The Unusual Anodic Reactivity of Tertiary Enamines in the Presence of Base: the Effect of the Nature of the Base on the Product Distribution

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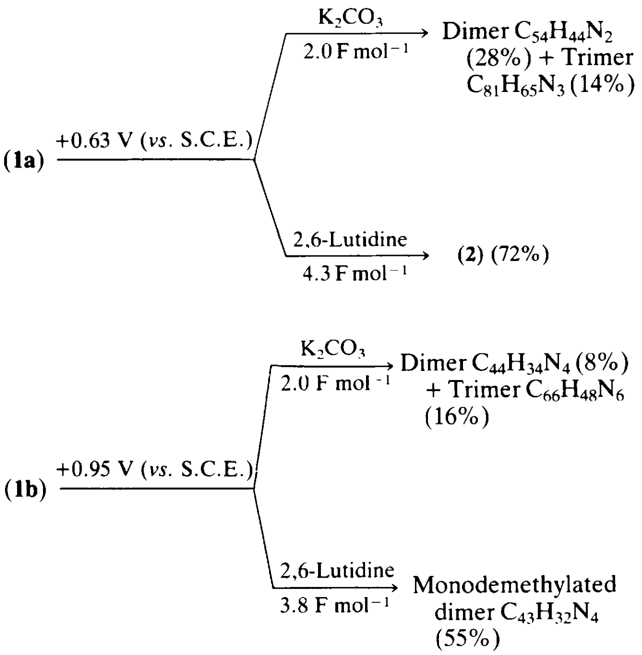
The anodic oxidation of aromatic *N*-methyl-*N*-phenylenamines leads to dimers and trimers in the presence of K_2CO_3, whereas in the presence of 2,6-lutidine demethylation occurs and, in one case, this is subsequent to cyclisation and results in a new 3*H*-indole.

Tertiary amines are known[1] to react anodically and this generally results in substitution or dimerization products where the nitrogen atom is not involved. However, with arylalkylamines, it has been established that in most cases the intermediate is the iminium salt which is slowly decomposed by the nucleophiles present in the medium, giving α-substituted amines. For less acidic cation radicals, the route *via* an iminium salt is not observed and the main products are the result of an anodic aryl–aryl coupling giving rise to more or less complex benzidine derivatives.

Curiously enough, there are no reports of work on enamines in general and enamines of the general formula (**1**) in particular. Work on symmetrical enediamines showing reversible two-electron oxidation has been reported[2,3] as has the fate of the transient dications slowly decomposed in the anode electrolyte, resulting in indolo-oxazolidines in good yield.[4]

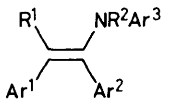
Here we report our initial results on the anodic behaviour of the enamines (**1a**) and (**1b**). Macroscale electrolyses (in 0.3 M acetonitrile–$LiClO_4$) were carried out in a divided H cell, with a platinum anode (A = 16 cm^2) and a graphite cathode. To the magnetically stirred anode compartment (volume = 60 ml) containing the enamine (**1**) (concentration 4 mM), was added either an insoluble base [K_2CO_3 (1.5 g)] or a soluble base [2,6-lutidine (concentration 20 mM)]. Depending on the enamine used [(**1a**) or (**1b**)] and the nature of the base, quite different electrolysis products were isolated and characterized (Scheme 1).



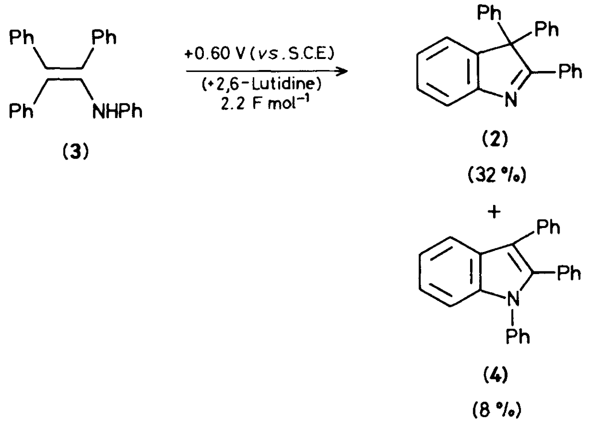
Scheme 1. S.C.E. = saturated calomel electrode.

Several observations can be made, from the product distribution, after the electrolyses.

(i) The dimers are not formed *via* Ph^3–Ph^3 coupling. The symmetrical dimer (unambiguously synthesised by methylation of the reaction product of benzidine with benzoylphenylacetonitrile) that would result from Ph^3–Ph^3 coupling, was not found among the products of electrolysis of (**1b**). For this reason and since trimers were also formed, a Ph^1–Ph^3 coupling is likely, because it is most favourable for such oligomerisations.



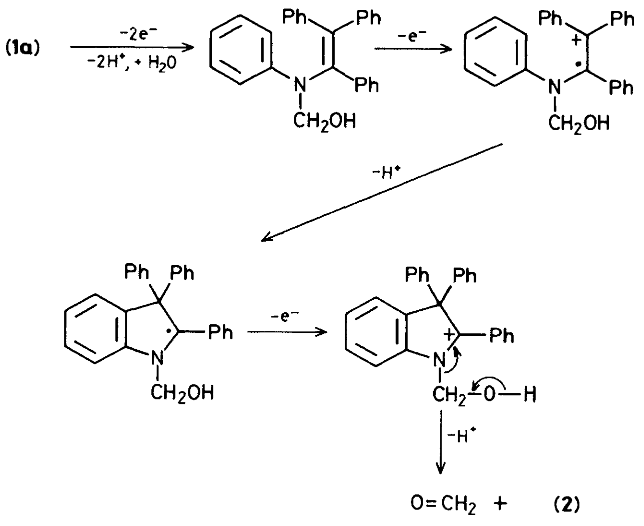
(1) a; R^1 = Ph
b; R^1 = CN
R^2 = Me; Ar^1 = Ar^2 = Ar^3 = Ph



Scheme 2

(ii) The use of a soluble base promotes the fast deprotonation process, according to the classical e.c.e. mechanism, very common for tertiary arylalkylamines. However, for the enamines (**1a**) and (**1b**), demethylation is observed. Therefore the loss of the methyl group already noticed for some diarylmethylamines[5] also occurs for other types of amines.

(iii) From (**1a**), 2,3,3-triphenyl-3*H*-indole (**2**) was isolated in good yield [m.p. 153 °C (di-isopropyl ether)]. This new indole was identified unambiguously by a Fischer indole synthesis (reaction of phenylhydrazine with 1,2,2-triphenylethanone). The anodic synthesis of (**2**) can also be achieved *directly*, from the corresponding secondary enamine (**3**), but the yield is much lower and the indole (**2**) is accompanied by 1,2,3-triphenylindole (**4**)[6] (Scheme 2).



Scheme 3

The high yield from the electro-oxidation of (**1a**) leading only to (**2**), contrasts strongly with the lower yield obtained and the mixture formed from (**3**). This would suggest that demethylation occurs after cyclisation in the oxidation product of the enamine (**1a**), especially since such a mechanism would prevent the formation of the isomeric indole (**4**) (Scheme 3).

Received, 21st May 1984; Com. 702

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