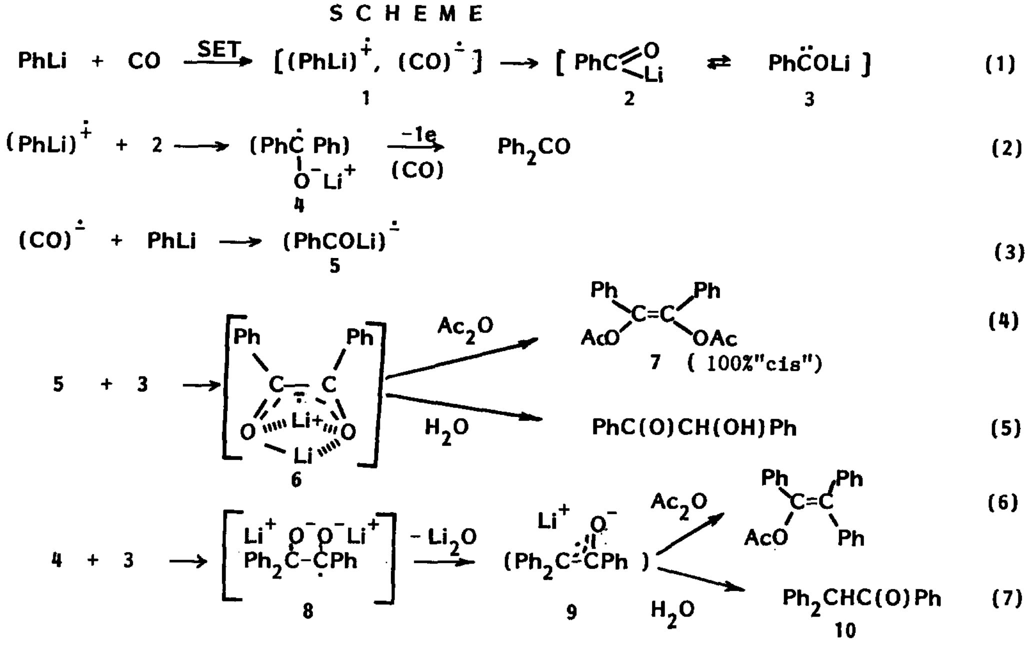
α,α-diphenylacetophenone at 110°C.[15] In the present work once the CO absorption ceased, a known amount of THF was added to the reaction mixture in diethyl ether or hexane; for reactions with solid phenyllithium, the purple solid product was diluted with THF, while reactions in THF were analyzed without any work-up. Some representative runs are shown in Table 1, the so called ["Ar"] represents the overall concentration of species (considering one benzene ring/molecule, in mmoles/ml THF) after treatment with THF. A satisfactory correlation is found between ["Ar"] and Δν (because of the effects of co-solvents,[14] proportionality holds better for reactions carried out in THF). Although, likely more than one e-unpaired species is present in the reaction mixture, a rough estimation of the overall radical-anion concentration indicates a high conversion of the reagent into radical intermediates. When the reaction is carried out in the presence of a good *electron acceptor* such an alkyl bromide, the signal broadening is lost, indicating the absence of radical anions.

Table 1. Reaction of Phenyllithium with CO. Changes in the THF α-carbon ^{13}C NMR signal width (Δ ν, Hz) by the Presence of Radical Anions in the Reaction Mixture.

Reaction Conditions	[PhLi]	["Ar"]	Δ ν	["Radical"][a]
THF / 25°C	0.33	0.33	5.1	0.33
	0.67	0.67	12.8	0.84
	1.00	1.00	23.8	1.50
	1.40	1.40	27.6	1.80
Hexane/ 25°C	1.00	0.62	5.6	0.37
	1.00	0.83	10.3	0.67
	1.00	1.66	15.9	1.05
	1.00	2.00	32.8	2.10
Diethyl ether/25°C	1.00	0.77	7.0	0.46
	1.00	1.03	7.2	0.47
	1.00	2.05	11.2	0.73
Solid / 110°C	7.0 mmol	4.2	22.9	1.3
THF/-78°C/C_3H_7Br	1.00	1.00	2.0	0.0
THF/-78°C/C_4H_9Br	1.00	1.00	2.0	0.0

[a] Overall concentration of "radical equivalents" estimated from the plot of Δν vs. [3].[14]

SCHEME



The determination of radical anions in concentrations similar to the reagent concentration suggests that radical anions are real intermediates in the reaction pathway and not a mere blind step. Preliminary studies of reactions of 1-naphtyl-, 1-mesityl- and 9-anthryllithium with CO in THF also show increase of the bandwidth in the ^{13}C NMR signals of THF. In the reactions of these compounds the main products are 1,2-diarylketones,[3,16] since these compounds are formed by dimerization of the first reaction intermediate,[3] the fact that paramagnetic species are observed in these reactions suggest that radical anions are formed in the first steps.

A mechanism consistent with the above and additional observations is presented in the Scheme.[17] The first step is electron transfer from PhLi to the highly electron deficient CO, producing the radical anion-radical cation pair **1**. This may react in the solvent cage to form the lithium acyl-anion **2**, which is in equilibrium with an oxy-carbene structure, **3**, (eq.1) as it has been previously demonstrated.[2] $(PhLi)^{\dot{+}}$ may escape the cage and react with **2** to form **4**, which by one-e oxidation renders benzophenone after work-up (eq. 2). This mechanism is simpler than the one we initially proposed for the formation of benzophenone that required a two-e oxidation,[6] and explains the finding of *benzopinacol* (formed by dimerization of **4**) in low yield. Reaction of $(CO)^{\dot{-}}$ with unreacted PhLi produces the radical anion **5** (eq. 3), which by reaction with **3** forms the lithium benzoin ketyl **6** (the *cis* configuration allows coordination of both lithium atoms) which renders 100% *cis-benzoin diacetate*, **7**, after treatment with acetic anhydride (eq. 4).[2,4] Eqs. 5-7 explains formation of the other main products.

The fact that in the reaction with solid phenyllithium at 110°C (which only produces **10**) significant concentrations of radical anions are also observed (Table 1) requires an e-unpaired precursor for **10** (such as **9** in eq. 7) instead of the initially proposed.[6] Finally, the trapping of the first intermediate with alkyl bromides, and the fact that alkyl chlorides do not react under similar reaction conditions, are also in favour of the electron transfer mechanism.

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(17) Although phenyllithium is written as a monomer, aggregation of the reagent in the solvents used is well stablished. See for instance ref. 18. See also ref. 19.

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(19) The proposed Scheme does not preclude other possible pathways to products.

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