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THE OXIDATION OF AROMATIC ANILS WITH LEAD TETRAACETATE

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The reaction of lead tetraacetate with substances containing carbon-carbon double bonds is known to lead to addition products or to allylic substitution$^{(1)}$.

Although the Pb^{IV} oxidation of nitrogen compounds has been recently reviewed$^{(2)}$, no datum is available concerning the reactivity of anils, we therefore submitted to the action of lead tetraacetate in the scope of studying if they were able to react via nitrene intermediates.

Benzaldehyde anil, oxidised in anhydrous benzene solution at room temperature$^{(3)}$ (Reaction A), yielded azobenzene, benzaldehyde and a small amount of anilin (Table 1). A similar experiment with p-methoxybenzaldehyde anil furnished (Reaction B) again azobenzene, the aldehyde and anilin, but the reaction time was much shorter, whereas p-nitrobenzaldehyde anil did not react under the same conditions. Being the production of aromatic azoderivatives indicative of the involvement of a nitrene$^{(4)}$, a further proof was obtained by oxidation of the same anils in cumene solution, a solvent which has been shown to give rise to bicumyl when used in nitrene-forming reactions$^{(5)}$. In this case the reaction mixtures contained respectively 12% and 4% of bicumyl, together with the normal reaction products, and the amount of anilin was stronger. Again, p-nitrobenzaldehyde anil did not react. Furthermore, no trace of bicumyl could be noted in a control experiment performed by suspending lead tetraacetate in anhydrous cumene for a long period, and the anils used were not altered when left for many days in benzene or cumene solution.

To clarify the mechanistic problem correlated with these reactions, anilin was submitted to oxidation in the same solvents at room temperature, giving azobenzene in a much faster reaction (Reaction C), no bicumyl being formed in cumene solution. As literature data show that aromatic amines are oxidised via amino cation radicals(6) or amino radicals(7), it was necessary to rule out these intermediates in the oxidation of anils, thus reinforcing the suggestion that they were cleaved via arylnitrene. A further proof for this could be obtained by the results of the lead tetraacetate treatment of the benzaldehyde or p-methoxybenzaldehyde anils of o-aminobiphenyl in dry benzene at room temperature (Reaction D and E respectively). The reaction products were again the corresponding aldehydes, the azoderivative and o-aminobiphenyl, the latter substrate giving also 1% of carbazole, which has been reported in the photolysis of o-azidobiphenyl in benzene(8). Again, the p-methoxyderivative reacted faster than the unsubstituted compound, whereas a control experiment performed treating o-aminobiphenyl with lead tetraacetate in benzene yielded the same azoderivative in a much faster reaction and no carbazole was formed (Reaction F).

The observation of the reactivity order of different anils suggests some conclusions about the oxidative attack. The increased ability of p-methoxy-derivatives to be transformed by lead tetraacetate can be explained in terms of an electrophilic attack of the metal oxidant on the negatively polarised nitrogen atom as the rate-limiting step. In fact, the presence of a p-methoxy group on the aldehydic part of the anil gives a resonance stabilisation to structures in which the nitrogen atom bears a negative charge. This effect would conversely render the nitrogen atom of the p-nitroderivative unreactive toward the electrophilic metal oxidant. It is then likely to admit the formation of the intermediate (I) through an ionic pattern, whereas radical intermediates have to be excluded since, once formed, would give rise to dimeric products, as shown by the reaction of anils with metals(9) or their photolysis(10). Fragmentation of (I) yields phenylnitrene, with subsequent dimerisation, interaction with the solvent or, when possible, insertion into carbon-hydrogen bonds. The other fragment gives an aldehyde with a reaction course which closely resembles the not yet mechanistically clarified formation of an aldehyde and a substituted acetamide in the oxidation of aryldialkylamines with lead tetraacetate(11).

The obtainment of some amine in all the reactions performed reflects the ability of arylnitrenes to abstract a hydrogen atom from a suitable donor giving rise to amino radicals which are transformed by subsequent reactions(4) into azoderivatives, passing either through the amine via a second abstraction step or through hydrazobenzene. The latter would be oxidised instantly, whereas the former could partly survive owing to the lack of complete oxidation in the experimental conditions used. o-biphenyl-nitrene appear to prefer this fate owing to combined steric and electronic effects.

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3) In a typical experiment, 100 mg of substrate in 10 ml of the solvent used were oxidised with 1 eq. mol. of lead tetraacetate free from acetic acid. After consumption of the oxidant, the mixture contained still some unreacted anil owing to the non stoichiometric course of the reactions of lead tetraacetate (see ref. 1) and some polymeric material, together with the reaction products. Dilution to 25 ml with anhydrous benzene and filtration from lead diacetate of the obtained suspension allowed g.l.c.-m.s. and quantitative g.l.c. measurements.

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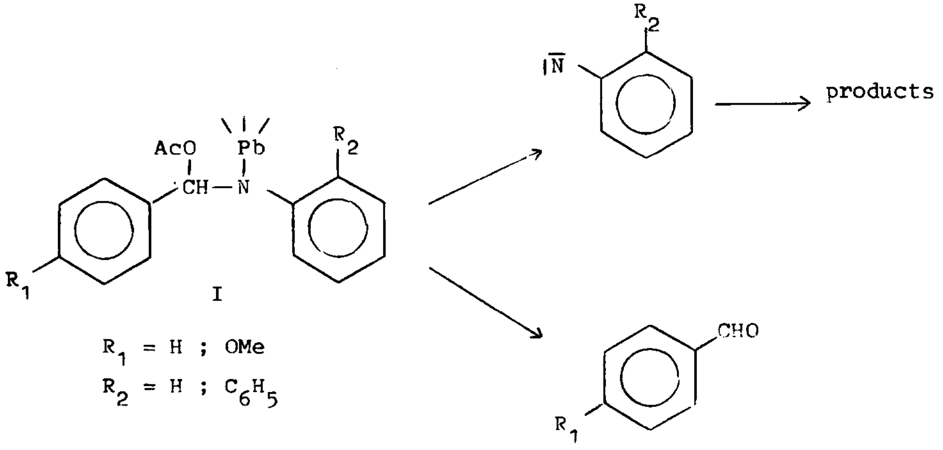
TABLE 1

Molar yields of the products in the reactions in benzene

Reaction	Anil	Aldehyde	Azoderiv.	Amine	Reac. time
A	23	11	9	≈1	96 h
B	8	30	21	≈1	35 h
C	—	—	28	4	150 min.
D	62	11	4	14	45 h
E	26	25	6	28	35 h
F	—	—	45	33	150 min.



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R_1 = H ; OMe

R_2 = H ; C_6H_5