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Electron-Transfer-Induced Reductive Demethoxylation of Anisole: Evidence for Cleavage of a Radical Anion

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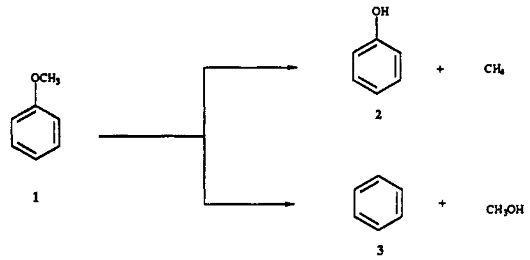
The electron-transfer induced cleavage of anisole with alkali metals (mostly potassium) in the absence of proton donors was studied in solvents of low polarity under a variety of conditions. In THF exclusive demethylation to phenol was observed, regardless of the temperature, whereas in solvents of very low dielectric constant (aliphatic hydrocarbons, toluene, tributylamine, dioxane) demethoxylation to benzene was the main reaction pathway, particularly at the lowest temperatures investigated. Investigation of the mechanism of demethoxylation, with the aid of labeling experiments, provided strong evidence for fragmentation of the radical anion of anisole to methoxide anion and phenyl radical; in a subsequent step, the latter abstracts a hydrogen atom from components of the reaction medium or undergoes one-electron reduction to phenyl anion. The influence of solvent and temperature on the regioselectivity of cleavage is discussed.

The alkali metal-induced cleavage of the alkyl-oxygen bond of alkyl aryl ethers to give phenols (dealkylation) is known to occur readily in a variety of solvents, e.g., liquid ammonia, tetrahydrofuran (THF), or hexamethylphosphoric triamide (HMPA); reaction mechanisms involving fragmentation of either a radical anion or a dianion have been proposed.[1-8] On the other hand, few reports concern the reductive cleavage of the aryl-oxygen bond of such ethers to give aromatic hydrocarbons (dealkoxylation); in fact, dealkoxylation has been observed only in particular cases, e.g., in the reduction of alkyl naphthyl ethers with sodium or potassium in HMPA or in THF/HMPA,[5] of decyl phenyl ether with lithiumbiphenilide in THF,[6] and of 1,2,3-trimethoxybenzene with sodium or potassium in THF; the latter gave highly regioselective demethoxylation to 1,3-dimethoxybenzene.[9,10]

Under all the above conditions anisole, the simplest alkyl aryl ether, undergoes exclusive demethylation;[1-5,8] only under the typical conditions of the Birch reduction,[11] in the presence of an alcohol, minor amounts of a demethoxylation product can be obtained, but after the well-known partial reduction of the aromatic ring to cyclohexadienyl derivatives.[12] Furthermore, anisole is one of the few substrates which were found to be unreactive under standard $S_{RN}1$ conditions.[13] Interestingly, in the course of their work on the metalation of aromatic substrates, Morton et al.[14] reported the preparation of phenyl potassium by treatment of anisole with a dispersion of potassium metal in *n*-heptane at room temperature; however, owing to the synthetic scope of the work, the mechanism of reaction and the formation of other reaction products were not investigated.

Scheme I



In a recent review,[9] Maercker discussed in detail the cleavage of alkyl aryl ethers by alkali metals, pointed out the great influence of the reaction conditions on the regioselectivity of cleavage of carbon-oxygen bonds, and suggested fragmentation of a radical anion as the most likely mechanistic pathway for both dealkylation and dealkoxylation. More recently, on the basis of a theoretical interpretation of ESR spectra of radical anions of various aromatic ethers, Herold and co-workers proposed the same mechanistic pathway for the cleavage of anisole.[15] Fragmentation of a radical anion has been invoked for scission of diaryl ethers as well.[8,16]

In view of our interest in the electron-transfer reduction of simple models for the monomeric units of lignin,[17] we have investigated the reduction of anisole, **1**, with alkali metals under various reaction conditions, according to the general Scheme I, in order to get more detailed informations on the mechanism(s) of cleavage.

Results

The reactions were carried out by vigorous stirring of a ca. 1-1.2 M solution of **1** in anhydrous, freshly distilled solvents with the appropriate amount of alkali metal under nitrogen or argon. In some experiments the alkali metal was added in one or few pieces; in others, a metal dis-

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(1) Freudenberg, K.; Lautsch, W.; Piazolo, G. *Chem. Ber.* **1941,** *74,* 1879.

