

DEMETHYLATION AND DEALKYLATION IN THE OXIDATION OF ARYLDIALKYLAMINES WITH  
METAL ACETATES

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Some recent papers report the oxidation of tertiary amines with various metal oxidants. Aryldialkylamines are transformed by  $\text{CuCl}_2$  into complex reaction mixtures derived by di- or trimerisation reactions<sup>(1)</sup>. Lead tetraacetate (LTA) in chloroform-acetic anhydride dealkylates these compounds giving the corresponding arylalkylacetamides<sup>(2)</sup>. Tertiary amines are transformed by Fe (III)<sup>(3)</sup> or by anodic oxidation<sup>(4)</sup> into secondary amines. The positive ion radical is always indicated as an intermediate and is evidenced by cyclic voltammetry<sup>(5)</sup>. With tertiary amines having three different groups bonded to the nitrogen atom a preference for the demethylation reaction was noted<sup>(6)</sup>. These reactions, however, occur in low yield and in severe conditions and cannot easily be used for preparative purposes.

This paper is concerned with the oxidation of dimethylaniline (I), (DMA), ethylmethylaniline (II), (EMA) and n-butylmethylaniline (III), (BMA) with LTA, manganese triacetate (MTA), cobalt triacetate (CTA) and thallium triacetate (TTA) in chloroform-acetic anhydride 1:1 at room temperature under nitrogen atmosphere. The reaction product from DMA was (IV), those from EMA and BMA were (IV) and (Va) or (Vb). The results are shown in Table 1<sup>(7)</sup>.

The results show that among the oxidants used higher yields and a cleaner reaction are obtained with MTA. The reactions with LTA and CTA give also some coloured material deriving from further oxidation. The reaction with LTA is sensi-

tive to the procedure of mixing the reagents. Also TTA reacts with these substrates, probably through a reaction path concurrent with the reversible electrophilic aromatic thallation reaction already reported for many aromatic substrates other than amines<sup>(8)</sup>. The recent e.s.r. evidence for the one-electron oxidation of arenes by Tl (III)<sup>(9)</sup> suggests the conclusion that TTA reacts with the substrates through an initial charge-transfer complex analogous with that formed with the other metal oxidants. The intermediate cation radical (i.e. VI) derived from this evolves by loss of a proton to give the radical (i.e. VII) which is oxidised by the metal to the mesomeric cation (i.e. VIII) subsequently cleaved by acetic anhydride to give the acetamides.

As it has been pointed out by other groups<sup>(6)</sup>, the oxidative demethylation reaction of tertiary amines bearing different N-alkyl groups prevales on the dealkylation reaction. This fact has been indicated to depend on the major acidity of the hydrogens of a  $\text{CH}_3$  group when confronted with that of a  $\text{CH}_2\text{-R}$  group. The alteration of this acidity scale by changing the electronic properties of the groups attached to the nitrogen atom has been suggested (i.e. electron-donating *para* substituents in an aromatic ring favour the demethylation reaction). The possibility of the participation of statistical factors has been taken into consideration. Alternatively, the difference in the oxidation rate of the two possible radicals from (VII) to the carbocations related to (VIII) has been considered to drive the reaction toward demethylation. In our case, a metal-amine complex initially formed could significantly differentiate the acidities of the hydrogens involved in the elimination reaction. Moreover, the lack of dimeric materials such as those found in the oxidation of these amines with LTA, MTA and CTA in chloroform<sup>(10)</sup> seems to indicate that the whole oxidative process occurs in a metal-substrate complex.

Studies are in progress in order to define the sensitivity of the demethylation/dealkylation ratio toward nuclear substituents and to obtain a kinetic des-

cription of the reaction.

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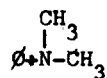
TABLE 1

		LTA*	MTA**	CTA**	TTA*
DMA	(IV)	33%	58%	46%	9%
	(IV)	29%	61%	18%	8%
EMA	(Va)	2%	8%	4%	2%
	(IV)	46%	83%	37%	42%
BMA	(Vb)	6%	1%	4%	3%

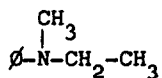
\* 1 mole/mole. Reaction time: 40' for LTA, 2 days for TTA.

\*\* 2 moles/mole. Reaction time: 16 h.

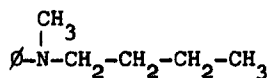
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(I)



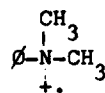
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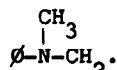
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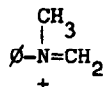
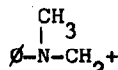
(IV)

(Va) : R = -CH<sub>2</sub>-CH<sub>3</sub>(Vb) : R = -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>

(VI)



(VII)



(VIII)