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THE ANISOLE ANION-RADICAL: ASPECTS OF THE BIRCH REDUCTION.

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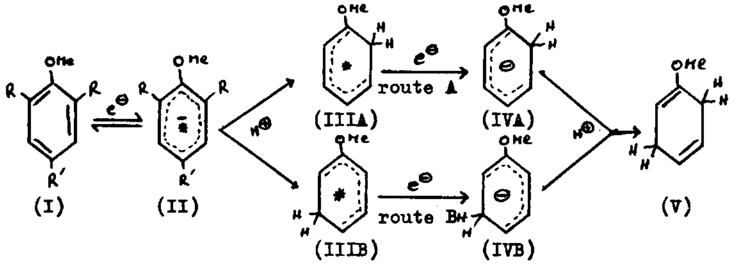
The reduction of aromatic compounds by solutions of metals in liquid ammonia, generally known as the Birch reduction, has been discussed at length by several authors[1]. It is generally accepted that in the case under discussion, the reaction involves reversible reduction of anisole (I, R=R'=H) to the anion-radical (II, R=R'=H), followed by protonation in the rate-determining step, the resulting radical being further reduced and protonated to yield the product (V)[2]. The site of the initial protonation is in doubt.



Calculations of charge-density distribution in the anion-radical (II, R=R'=H) using the simple HMO method, suggest that the *ortho*-position bears the highest charge. This result has been interpreted as favouring *ortho*-protonation (route A)[3]. *Ortho*-attack would also be anticipated on the grounds that it leads to the more stable of the two possible products (IIIA and IIIB)[4]. The alternative (route B) has been supported[5] on the basis of the argument that the extra electron-density in the anion-radical should reside largely on the *meta*-position, leading to a high overall charge-density at that position.

In this communication we present data regarding the spin-density distribution in the anion-radical (II, R=R'=H) together with some results bearing on its mode of reaction with protonating agents in ethereal solvents.

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A solution of anisole in tetrahydrofuran (THF), prepared from reagents which had been thoroughly dried and distilled from potassium, when placed in contact with a potassium mirror at -80° produced a pale yellow solution which exhibited the electron spin resonance spectrum shown in Fig.1.*

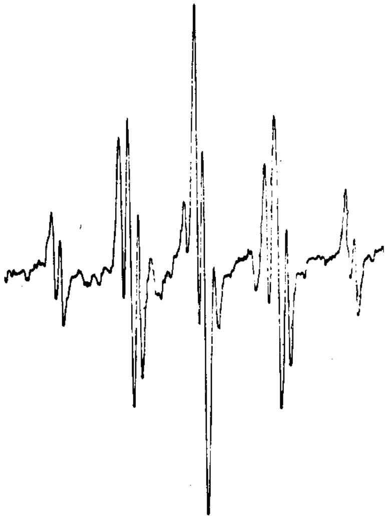

Fig. 1.

This has been interpreted as arising from two equivalent protons with a hyperfine splitting of 6.18 ± 0.07 gauss, two of 5.38 ± 0.07 gauss and one of 0.61 ± 0.08 gauss and hasbeen assigned to the anisole anion-radical (II, R=R'=H). The spectrum is entirely in accord with

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* A trace impurity, 2-methoxynaphthalene, originally present in the sample of anisole used, was found to have a very marked effect in giving observable concentrations of the anion-radical. On the assumption that this impurity had a catalytic action, comparable concentrations ($\sim 10^{-4}$ molar) of naphthalene were used with a pure sample of anisole and were shown to have a similar effect. These observations are being investigated in further detail.

expectation for the unpaired electron distribution in a benzene structure perturbed by an electron-releasing substituent, with relatively large, and similar spin-densities at the ortho- and meta-positions and a small spin-density at the para-position. The splitting associated with the methyl-group protons are not resolved; from the line-widths this is estimated as not greater than 0.09 gauss. The spectrum decayed rapidly in the temperature range -70 to -60°.

Simple HMO calculations lead to spin-densities of 0.25, 0.25 and 0 at the ortho-, meta- and para-positions for the anion-radical (II, R=R'=H). Modifications using the ω-technique[6] result in a small increase in the ortho-spin-density over that at the meta-position. The approximate S.C.F. method of McLachlan[7] gives an extremely small spin-density difference, in the same sense, and a negative spin-density at the para-position of 0.084, which corresponds to a splitting of approximately 2 gauss. This considerable discrepancy between the calculated and observed para-splitting may arise because of the mixing of the symmetric and antisymmetric anti-bonding orbitals through vibronic[8] and thermal effects[9, 10], which would lead to a reduction in the para-spin-density. In the simple HMO approximation these orbitals are nearly degenerate.