(2) Birch, A. J. *J. Chem. Soc.* **1947,** 102.

(3) Hurd, C. D.; Oliver, G. L. *J. Am. Chem. Soc.* **1959,** *81,* 2795.

(4) Eisch, J. J. *J. Org. Chem.* **1963,** *28,* 707.

(5) Normant, H.; Cuvigny, T. *Bull. Soc. Chim. Fr.* **1966,** *10,* 3344 and references cited therein.

(6) Itoh, M.; Yoshida, S.; Ando, T.; Miyaura, N. *Chem. Lett.* **1976,** 271.

(7) Testaferri, L.; Tiecco, M.; Tingoli, M.; Chianelli, D.; Montanucci, M. *Tetrahedron* **1982,** *47,* 4250.

(8) Patel, K. M.; Baltisberger, R. J.; Stenberg, V. I.; Woolsey, N. F. *J. Org. Chem.* **1982,** *47,* 4250.

(9) Maercker, A. *Angew. Chem., Int. Ed. Engl.* **1987,** *26,* 972.

(10) Azzena, U.; Denurra, T.; Fenude, E.; Melloni, G.; Rassu, G. *Synthesis* **1989,** 28.

(11) For leading reviews see: (a) Birch, A. J.; Subba Rao, G. S. R. *Advan. Org. Chem.* **1972,** *8,* 1. (b) Hook, J. M.; Mander, L. N. *Nat. Prod. Rep.* **1986,** *3,* 35. (c) Rabideau, P. W. *Tetrahedron* **1989,** *45,* 1579.

(12) Birch, A. J.; Subba Rao, G. S. R. *Aust. J. Chem.* **1970,** *23,* 1641.

(13) Rossi, R. A.; Bunnett, J. F. *J. Am. Chem. Soc.* **1974,** *96,* 112.

(14) Morton, A. A.; Lanpher, E. J. *J. Org. Chem.* **1958,** *23,* 1636.

(15) Lazana, M. C. R. L. R.; Franco, M. L. T. M. B.; Herold, B. J. *J. Am. Chem. Soc.* **1989,** *111,* 8640.

(16) Fish, R. H.; Dupon, J. W. *J. Org. Chem.* **1988,** *53,* 5230 and references cited therein.

(17) Azzena, U.; Denurra, T.; Melloni, G.; Rassu, G. Proceedings of the V European Symposium on Organic Chemistry, Jerusalem, Israel, 1987; 190.

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Table I. Reduction of 1 with Alkali Metals

entry	solvent	metal (equiv)	*T*, °C	*t*, h	% conv	**2**[a]	**3**[b]
1	THF	K (1.2)	20	24	22	18	
2	THF	K (1.2)	66	24	62	60	
3	THF	K (2)	66	24	98	94	
4	heptane	Li (2)	20	336			
5	dodecane	Li (2)	100	336		trace	
6	pentane	Na (2)	20	96	2	2	
7	heptane	Na (1.2)	98	24	3	3	
8	heptane	K (2)	20	24	59	3	51
9	isooctane	K (1.2)	20	120	39	3	32
10	isooctane	K (1.2)	60	24	58	7	35
11	isooctane	K (1.2)	70	24	69	16	41
12	isooctane	K (1.2)	80	24	90	23	47
13	isooctane	K (1.2)	98	5	100	27	49
14	heptane	K (1.2)	91	24	79	19	35
15	toluene	K (1.2)	100	24	100	32	48
16	dioxane	K (1.2)	100	24	35	7	15
17	(butyl)$_3$N	K (1.2)	70	24	66	13	45
18	(butyl$_3$N	K (1.2)	100	24	100	29	48

[a] Recovered yield determined by weight; estimated error ±2%. [b] Recovered yield determined by GC; estimated error ±4%.

persion was used. In such a manner it was realized that the form of the metal had no influence on the results of the reactions and a small influence, if any, on the rate of the reduction.[18] Potassium was used in most experiments. In some tests in hydrocarbon solvents also lithium and sodium were used; however, at variance with Maercker's report,[9] practically no reaction was observed. In most cases the reactions were quenched with water or ethanol (*caution!*); after standard workup, the significant products, i.e., phenol, **2**, benzene, **3**, and methanol, were recognized by GC/MS and ^{1}H NMR; no attempts were made to detect gaseous reaction products such as methane.[19] No products of partial reduction of the aromatic ring nor biphenyl were detected. The results are reported in Table I.

