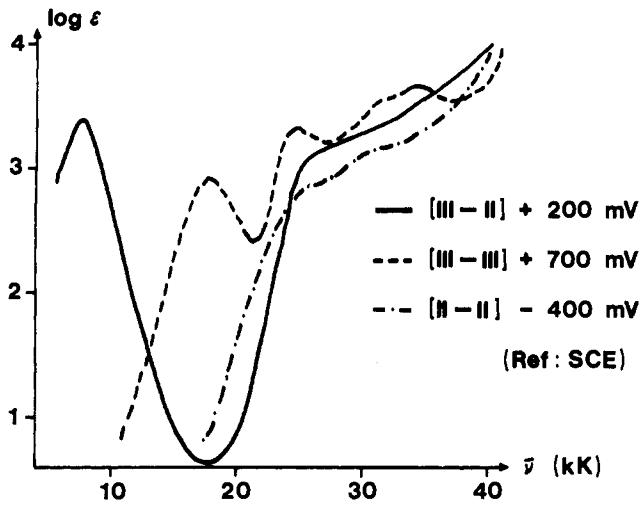

Figure 2. Absorption spectra of $Fe_2(CN)_{11}^{x-}$ at different, constant minigrid potentials.

peatedly and reversibly scanned reaction can be conveniently followed by recording the intensity of the 1300-nm band as a function of time, *i.e.*, the minigrid potential. The optical density at this wavelength is zero at −400 mV/sce, reaches a maximum around +200 mV/sce, and vanishes again at higher potentials (Figure 1). This redox behavior is interpreted in terms of a two-step mechanism involving the binuclear species [II-II], [III-III], and [III-II] as an electrochemical intermediate according to

$$[\text{III-III}] \overset{+e}{\rightleftarrows} [\text{III-II}] \overset{+e}{\rightleftarrows} [\text{II-II}]$$

$$Fe_2(CN)_{11}^{5-} \overset{+e}{\rightleftarrows} Fe_2(CN)_{11}^{6-} \overset{+e}{\rightleftarrows} Fe_2(CN)_{11}^{7-}$$

The spectra recorded at the different potentials are accordingly assigned to these three binuclear complexes (Figure 2). Defined oxidation states of this binuclear iron cyano complex can thus be produced which otherwise are difficult to obtain.[10] Similar complexes having pyrazine as bridging ligand are presently investigated in our laboratory. In the case of $[(CN)_5Fe^{III}pyrFe^{II}(CN)_5]^{5-}$ (pyr is pyrazine) an intervalence band is observed at 1180 nm.[11]

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(10) G. Emschwiller, *C. R. Acad. Sci.*, **268**, 692 (1969).
(11) F. Wenk, to be submitted for publication.

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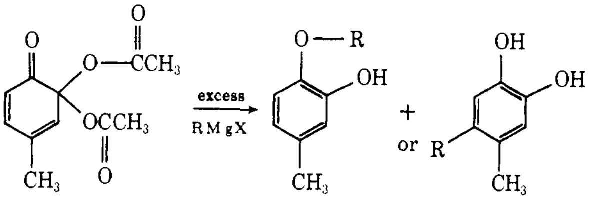
Attack of Carbanionoid Reagents at the Oxygen Atoms of Carbonyl Groups in *o*-Quinol Acetates[1]

Sir:

It is commonly observed that Grignard and lithium reagents add to the carbonyl carbons of ketones or to the β carbons of α,β-unsaturated ketones. In contrast, attack by these reagents at the oxygen atoms of carbonyl groups is almost unknown. One striking exception is the report by Wessely and Kotlan that ethylmagnesium bromide reacts with the quinol diacetate **1** to give principally the corresponding ethyl ether **2**. In contrast, methyl- and phenylmagnesium bromides reacted with **1** to give good yields of **3**, resulting from the expected conjugate addition to the unsaturated ketone.[2] Quinol monoacetates, such as **4**, were reported to react with lithium and Grignard reagents (including ethylmagnesium bromide) to give the normal conjugate addition. No formation of ethers was observed in these reactions.[3]



1 **2** **3**

In this communication it is reported that ether formation in the reaction of carbanionoid reagents with *o*-quinol monoacetates is a general phenomenon. Remarkably, as the reagent employed changes from primary to secondary, and then to tertiary or benzylic Grignard or lithium reagents, ether formation changes from a very minor process to the major process, and frequently is the only observable addition reaction.

