

THE OXIDATION OF AROMATIC ANILS WITH LEAD TETRAACETATE - II -

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In a previous paper<sup>(1)</sup> we reported the oxidation of some aromatic anils with lead tetraacetate (LTA) in benzene. The results of four substrates indicated a reaction mechanism occurring via the formation of a nitrene. Here we report the oxidation with LTA of aromatic anils substituted at the amine-derived nucleus.

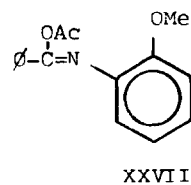
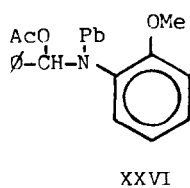
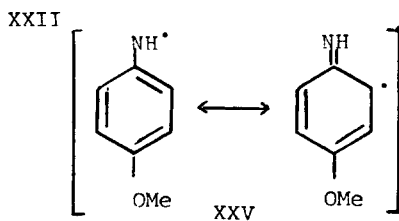
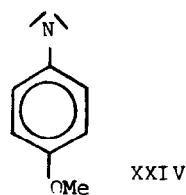
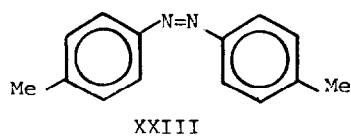
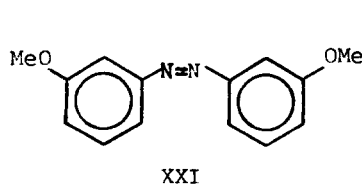
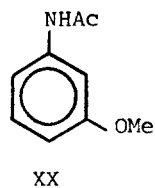
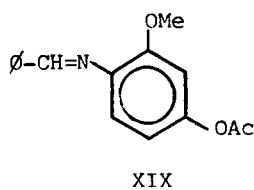
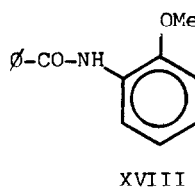
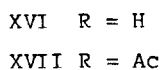
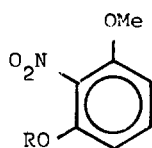
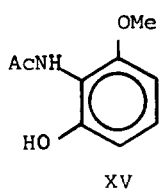
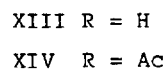
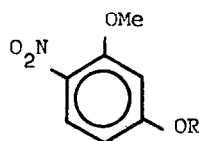
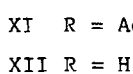
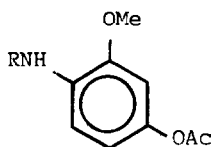
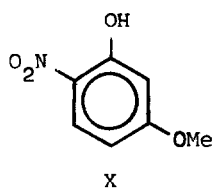
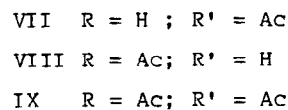
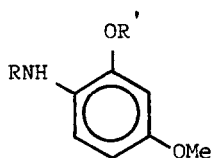
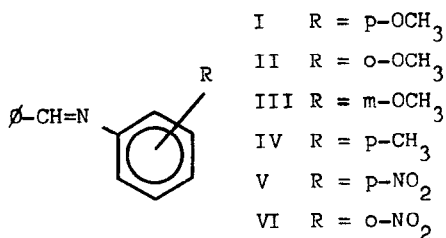
The oxidation of (I) with LTA<sup>(2)</sup> yielded benzaldehyde, 43%, and a mixture of (VII) and (VIII), 32%, which could be converted into the diacetyl derivative (IX) by acetylation. Compound (IX) was prepared from (X)<sup>(3)</sup> via a PtO<sub>2</sub>-catalysed reduction followed by acetylation and had m.p. 114-7°. Compound (VII), isolated by silica-gel chromatography, had m.p. 156-60°,  $\nu_{\max}$  (nujol) 1658 cm<sup>-1</sup>. The isomer (VIII), present in minor amount, could never be obtained pure.

The oxidation of (II) with LTA yielded benzaldehyde, 18%; (XI), 7%; (XV), 19%; (XVIII), 3%; (XIX), 12% and starting material, 2%. Compound (XI) was prepared from (XIII)<sup>(4)</sup> by acetylation to yield (XIV), m.p. 82-4°, subsequently reduced to the unstable (XII). Acetylation of this yielded (XI), m.p. 173-6°. The reaction of benzaldehyde and (XII) gave (XIX), b.p. 130° at 10<sup>-5</sup> mm/Hg. Compound (XV) was obtained by acetylation of (XVI)<sup>(5)</sup> to oily (XVII) and this hydrogenated using PtO<sub>2</sub> as catalyst. The amide (XV) had m.p. 89-90°,  $\nu_{\max}$  (nujol) 1635 cm<sup>-1</sup>.