Reductions in THF. The reduction of **1** in THF was carried out only with potassium. As shown in Table I (entries 1–3), the only reaction observed was demethylation to **2**, which was present at the end of the reaction as potassium phenoxide; **3** was never detected. Comparison of entries 2 and 3 shows that 2 equiv of metal are necessary to bring the reaction to completion, according to a two-electron reduction process.

Reductions in Solvents of Low Polarity. The reduction of **1** in solvents of very low polarity was studied in more detail, as demethoxylation was expected to occur under such conditions.[9,14] The initial experiments were carried out with 2 equiv of metal; however, it was soon realized that complete conversion of **1** could be achieved with just 1.2 equiv, at least at high temperatures (Table I, entries 13, 15, and 18); therefore, for comparison purposes, most reactions were run under such conditions, although reactions run at room temperature were quite sluggish (Table I, entry 9). Isooctane (2,4,4-trimethylpentane) was chosen for the experiments at different temperatures since higher percentages of conversion of **1** were usually obtained in respect to heptane.

The results obtained showed that, with potassium as a reducing agent, formation of **3** is the main reaction either in saturated hydrocarbons or in non-hydrocarbon solvents (tributylamine and dioxane), as well as in toluene. Demethoxylation to **3** was accompanied by demethylation under all the conditions investigated, with small amounts of **2** formed also at room temperature (not detected in Morton's work).[14] It is worthy of noting that the ratio **2**/**3** increased with increasing reaction temperature (Table I, entries 9–13 and 17, 18).

Table II. Product Distribution in Deuterium Labeling Experiments[a]

substr	solvent	*T*, °C	**3**:**7**:**8**[b] ratio, %
1	octane-d_{18}	20	100:0:0[c]
1	octane-d_{18}	100	100:0:0[c]
1	cyclohexane-d_{12}	20	100:0:0[c]
1	cyclohexane-d_{12}	81	100:0:0[c]
5	isooctane	20	100:0:0[c]
5	isooctane	99	70:30:0
1[d]	isooctane	99	55:33:12
1[e]	isooctane	20	52:48:0
1[e]	isooctane	99	88:12:0

[a] The reactions were run with 1.2 equiv of K metal for 24 h. [b] Determined by GC–MS from the $M^{\bullet+}/M^{\bullet+} + 1/M^{\bullet+} + 2$ ratio, taking into account isotopic abundancies; the results are the average of three determinations. [c] 100:0:0 means that the ratio $M^{\bullet+}/M^{\bullet+} + 1/M^{\cdot+} + 2$ reflects isotopic abundancies. [d] In the presence of 1 equiv of CD_3OK. [e] D_2O quenching.

At variance with the reactions in THF, under these conditions secondary products and dark tars were formed, particularly at high temperatures. Benzyl alcohol, **4**, was identified as the major byproduct in yields up to 10%; no attempts were made to determine the composition of tars.

Quenching with Carbon Dioxide and Deuterium Oxide. These experiments were performed in order to determine the amount of phenyl potassium present in the reaction mixtures before quenching. They were carried out in particular for the reductions of **1** in isooctane. Quenching with CO_2 to afford benzoic acid, according to Morton's procedure,[14] permitted us to ascertain that under our conditions significant amounts of **3** were formed before quenching, particularly in the reactions carried out at high temperature. Indeed, while in Morton's experiment, in the presence of 2 equiv of potassium metal at room temperature, **1** afforded 60% benzoic acid, we recovered only 7% benzoic acid upon CO_2 quenching of the reaction carried out at 100 °C (see Table I, entry 13 for the overall amount of **3**). These data were confirmed by D_2O quenching of reactions run at 20 and 100 °C, respectively, followed by GC/MS analysis of the amount of deuterium incorporated in the recovered benzene (Table II).