The products obtained from reaction of quinol acetates with carbanionoid reagents are listed in Table I. The final column in the table lists the ratio of attack at the carbonyl oxygen to conjugate addition. Since the presence of isomeric reaction products interfered with attempts to estimate the maximum possible yield of **6** from reaction with **4c**, the column is blank in those cases.

Wessely and Kotlan[2] originally suggested that **2** was formed by initial 1,2 addition of ethylmagnesium bromide to the carbonyl group of **1**, followed by rearrangement of the ethyl group from carbon to oxygen. An attempt to explain the data in Table I by a similar "reverse Wittig rearrangement" mechanism would require the assumption that the ratio of 1,2 to 1,4 addition to unsaturated ketones should increase sharply as the degree of substitution at the carbanionoid center of the organometallic reagent increases. Little support for such a proposition is available. Indeed, appreciable evidence suggests that the opposite is true.[4] Furthermore, it seems improbable that the *tert*-butyl Grignard reagent would add to the carbonyl of **4b** in preference to the much less hindered β carbon of the double bond. Finally, the observation that the reaction of the *sec*-butyl Grignard with **4c** is complete within a few seconds seems inconsistent with a mechanism for ether formation requiring attack at the highly crowded carbonyl carbon.

The data in Table I suggest that the ratio of formation of ethers to meta-substituted phenols from aliphatic

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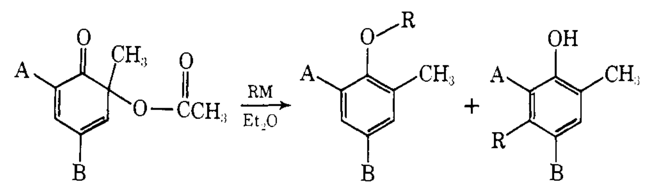
(1) Reactions of Cyclohexadienones. XXXI. Part XXX: B. Miller and M. R. Saidi, *Tetrahedron Lett.*, **4391** (1972).

(2) F. Wessely and J. Kotlan, *Monatsh. Chem.*, **84**, 124 (1953).

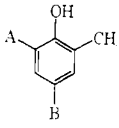
(3) F. Wessely, L. Holzer, and H. Vilcsek, *ibid.*, **83**, 1253 (1952).

(4) P. G. Stevens, *J. Amer. Chem. Soc.*, **56**, 1425 (1934); **57**, 1112 (1935); F. C. Whitmore and G. W. Pedlow, Jr., *ibid.*, **63**, 758 (1941); E. R. Alexander and G. R. Coraor, *ibid.*, **73**, 2721 (1951); H. O. House, D. D. Traficante, and R. A. Evans, *J. Org. Chem.*, **28**, 348 (1963).