The problem of the assignment of the ortho- and meta-spin-densities was resolved by a study of the anion-radical of 2,4,6-trideuteroanisole (II, R=R'=D). This showed clearly that the ortho-splitting was the smaller, and thus that the above treatments were unable to predict the correct spin distribution in this respect. More sophisticated approaches are being explored in an attempt to improve the agreement.

From the standpoint of mechanism, the most significant conclusion from the e.s.r.spectrum is that the difference between the ortho- and meta-spin-densities is small (approx. 0.03). It is therefore valid to suggest that the charge density in the anion-radical does not differ significantly at these positions. Arguments as to the preferred site of protonation in this species then, cannot profitably be based on charge-density considerations.

When 1,2-dimethoxyethane (DME) was substituted for THF, the anisole anion-radical was not observed; instead a brown solution was produced which exhibited the e.s.r. spectrum shown in Fig. 2. This e.s.r. pattern has a close similarity to that published for the diphenyl anion-radical[11] (IX), and the measured splittings were within experimental error, the same as those reported. On opening the sample to air the colour faded, and gas-liquid chromatographic analysis revealed peaks with the correct retention times for diphenyl, the metal in ammonia reduction products of diphenyl, and phenol.

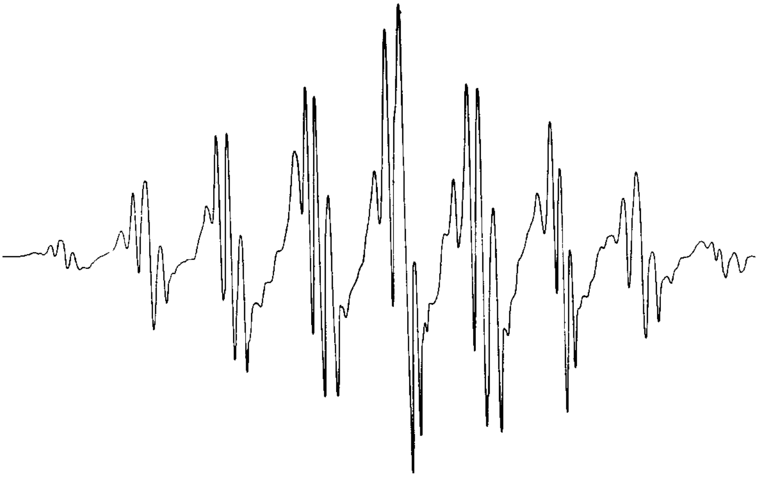

Fig. 2.

The interpretation of these observations is not certain, but a reasonable rationalisation is as follows:

The anisole anion-radical decomposes more rapidly in DME than in THF *, giving rise to the phenoxyl radical and the methyl

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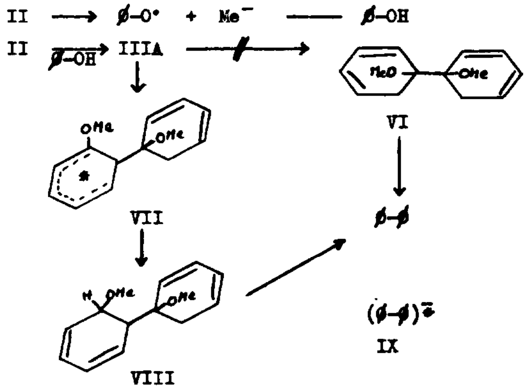
* This profound solvent effect may be associated with stabilisation via ion-pairing in THF, but not in DME solution[cf.12].

anion *. The phenol produced by hydrogen abstraction from the solvent might then fuction as a proton source, yielding the radical (IIIA). Dimerisation of this radical through the carbon atom bearing the methoxyl group (I → → VI) was considered as a possible route to diphenyl, but was ruled out by substituting 4-deuteroanisole for anisole. The e.s.r. spectrum obtained in DME was not compatable with the expected 4,4'-dideuterodiphenyl; the major product appeared to be 3,4'-dideuterodiphenyl. The route currently under consideration is that involving attack of the radical (IIIA) on anisole to give the radical (VII), followed by hydrogen abstraction from the solvent to give the compound (VIII)[13]. It will be noted that the production of a phenyl radical from the anisole anion-radical would also serve as an initiation process for this sequence of reactions. Its production would not be anticipated however on the basis of the metal in ammonia reduction of anisole. It will further be noted that <u>meta</u>-protonation of II (R=R'=H) to give the radical (IIIB) cannot lead, by any reasonable sequence of reactions, to the production of diphenyl.



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* The alternative mode of decomposition, to the phenate ion and methyl radical, could involve methanol as a proton source through an attack by methyl on the solvent, with subsequent disproportionation of a solvent radical to give MeO^- . This alternative does not change the proposed mechanism for the later stages. Evidence bearing on this point will be presented elsewhere.

Certain aspects of this work will be discussed at greater length in full communications. Work is in hand to test some of the more speculative points in the argument.

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