Experiments with Deuteriated Solvents and Substrates. These reactions were carried out in order to shed light on the mode(s) of direct formation of **3** in the reaction mixtures before quenching and to find out possible relationships with the low amount of metal necessary to the complete reduction of **1**. Indeed, both facts are strong indications of the intermediacy of a phenyl radical in the demethoxylation reaction, in accordance to what was recently proposed for the reductive cleavage of aryl ethers.[8,9,16] Furthermore, **3** is often a byproduct in $S_{RN}1$ reactions of monosubstituted benzenes,[20] where it is formed from a phenyl radical by hydrogen atom abstraction. In the present case, the amount of metal consumed in our reactions, lower than expected for an overall two-electron process, indicates that other reduction equivalents, such as hydrogen atoms, are supplied by the reaction medium.

For the purpose of identifying all possible sources of such hydrogen atoms, four kinds of experiments were performed: i, reactions in deuteriated solvents; ii, reactions with methyl-d_3 phenyl ether, **5**; iii, reactions in the presence of potassium methoxide-d_3 (CD_3OK); iv, reactions with methyl phenyl-d_5 ether, **6**; the results of experiments i–iii are reported in Table II.

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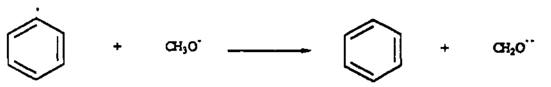
(18) See, however, Morton's procedure (ref 12).

(19) Shorigin, P. *Chem. Ber.* **1923**, *56*, 176.

(20) Bard, R. R.; Bunnett, J. F.; Creary, X.; Tremelling, M. J. *J. Am. Chem. Soc.* **1980**, *102*, 2852.

Involvement of the solvent as a source of hydrogen atoms, as suggested in potassium-promoted aromatic $S_{RN}1$ reactions in liquid ammonia[13,20] and in the reductive cleavage of aromatic ethers and esters with potassium metal/18-crown-6/THF,[16] was ruled out in the present case by the results of the reductions of 1 in octane-d_{18} and cyclohexane-d_{12}, which afforded no deuteriated benzene. As the solvent does not constitute a source of hydrogen atoms, at least to a detectable extent, 1 itself must be involved, either before and/or after the cleavage. Accordingly, 5 was allowed to react with potassium metal in isooctane both at 20 and 100 °C: in the first case only a minor amount of benzene-d_1, 7, could be detected by GC/MS, while in the second case a mixture of 3 and 7 in the ratio 70:30 was obtained. Comparable results were obtained in the reduction of 1 in isooctane at 100 °C carried out in the presence of a stoichiometric amount of added CD_3OK, which afforded, after quenching with H_2O, a mixture of 3 and 7 in the ratio 55:33; in this reaction, the formation of a significant amount of benzene-d_2, 8, was evidenced, as well as 33% deuterium incorporation in the aromatic nucleus of 2.

On the light of the well-known properties of the methoxide anion to behave as hydrogen atom donor towards neutral radicals,[21] this finding strongly supports the occurrence of the following reaction, leading to the formation of formaldehyde radical anion (eq 1). The formaldehyde



(1)

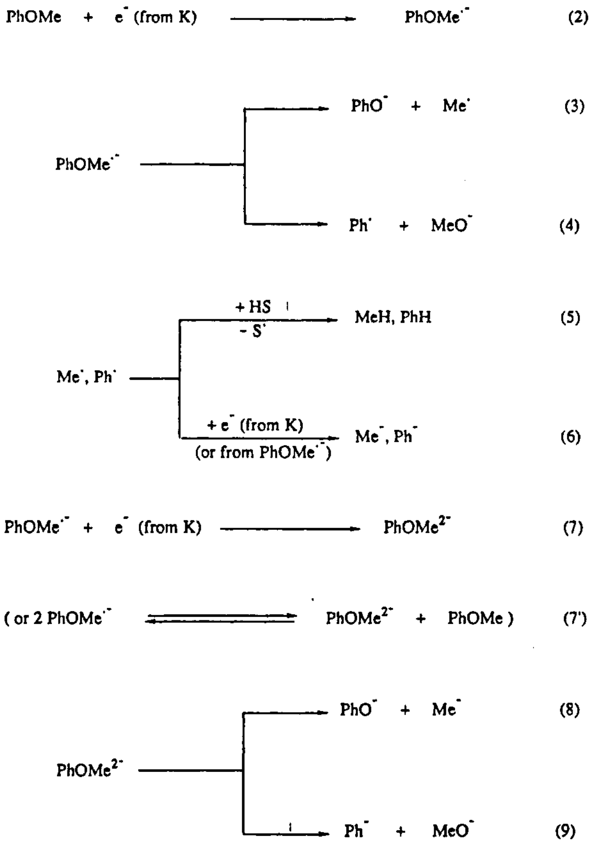
radical anion, if stable enough to survive under our reaction conditions, should afford, upon quenching with water, methanol and formaldehyde by disproportionation. While methanol is a product of our reactions, where it is formed anyway by demethoxylation according to Scheme I, we were unable to detect the presence of formaldehyde in our reaction mixtures, despite several attempts with a very sensitive analytical method.[22]