The oxidation of (III) with LTA gave benzaldehyde, 16%; (XX), 4%; (XXI), 14% and starting material, 62%.

The oxidation of (IV) with LTA gave benzaldehyde, 26%; (XXII), 23%, starting material, 20% and traces of (XXIII).

Compounds (V) and (VI) did not react under the reaction conditions used.



In a control experiment, the oxidation of o-, m-, p-anisidine and p-toluidine did not give the corresponding N-acetyl derivatives. In these reactions, the corresponding azoderivatives were formed in poor yields. Furthermore, o-, m-, p-methoxyphenyl and p-methylphenyl acetamides were not altered by LTA.

The interpretation of these results derives by the consideration that the stability of aromatic nitrenes depends<sup>(6)</sup> from the nuclear substituent with the order  $\text{NO}_2 > \text{H} > \text{Me} > \text{OMe}$  (referred to o- or p-substituents). Hence, an o- or a p-methoxyphenyl nitrene is expected to be less stable than the unsubstituted nitrene, the p-methyl or the m-methoxy derivative; the latter intermediates giving preferentially hydrogen abstraction reactions, the former preferentially dimerising to azoderivatives. In our case, o- or p-methoxyphenyl nitrene formed in the oxidation of (I) or (II) (i.e. XXIV) abstract a hydrogen atom from a suitable donor giving rise to the corresponding mesomeric amino radical (i.e. XXV). The radical nuclear acetoxylation of this gives, after eventual acetyl transfer, (VII), (VIII), (XII) or (XV). On the contrary, m-methoxyphenyl nitrene and p-methylphenyl nitrene prefer either to trap an acetyl radical or to dimerise to the corresponding azoderivative, according to their higher stability. This reaction occurs even in the case of the oxidation of (II), forming the diacetate (XI), via the amine (XII). (VII) and (VIII) are not further transformed probably owing to their insolubility in benzene. The intermediate formation of (XII) can also account for the formation of the anil (XIX) through equilibration in the reaction medium. The radical nature of the acetoxylation step is confirmed by the 1:1 ratio in o- and p-isomers as deduced by the yield of (XV) and (XI)+(XIX). Furthermore, the presence of the amide (XVIII) in the reaction of (II) permits some insight in the early stages of the reaction mechanism. It can be thought in fact that the intermediate (XXVI) formed through attack of the metal oxidant on the anil undergoes either a radical or ionic fragmentation leading to a nitrene and an aldehyde, or a  $\beta$ -elimination reaction with expulsion of lead diacetate and acetic acid, giving (XXVII) and consequently the amide (XVIII). The occur-

ce of this side-reaction could derive from the severe interaction between the lead fragment and the o-methoxy group in intermediate (XXVI).

The failure of compounds (V) and (VI) to react can be ascribed to the inductive effect of the nitro group, which makes less probable the electrophilic attack on the nitrogen atom.

The observation that neither nuclear acetoxylation nor N-acetylation is noted in the oxidation of the three isomeric anisidines or p-toluidine with LTA indicates that in these cases neither a nitrene nor an amino radical as (XXV) is formed. This suggests that the azoderivatives formed in these reactions derive from the attack of an amino positive ion (formed by fragmentation of an intermediate such as those hypothesised recently<sup>(7)</sup>) giving an hydrazobenzene derivative which is rapidly oxidised by LTA to an azoderivative.

#### REFERENCES AND NOTES

- 1) B. Rindone, E. Santaniello and C. Scolastico, *Tetrahedron Letters*, 19, (1972).
- 2) The ratio substrate:LTA was 1:1,2 except for (IV), where a ratio 1:2 was used; the solutions were 0,05 M in anhydrous benzene. After consumption of the oxidant (1-3 days at room temperature with stirring), the solutions were filtered and analysed by g.l.c.-m.s.. Per cent values are referred to the total reaction mixture.
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- 5) C. B. Jaeger, Jr., *Chem. Abs.*, 40, 1883, (1946).
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