Table I



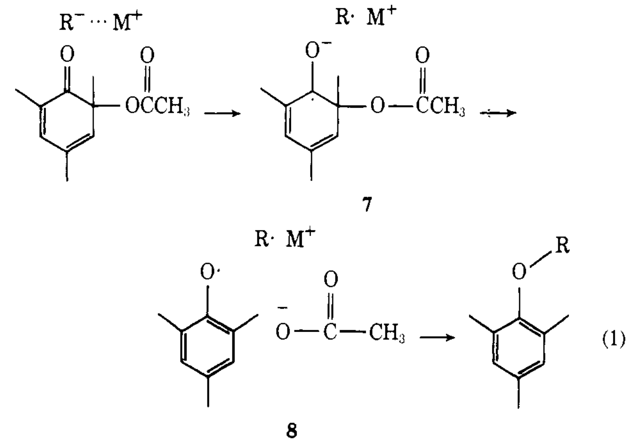
4 5 6

		Composition of products, %				
Ketone	Organo-metallic reagent	**5**	**6**		Other products (%)	% **5**/ % **6**
4a,[a] A = B = CH_3	CH_3MgBr	<0.1[b]	39	4	Pentamethylbenzene (42)[c] Unidentified nonaromatic product (15)	<0.003
	C_2H_5MgBr	4[b]	52	7	Unidentified nonaromatic ketone (31)[d]	0.08
	sec-BuMgBr	67[b]	16	17		4.2
	t-BuMgBr	28[e]	<0.1	72		>280
	t-BuLi	15[e]	<0.1	85		>150
	$PhCH_2MgCl$	91[b]	<0.2[f]	9		>450
4b,[g] A = CH_3; B = H	*sec*-BuMgBr	46[b]	27	32		1.7
	t-BuMgBr	38[e]	4	58	4-*tert*-Butyl-2,6-dimethylphenol (0.4)	9.5
4c,[g] A = *t*-Bu; B = H	*sec*-BuMgBr	16[b]		73	4-*sec*-Butyl-2-*tert*-butyl-6-methylphenol (11)[e]	
	$PhCH_2MgCl$	64[b]		22	3-Benzyl-5-*tert*-butyl-2-methylphenol (2.0)[h] 4-Benzyl-2-*tert*-butyl-6-methylphenol (12.5)[h]	

[a] F. Wessely and F. Sinwel, *Monatsh. Chem.*, **81**, 1055 (1950). [b] Identical with product obtained *via* a Williamson synthesis from the potassium phenoxide and alkyl halide. [c] Sample for comparison obtained from the Aldrich Chemical Co., Milwaukee, Wis. [d] This product is presumably identical with the compound isolated by F. Wessely, L. Holzer, F. Langer, E. Schinzel, and H. Vilcsek, *Monatsh. Chem.*, **86**, 831 (1955), and assigned the structure 2,5-diethyl-2,4,6-trimethylcyclohex-3-en-1-one. [e] Structure assigned from elemental analysis and ir and nmr spectra. Details will be provided in the full paper. [f] A comparison sample was synthesized by acid-catalyzed rearrangement of 6-benzyl-2,4,6-trimethylcyclohexa-2,4-dien-1-one. [g] Prepared by reaction of the corresponding phenol with lead tetraacetate, following the procedure of footnote *a*. [h] B. Miller, *J. Amer. Chem. Soc.*, **92**, 6252 (1970).

Grignard reagents increases with the size of the reagent. However, the very high yields of ethers from reaction with the benzyl Grignard argue against steric effects being the determining factor favoring ether formation—particularly in view of the report that phenylmagnesium bromide gives good yields of *m*-phenylmesitol from reaction with **4a**.[3]

The increase in the **5**/**6** ratio in the products appears to parallel most closely the electron donating abilities of the organometallic reagents. Increased alkyl substitution at a carbanionoid center would decrease carbanion stability (in solution) while increasing the stability of the radicals (or carbonium ions) formed by electron transfer. A comparison of the electron donating ability of the benzyl Grignard reagent with those of aliphatic Grignard reagents is more difficult to obtain. However, the benzyl radical has been shown to have a lower electron affinity than the methyl radical, presumably due to a lower energy gain in placing a second electron into a half-occupied p orbital as compared to a hybrid orbital.[5] Thus, the benzyl Grignard should be a good electron donor, although a direct numerical comparison with secondary or tertiary Grignards is not yet available.



7

8

(1)

The following mechanism (eq 1) is suggested for the formation of ethers in the reaction of organometallic reagents with *o*-quinol acetates. If phenoxy and hydrocarbon radicals are indeed intermediates in the reaction, combination of these radicals at the para positions of the phenoxy radicals, as well as at the oxygen atoms, might be anticipated. As can be seen in Table I, this prediction is borne out, particularly when approach to the oxygen atom is sterically inhibited. However, the possibility that these by-products might arise *via* processes independent of those leading to ethers cannot yet be eliminated. Attempts to use CIDNP techniques to verify that ethers are formed by a combination of radicals have thus far been fruitless. No negative peaks or clearly enhanced peaks have been observed.