The formation of 8 and of deuteriated phenol in the reduction of unlabeled 1 in the presence of CD_3OK is somewhat puzzling; these results and the formation of 70% unlabeled 3 in the reduction of 5 seem to indicate the occurrence of an exchange of the aromatic hydrogens of either anisole and/or benzene. This was confirmed by the result of the reduction of equimolar amounts of 1 and 6 in isooctane at reflux, quenched at ca. 70% conversion, which showed, by GC/MS analysis, complete H/D scrambling of the aromatic hydrogens in both recovered anisole and benzene.

Discussion

The results obtained in this work confirm the scanty reports that it is possible to achieve the uncommon demethoxylation of aromatic substrates with preservation of the aromaticity of the nucleus, though under particular conditions. They also indicate that reductive demethoxylation can occur in the absence of particular substituents, as well as of particular conformational constraints.[9,15,23] This fact appears of considerable importance, since the methoxyl group is one of the most common groups in natural organic matter and has been used, because of its stability, in a wealth of synthetic and mechanistic studies as a typical substituent, under a variety of conditions. In addition, it must be taken into account that the phenyl-oxygen bond constitutes the principal linking between the monomeric units in lignin and is likely responsible for the exceptional chemical stability of such constituents of vegetable biomass; it constitutes as well an important linkage in coal.[16] Indeed, lignin is known to undergo extensive degradation under electron-transfer reductive conditions (Birch reduction);[24] besides, it has been suggested in recent work that finding a simple means of cleavage of the phenyl–oxygen bond would provide an easier approach to liquefaction of coal.[16,25]

Scheme II



Furthermore, this work provides the first experimental evidence that demethoxylation of anisole can occur by fragmentation of its radical anion, formed in the first one-electron transfer, to afford a methoxyl anion and a phenyl radical, precursor of benzene.[9,16,20]

At a closer examination, however, our data appear of considerable complexity, which makes somewhat problematical their interpretation. On the whole, they appear to be the outcome of several competition reactions, whose balance is seriously influenced, inter alia, by variables such as the metal (either as electron transfer agent or as counterion), solvent, and temperature. For instance, there is competition between demethoxylation and demethylation, which is influenced by metal and solvent, and, less drastically, by temperature and that, at the phenyl radical level, between reduction to phenyl anion and abstraction of an hydrogen atom; also, taking into account the eventual formation of an intermediate dianion, its mode(s) of

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(21) Boyle, W. J.; Bunnett, J. F. *J. Am. Chem. Soc.* **1974**, *96*, 1418.

(22) Schmitz, E.; Ohme, R. *Monatsber. Deut. Akad. Wiss. Berlin* **1959**, *1*, 366; *Chem. Abstr.* **1960**, *54*, 14263c.

(23) Azzena, U.; Denurra, T.; Melloni, G.; Piroddi, A. M. *J. Org. Chem.* **1990**, *55*, 5386.

(24) Pernemalm, P. A.; Dence, C. W. *Acta Chem. Scand., Ser. B* **1974**, *28*, 453 and references cited therein.

