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THE CONVERSION OF UNBRANCHED PRIMARY ALKYL AND ARYLALKYL AMINES TO NITRILES BY MEANS OF LEAD TETRAACETATE[a]

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The only amino compounds oxidized so far with lead tetraacetate were primary aromatic amines, which gave mainly the corresponding azo compounds /1/, and some tertiary aryldialkyl amines, which in glacial acetic acid in the presence of acetic acid anhydride underwent oxidative dealkylation with the formation of acetylated secondary amines /2/.[c]

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[c] Similarly to the fission of 1,2-glycols, primary and secondary 1,2-aminoalcohols are easily cleaved at the C-C bond when subjected to the action of lead tetraacetate in the cold /3/, while tertiary 1,2-aminoalcohols are decomposed only at higher temperatures /in acetic acid/, with rupture of the C-N bond, to give secondary amines and glycolaldehyde or glyoxal /4/.

We have now undertaken a systematic study on the action of lead tetraacetate on amines, and in the present paper we wish to report the results obtained with unbranched aliphatic amines / n-butylamine, n-hexylamine, n-heptylamine and n-octylamine/ and with benzylamine. These compounds reacted with lead tetraacetate to give as major products the corresponding nitriles, probably by a two-step dehydrogenation process involving as intermediate an unstable aldimine:

$$RCH_2NH_2 \xrightarrow{Pb/OAc/_4} [RCH{=}NH] \xrightarrow{Pb/OAc/_4} RCN$$

The oxidations were carried out in boiling benzene /100ml per 0.1 mole of amine/. When the reactants were used in a 1:1 molar ratio, the reaction was completed in less than one hour and the yields of nitriles ranged from 20 to 36% / Table 1/. With two moles of lead tetraacetate per mole of amine the time required for complete consumption of the tetravalent lead reagent was considerably prolonged, and the yields of nitriles were nearly doubled / see Table 1/. Addition of pyridine, calcium carbonate or acetic acid did not improve the yields of cyanides.

Nitriles were identified on the basis of their physical constants, infrared spectra and by hydrolysis to the corresponding acids. In the case of benzylamine, the obtained benzonitrile was accompanied by a small amount of benzaldehyde / 2-4%/, which probably arose from hydrolysis of intermediate benzaldimine. Under identical conditions aliphatic amines did not produce detectable amounts of the corresponding aldehydes.

TABLE 1

Yields of Nitriles Obtained in the Lead Tetraacetate Oxidation of Amines

Amine	Molar Ration of Amine to $Pb/OAc/_4$	Nitrile / in %/
n-Butylamine	1:1	20
n-Butylamine	1:2	39
n-Hexylamine	1:1	30
n-Hexylamine	1:2	59
n-Heptylamine	1:1	32
n-Heptylamine	1:2	61
n-Octylamine	1:1	31
n-Octylamine	1:2	60

Other products formed in these reactions were high-boiling amides, nitrogen containing acetates and partially polymerized material.[d] One of the amides, isolated upon oxidation of *n*-hexylamine, was found to be N-hexyl hexanoic acid amide. The formation of these by-products may be accounted for by assuming primary attack of the starting amine on the nitrile or the intermediate aldimine and/or acetoxylation

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[d] Benzyl acetate, resulting from attack of methyl radicals /generated by the decomposition of acetoxy radicals formed from lead tetraacetate in the course of the reaction/ on benzene, was always isolated in low yields.

of various intermediates and products in the reaction mixture. In no case did we isolate products resulting from oxidative coupling /hydrazines/ or intramolecular cyclization /pyrrolidines or piperidines/.

The dehydrogenation of primary amines by means of lead tetraacetate might be of synthetic value, since the nitriles are easily isolated and are obtained in satisfactory yields. The conversion of amines to nitriles has so far been possible only by catalytic dehydrogenation /5/ and, in a few cases, by oxidation with iodine pentafluoride /6/.

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