In summary, a mechanism similar to that of eq 1 appears consistent with the observations reported above. It is not yet certain, however, whether radicals such as

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(5) A. F. Gaines and F. M. Page, *Int. J. Mass. Spectrom. Ion Phys.*, **1**, 315 (1968); *Trans. Faraday Soc.*, **59**, 1266 (1963).

7 or **8** are genuine intermediates in the reaction, or whether they simply represent resonance contributors to the transition state of a single step displacement on oxygen.

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Role of Hexamethylphosphoramide in Facile, High-Yield One-Electron Reductions by Organometallic Compounds

Sir:

It was recently reported that trimethylsilylsodium is a good one-electron reducing agent in hexamethylphosphoramide (HMPA) solution.[1] We wish to report that HMPA facilitates the one-electron reduction of a variety of compounds by organolithium and -magnesium compounds.[2] For example, 0.1 *F* HMPA solutions of methyl-, *n*-butyl-, or *tert*-butyllithium or benzylmagnesium chloride will quantitatively reduce 10^{-4} *M* biphenyl to its radical anion in less than 10 min.

Investigations of the reactions of *n*-butyllithium with biphenyl and anthracene in mixed solvent systems indicate that the concentration of HMPA is the most important variable in determining the extent of one-electron reduction observed. No apparent reaction occurs between *n*-butyllithium and biphenyl in tetrahydrofuran (THF) solution within 1 hr. Incremental replacement of THF by HMPA leads to a concurrent increase in the formation of biphenyl radical anion (Table I). The amount of reduction which occurs is not related to any particular stoichiometric ratio of HMPA to *n*-butyllithium or biphenyl, but is dependent on the HMPA concentration.

Table I. Yield of Biphenyl Radical Anion as a Function of HMPA Concentration[a]

[HMPA], *M*	Yield, %[b]	[HMPA], *M*	Yield, %
0.0	*c*	2.95	10.0
0.95	*c*	4.35	38.0
1.91	3.0	5.40	100.0

[a] THF was the cosolvent, [biphenyl] = 1.10×10^{-3} *M*, [*n*-butyllithium] = 0.10 *F*. [b] Calculated using an extinction coefficient of 4.0×10^4 at 407 nm (J. Jagar-Grodzinski, M. Field, S. L. Yang, and M. Szwarc, *J. Phys. Chem.*, **69**, 628 (1968); M. Szwarc, "Carbanions, Living Polymers, and Electron Transfer Processes," Interscience, New York, N. Y., 1968, p 174). [c] Not detected by visible or epr spectra.

This conclusion was confirmed by a detailed study of the reaction between anthracene and *n*-butyllithium. Anthracene does not react rapidly with *n*-butyllithium in diethyl ether solution in the dark.[5] However, in THF solution,[6] in diethyl ether–tetramethylethylenediamine (TMEDA),[7] and in diethyl ether–HMPA solvent mixtures rapid reaction occurs. The reaction products are anthracene radical anion and the alkylate, 10-*n*-butyl-9-lithio-9,10-dihydroanthracene. The alkylate is the major product in THF solution and the diethyl ether–TMEDA and diethyl ether–HMPA (when HMPA/*n*-butylithium < 15) solvent mixtures (Table II). When diethyl ether or THF is successively replaced by larger quantities of HMPA (HMPA/*n*-butyllithium > 15), the amount of anthracene radical anion observed increases at the expense of the alkylate (Table II). The anthracene radical anion is not formed by decomposition of the alkylate nor is the amount observed a function of any particular stoichiometric ratio of HMPA to *n*-butyllithium or anthracene. Only when the HMPA concentration is high (and HMPA/*n*-butyllithium is large) does electron transfer become the major reaction. A reasonable hypothesis is that the high dielectric constant of HMPA (E = 30/20°)[8] favors these electron transfer reactions.