(25) Bond dissociation energies of the C–O bonds of anisole are as follows: Me–O, 64.7 kcal/mol (Suryan, M. M., Kafafi, S. A., Stein, S. E. *J. Am. Chem. Soc.* **1989**, *111*, 1423); Ph-O, 98 kcal/mol (*Handbook of Chemistry and Physics*, 66th ed.; CRC Press: Boca Raton, 1985–1986, F-193).

cleavage would be in competition with that (those) of the radical anion.

Based on these considerations and on data reported in the literature for these and analogous reactions,[6-9,15,16,26] a mechanistic scheme accounting for the results of the present work is reported in Scheme II, where the metal has been omitted for simplicity and HS represents the solvent or other components of the reaction medium. Less likely mechanistic pathways, such as the cleavage of $1^{\bullet-}$ to Ph^- and $CH_3O^\bullet$ or to $PhO^\bullet$ and CH_3^- have been omitted in Scheme II, since similar modes of cleavage have been ruled out in recent electrochemical work on diaryl ethers.[26] On the other hand, the possibility of formation of the anisole dianion, 1^{2-} (eq 7 or, more likely, eq 7′) and its fragmentation into the four possible negative species (eqs 8 and 9) could not be excluded a priori, at least for the reactions carried out with 2 equiv of metal or for those showing low conversions of 1.

On the light of the results obtained in solvents of low polarity, it can be confidently assumed that formation of $1^{\bullet-}$ and its subsequent cleavage (eqs 2–4), as well as the decay of the phenyl radical, represent a relevant pathway of our reactions. It would be of interest to establish which of these steps (except for the decay of the phenyl radical, which is reported to be an extremely fast process)[27] is rate determining; however, in the absence of kinetic measurements, which would be problematical owing to the heterogeneity of our reaction mixtures, we could not establish this with certainty. Nevertheless, the fact that $1^{\bullet-}$ does not accumulate under our reaction conditions but suffers fragmentation in either way, as indicated by the absence of products of reduction of the aromatic ring upon quenching, and the recent report based on kinetic work of a fast cleavage of the carbon–oxygen bond in radical anions of various aromatic ethers[26] tend to indicate formation of $1^{\bullet-}$ as the rate-determining step. This is also in accordance with the very negative reduction potentials of ethers.[26]

A second question immediately arises: which is the product-determining step of our reactions? In other words, does the competition between demethylation and demethoxylation occur at the level of radical anions of different structures or at the level of differently structured ion pairs? In his review,[9] Maercker proposed that, after the primary formation of a π radical anion, the two modes of scission must be ascribed to the formation of two different σ radical anions. More recently, Herold and coworkers, on the basis of a theoretical interpretation of the ESR spectra of radical anions of various aromatic ethers,[15] discussed the matter in terms of two different conformations of the methoxyl group, planar or orthogonal with respect to the plane of the aromatic ring, in the radical anion of anisole, $1^{\bullet-}$, and in the corresponding ion pair. On the other hand, in an earlier theoretical work based on INDO SCF-MO computations, not taking into account interactions with the counterion, Bernardi and co-workers[28] had indicated the planar conformation in the antisymmetric electronic configuration Ψ_A as the most stable conformation for $1^{\bullet-}$. Since the matter is highly complex, and we have no evidence in favor of any of the above suggestions, we prefer to discuss it from a more general point of view, considering the $1^{\bullet-}$/metal ion pair as a single entity and restricting the comments to the available experimental data for the reduction of 1.

Table III. Literature Data for the Reduction of 1 with Alkali Metals

entry	solvent	metal (equiv)	T, °C	t, h	yield, % 2	yield, % 3	ref
1	NH_3	Na (3.6)	−33	7	27		2
2	NH_3	Na (5)	−33	5	63		3
3	NH_3	K (2.8)	20		92		1
4	THF/NH_3	Na (2)	−78	4	1		8
5	THF/HMPA	Na (2)	20	24	5–48		8
6	THF/HMPA	K (2)	20	16	80		5
7	THF	Li-biPh (2)[a]	66	4.5	80		4
8	heptane	Li (2)	20	336		75	9
9	heptane	K (2)	20	1		60[b]	14

[a] Li-biPh = Li-biphenyl. [b] Isolated as benzoic acid after CO_2 quenching.

