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Rearrangements of Tertiary Amine *N*-Oxides. XXVI. Reactions of Arylnitrones with Lead Tetraacetate

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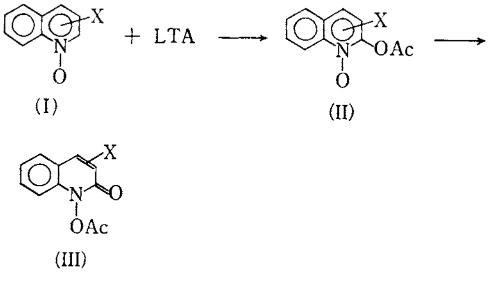
Lead tetraacetate (LTA) has been used widely as a reagent for electron-oxidation of many organic compounds, for instance, the oxidation of alcohols or phenols to the corresponding ketones or quinones. An interesting example is the oxidation of quinoline *N*-oxide (I).[1] In this case, the heterocyclic carbon α to the *N*-oxide function is oxidized to afford the corresponding *N*-acetoxycarbostyril (III) which appears to be produced through the formation of α-acetoxyquinoline *N*-oxide (II) as shown below.



According to Ochiai and Ohta, electron-donating groups on the ring afford the corresponding carbostyrils in higher yields than electron-withdrawing groups.[1]

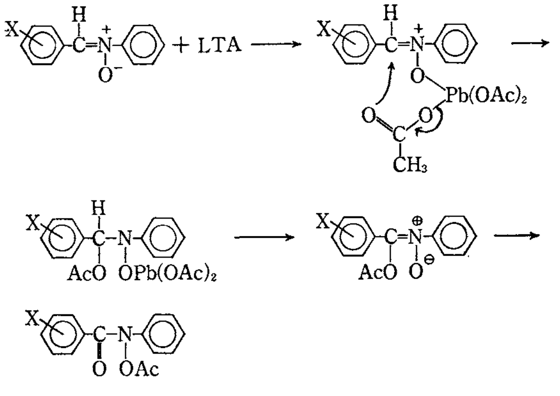
In extending this oxidation reaction by LTA to other tertiary amine *N*-oxides, we have examined the oxidation of arylnitrones which are considered to be the analogs of quinoline *N*-oxide.

When LTA was added portionwise into arylnitrones in dry benzene, the colorless powder precipitated immediately. When the precipitate was filtered off and benzene was removed from the filtrate by evaporation, either crystalline or oily products was obtained quantitatively irrespective of the nitrone employed. For instance, α,*N*-diphenylnitrone afforded *N*-acetoxy-*N*-benzoylaniline as the sole product.

Other examples of stoichiometries are tabulated in Table 1.

The structures of the products were determined by means of NMR, IR, elemental analysis as well as by chemical conversion to the corresponding *N*-hydroxybenzamides.

The reaction appears to proceed through the following scheme.



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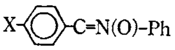
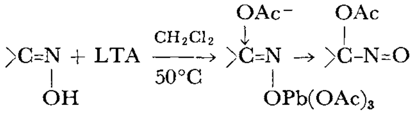
[1] E. Ochiai and A. Ohta, *Chem. Pharm. Bull.* (*Tokyo*), **10**, 1260 (1962). *ibid.*, **11**, 1586 (1963).

Table 1. Reaction of arylnitrones with lead tetraacetate in benzene

	Mp (bp) (°C)	*N*-Oxide	Lead tetraacetate (g)	Product	Lead diacetate
p-Cl	108	2.0	4.0	2.15	2.17
H	(165—170/2 mmHg)	1.0	2.2	1.0	1.46
p-CH_3	95—96	0.75	1.6	0.90	1.12

The reaction of nitrones with LTA takes place very readily without heating the reaction mixture, whereas that of quinoline *N*-oxide requires refluxing of the solution. In the reaction with acylating agents also, nitrones are much more reactive than quinoline or pyridine *N*-oxide. Thus, we can conclude that nitrones are in general more reactive in oxidation than the aromatic *N*-oxides.



$$>C=\underset{OH}{N} + LTA \xrightarrow[50°C]{CH_2Cl_2} >\overset{OAc^- \downarrow}{C}=\underset{OPb(OAc)_3}{N} \rightarrow >\overset{OAc}{C}-N=O$$

Apparently, the oxidation of oximes by LTA resembles that of nitrones. In this case, however, the transfer of acetyl group does not take place from the C–O group[2] perhaps because of the low basicity of nitroso group. More detailed investigations on the oxidation reactions of tertiary amine *N*-oxides with LTA are in progress.

Experimental

Typical Run. *a*,*N*-Diphenylnitrone (1.00 g) in benzene was treated with LTA (2.2 g). Exothermic reaction took place immediately. The solution was cooled down to room temperature and the precipitated white lead diacetate was filtered off. The solvent benzene was removed on boiling water bath. Distillation of the resulting oil under reduced pressure gave *N*-acetoxy-*N*-benzoylaniline, bp 165—170°/2 mmHg. IR: 1780, 1665 cm^{-1}. NMR: 7.82 (acetyl methyl proton); 2.67 (*N*-phenyl ring proton); 2.50 (*a*-phenyl ring proton).

Elemental analyss of other products;

N-Acetoxy-*N*-(*p*-chlorobenzoyl)aniline. Found: C, 62.7; H, 4.11; N, 5.04%. Calcd for $C_{15}H_{12}NO_3Cl$: C, 63.3; H, 4.04; N, 4.84%.

N-Acetoxy-*N*-(*p*-methylbenzoyl)aniline. Found: C, 71.28; H, 5.64; N, 5.39%. Calcd for $C_{16}H_{15}NO_3$: C, 71.24; H, 5.57; N, 5.20%.

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[2] H. E. Baumgarten, A. Stablis and E. M. Mille, *J. Org. Chem.*, **30**, 1203 (1965). C. C. Liffland and E. Cerda, *ibid.*, **28**, 2769 (1963).