Table II. Yields of Anthracene Radical Anion and Alkylate as a Function of HMPA Concentration[a]

[HMPA], *M*/Solvent[b]	Yield, %[c]		[HMPA], *M*/Solvent	Yield, %	
	Alkylate	Radical		Alkylate	Radical
0.00/T	>99	<1[d]	0.82/E	90	10
1.39/T	77	23	1.39/E	85	15
1.43/T[e]	72	28	1.48/E	83	17
2.15/T[e]	45	55	1.80/E	70	30
2.78/T	32	68	1.80/E[f]	71	29
4.17/T	13	87	2.46/E	50	50
5.21/T	7	93	3.77/E	15	85
0.16/E	87	13	4.17/E	16	84
0.33/E	81	19	5.07/E	8	92
0.33/E[f]	87	13	1.71/E[g]	>99	<1[d]
0.35/E	86	14	4.30/E[g]	89	11

[a] Unless noted otherwise, [*n*-butyllithium] = 0.10 *F* and [anthracene] = 8.2×10^{-4} *M*. [b] T = THF, E = diethyl ether. [c] Yield of radical anion calculated using an extinction coefficient of 2.4×10^4 at 366 nm (see references in Table I, footnote *b*). Yield of alkylate calculated using an extinction coefficient of 2.4×10^4 at 455 nm (HMPA containing solutions) or 425 nm (TMEDA containing solutions). The alkylate has two equally intense absorptions at 395 and 444 nm in THF solutions (ref 6a). [d] Not detected in sufficient quantity to accurately measure. [e] [*n*-Butyllithium] = 0.05 *F*. [f] [Anthracene] = 16.0×10^{-4} *M*. [g] TMEDA rather than HMPA added.

The radical anions of many aromatic hydrocarbons and compounds such as nitrobenzene[9] have been formed by reaction with organolithium or -magnesium compounds in HMPA solution. Since overreduction does not appear to be a problem, a large excess of the organometallic reagent can be used. The radical anion is formed rapidly and its destruction by trace amounts of

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(1) H. Sakurai, A. Okade, H. Umino, and M. Kira, *J. Amer. Chem. Soc.*, **95**, 955 (1973).

(2) One-electron transfers by organolithium compounds in low yield in THF solution[3] and upon photolysis in diethyl ether solution[4] have been observed.

(3) G. A. Russell, E. G. Janzen, and E. T. Strom, *J. Amer. Chem. Soc.*, **86**, 1807 (1964), and references therein.

(4) H. J. S. Winkler and H. Winkler, *J. Org. Chem.*, **32**, 1695 (1967).

(5) H. J. S. Winkler, R. Bellinger, and H. Winkler, *J. Org. Chem.*, **32**, 1700 (1967).

(6) (a) D. Nicholls and M. Szwarc, *J. Amer. Chem. Soc.*, **88**, 5757 (1966); *Proc. Roy. Soc., Ser. A*, 301, 223, 231 (1967); (b) R. G. Harvey and C. C. Davis, *J. Org. Chem.*, **34**, 3607 (1969).

(7) The TMEDA-*n*-butyllithium complex is very reactive. See C. G. Eberhardt and W. A. Butte, *ibid.*, **29**, 2928 (1964); C. G. Screttas and J. F. Eastham, *J. Amer. Chem. Soc.*, **87**, 3276 (1965); R. G. Harvey, L. Nazareno, and H. Cho, *ibid.*, **95**, 2376 (1973).

(8) H. Normant, *Angew. Chem., Int. Ed. Engl.*, **6**, 1046 (1967).

(9) G. R. Stevenson, L. Echegoyen, and L. R. Lizardi, *J. Phys. Chem.*, **76**, 1439 (1972), have reported the epr spectra of nitrobenzene radical anion as its lithium, sodium, and potassium salts in HMPA solution.