The comparison of the results of this work with all the data previously reported for the reduction of 1 with alkali metals (Table III) confirms that the ratio demethoxylation/demethylation is influenced by at least three variables: metal, solvent, and temperature. With Li and Na demethoxylation is almost completely absent, except for Maercker's report[9] (Table III, entry 8) that the reduction of 1 with Li in heptane afforded 75% yield of 3 in 2 weeks. As reported in Table I (entry 4) we were unable, however, to confirm this result. In the presence of K, on the other hand, demethoxylation, which does not occur in solvents of medium to high polarity, becomes the predominant reaction in solvents of very low polarity. For such reductions, indeed, a rough correlation can be made between the dielectric constant of the solvent and the value of the ratio demethoxylation/demethylation, with a turning point lying somewhere between THF ($\epsilon = 7.58$)[29a] and toluene ($\epsilon = 2.38$).[29a] As for the effect of temperature, the data of Table I show that in solvents of very low polarity the ratio 2:3 significantly increases with increasing temperature, suggesting a kinetic versus thermodynamic control.[25]

From the above discussion and from the almost complete coincidence of the ratios 2:3 observed in solvents of so widely different structure (saturated hydrocarbons, toluene, dioxane, tributylamine) but of very similar polarity it can be concluded that nonspecific solvation effects play a critical role in affecting the competition between demethoxylation and demethylation at the level of the $1^{\bullet-}$/metal ion pair, with less solvated or tight ion pairs favoring the former, though thermodynamically unfavored, and less tight or solvent-separated ion pairs favoring the latter. This finds support in the fact that demethoxylation occurs mainly with potassium, whose cation is the least solvated among the lower weight alkali metals.[29b] The effects of counterion[9,15] and of polarity of the solvent[9] on the reactivity of ion pairs of radical anions of methoxy-substituted aromatics with alkali metals were recently discussed.

Besides the effect on the demethoxylation/demethylation ratio, temperature was found to affect significantly the decay of the phenyl radical, as shown by the prevalence of the one-electron reduction to phenyl anion at 20 °C and of the hydrogen atom abstraction to afford 3 at 98–100 °C. This indicates the occurrence of a very tight competition between an electron transfer to a radical of high electron

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(26) Thornton, T. A.; Woolsey, N. F.; Bartak, D. E. *J. Am. Chem. Soc.* **1986**, *108*, 6497 and preceding papers of the series. For benzylic and related ethers see also: Santiago, E.; Simonet, J. *Electrochim. Acta* **1975**, *20*, 853 and references cited therein.

(27) Scaiano, J. C.; Stewart, L. C. *J. Am. Soc.* **1983**, *105*, 3609. Madhavan, V.; Schuler, R. H.; Fessenden, R. W. *J. Am. Chem. Soc.* **1978**, *100*, 888.

(28) Bernardi, F.; Mangini, A.; Guerra, M.; Pedulli, G. F. *J. Phys. Chem.* **1979**, *83*, 640.

(29) Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*, 2nd ed.; VCH: Weinheim, 1988; (a) Appendix; (b) p 32.

affinity (2.20 eV in the gas phase at 0 K for Ph•)[30] and a bimolecular hydrogen-atom transfer. This finds analogy in the literature in the work by Savéant and co-workers on the electrochemical reduction of aromatic halides in the presence of alkoxides, to whom we refer for an ample discussion.[31]

Concerning the direct formation of benzene in our reactions, the question arises whether it all comes from the phenyl radical or it derives, at least in part, by protonation of the phenyl anion by very weak proton donors present in the reaction media. The latter argument may be excluded according to the following discussion. According to Shatenshtein,[32] the most acidic protons in 1 are the ortho protons; their abstraction would lead to the *o*-anysil anion, which should afford *o*-anisic acid by CO_2 quenching; such product was never detected in our reaction mixtures. Furthermore, the absence of proton donors, even very weak, in our reaction mixtures is indicated, as pointed out above, by the absence of product(s) of Birch reduction.[33]

The detection of benzyl alcohol among the products of our reactions deserves some comments. Its formation must be related to the demethoxylation reaction, since it was never observed, both in the present work and in work reported in the literature, under conditions leading to exclusive demethylation of 1. Although no particular study was carried out on this point, formation of 4 could be put into relation with the disappearance of formaldehyde radical anion from our reaction mixtures. Indeed, the amount of 4 was found to increase in the reactions carried out at high temperature, where abstraction of an hydrogen atom from CH_3O^-, and hence formation of $CH_2O^{\bullet-}$, becomes important. As a hypothesis, 4 could be formed by the reaction of the phenyl anion with formaldehyde, formed by disproportionation of $CH_2O^{\bullet-}$; this might explain, in part, the disappearance of formaldehyde from our reaction mixtures.

Work is in progress to test the effect of substituents on the aromatic ring on the competition between demethoxylation and demethylation, as well as the effect of bulky substituents in the position(s) ortho to the methoxyl group.

Experimental Section

General Procedures. All products and reagents were of the highest commercial quality from freshly opened containers and were further purified by distillation. D_2O (minimum isotopic purity 99.9% deuterium) was purchased from Aldrich. Compound 5 was prepared from methanol-d_3 (Janssen, minimum isotopic purity 99.5% deuterium) and phenol according to a literature procedure.[34] Compound 6 was prepared from phenol-d_6 (Janssen, minimum isotopic purity 98% deuterium) and methyl iodide according to a literature procedure.[35] Solvents were dried over Na and distilled from sodium benzophenone ketyl under nitrogen immediately prior to use. ^1H NMR spectra were recorded on a Varian EM 360 (60 MHz) spectrometer in $CDCl_3$ solution with Me_4Si as internal standard. Mass spectra were recorded on a Finnigan MAT 1020-B mass spectrometer operating at 70 eV, interfaced with a Perkin-Elmer Sigma 3 gas chromatograph, equipped with a Supelco SP-2100 30-m capillary column (i.d. 0.25 mm). GC analyses were performed with a Hewlett-Packard Model 5890 gas chromatograph, equipped with a similar Supelco SP-2100 capillary column; the chromatograms were recorded on a Perkin-Elmer LC 100 integrator. Yields were calculated from the chromatograms after application of a predetermined response factor.

General Procedure for the Reductive Cleavage of 1. Whenever possible, metal dispersions were prepared by vigorous stirring of the freshly cut metal in the dry solvent under dry nitrogen or argon at a temperature above its melting point and then cooling to room temperature without stirring. To this suspension, or to the freshly cut metal (0.024 g-atom), in 20 mL of the dry solvent was added 1 (2.16 g, 20 mmol) at once, and the mixture was stirred at the appropriate temperature. The mixture was stirred for 24 h, chilled to 0 °C, and quenched by slow dropwise addition of H_2O or of EtOH (10 mL) (*caution!*). After stirring 1 h at room temperature the organic phase was carefully separated and analyzed by GC and GC/MS. The aqueous phase was extracted with Et_2O (2 × 20 mL) and dried over $CaCl_2$ and the solvent evaporated to afford benzyl alcohol. The aqueous phase was acidified with concentrated HCl, extracted with Et_2O (2 × 20 mL), and dried over $CaCl_2$, the solvent evaporated, and the residue analyzed by GC and by GC/MS.

CO_2 quenching was performed by slowly bubbling gaseous CO_2, dried over $CaCl_2$ and concentrated H_2SO_4, into the reaction mixture for 6 h; H_2O (10 mL) (*caution!*) was slowly added, and the resulting mixture worked up as described above. Benzoic acid was collected by filtration of the aqueous layer after acidification, washed with a minimum amount of ice-cold H_2O, and dried in vacuo.

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(30) Gaines, A. F.; Page, F. M. *Trans. Faraday Soc.* **1966**, *62*, 3086.

(31) Amatore, C.; Badoz-Lambling, J.; Bonnell-Huyghes, C.; Pinson, J.; Savéant, J. M.; Thiébault, A. *J. Am. Chem. Soc.* **1982**, *104*, 1979.

(32) Shatenshtein, A. I. *Tetrahedron* **1962**, *18*, 95.

(33) For a recent discussion on the Birch reduction of anisole see: Zimmerman, H. E.; Wang, P. A. *J. Am. Chem. Soc.* **1990**, *112*, 1280.

(34) Vowinkel, E. *Chem. Ber.* **1966**, *99*, 1479.

(35) Claisen, L.; Tietze, E. *Chem. Ber.* **1926**, *53*, 2344.