The Oxidation of Some Aldehyde Arylhydrazones by Lead Tetra-acetate: Formation of Some Novel Azo-compounds and Evidence for Nitrilimine Intermediates

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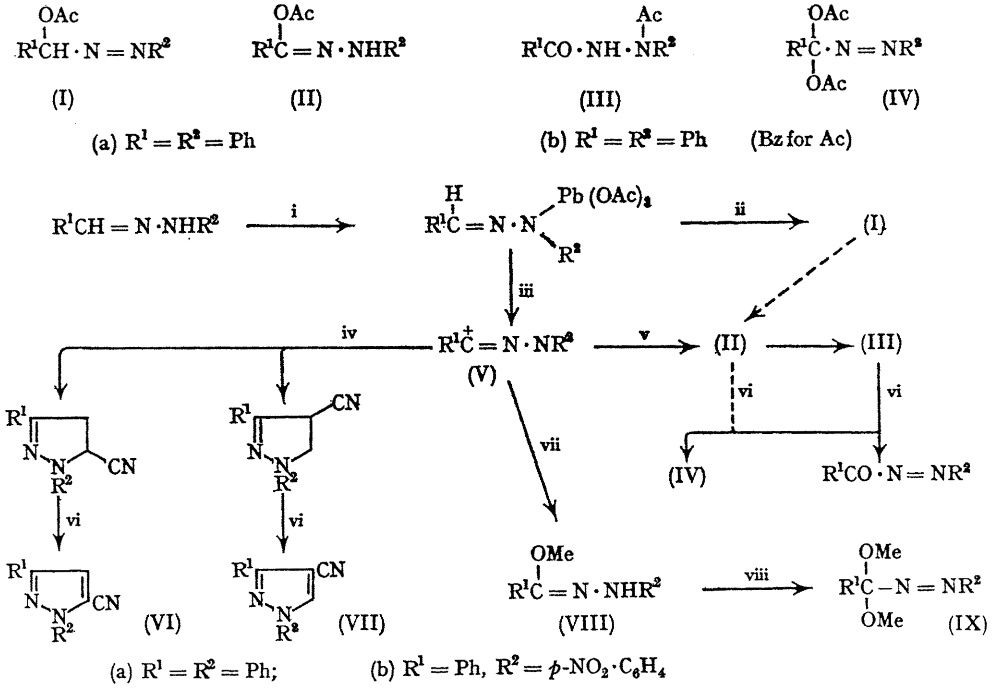
SUITABLY substituted aldehyde hydrazones undergo oxidative cyclisation with lead tetra-acetate.[1] The cyclised products are often accompanied by *NN'*-diacylhydrazines (III),[2] formation of which appears to be a general reaction of those aldehyde hydrazones which cannot cyclise.[2,3] Since ketone hydrazones give azoacetates[4] of the type $R^1R^2C(OAc)\cdot N:NR^3$, these *NN'*-diacylhydrazines have been assumed to arise from analogous azoacetates (I) by tautomerism to the hydrazidic acetates (II) and subsequent rearrangement. However, neither of these intermediates has been isolated. We now report the isolation of the azoacetate (Ia)‡ ($\leqslant 27\%$) from the lead tetra-acetate oxidation of benzaldehyde phenylhydrazone under nitrogen at room temperature, together with evidence that this compound is not an intermediate in the formation of other oxidation products, but that these arise independently *via* the 1,3-dipolar intermediate (V).

The structure of the compound (Ia), which is a stable yellow oil (b.p. *ca.* 125°/0·05 mm.), follows from its typical azo u.v. spectrum [λ_{max} 275 (log ϵ 4·13) and 403 nm. (2·32)], carbonyl absorption (1755 cm.$^{-1}$), mass [*m/e* 254 (M^+) and 149 (M − PhN:N·)], and ^{1}H n.m.r. spectrum [aromatic multiplet (10H), singlets at δ 7·13 (1H) and 2·22 (3H)]. Besides the azoacetate (Ia), oxidation of the phenylhydrazone also gave benzoylazobenzene[5] (*ca.* 35%) and the azodiacetate (IVa) ($\leqslant 5\%$) as a yellow solid m.p. 99—100°: these compounds were also formed by lead tetra-acetate oxidation of the diacylhydrazine (IIIa).

Under the conditions used for oxidation of the phenylhydrazone, the azoacetate (Ia) both rearranged to the diacylhydrazine (IIIa), and consumed lead tetra-acetate. However, both reactions proceeded so slowly that the azoacetate cannot be significantly involved in the formation of the other products. An alternative pathway involves formation of the nitrilimine (V) (*cf.* formation of nitrile oxides from *syn*-aldoximes and lead tetra-acetate)[6]; reaction of this nitrilimine with acetic acid would give the hydrazidic acetate (IIa) and thence the other products (Scheme). Evidence for this was obtained by trapping the nitrilimine; oxidation of the phenylhydrazone in acrylonitrile at 0° gave 1,3-diphenylpyrazole-5-carbonitrile[7] (VIa) (64%) and the corresponding 4-nitrile (VIIa) (2%).

Further studies have established the generality of these reactions. Oxidation of benzaldehyde phenylhydrazone with lead tetra-benzoate gave the azobenzoate (Ib) (16%) and the azodibenzoate (IVb) (35%), while lead tetra-acetate in methanol gave the azodimethyl ether (IXa) (62%), which must arise from further oxidation of the hydrazidic methyl



SCHEME

(i) $Pb(OAc)_4$–AcOH; (ii) $-Pb(OAc)_2$; (iii) $-Pb(OAc)_3^-$, $-H^+$; (iv) $CH_2{=}CH{\cdot}CN$; (v) AcOH; (vi) $Pb(OAc)_4$; (vii) MeOH; (viii) Pb $(OAc)_4$–MeOH.

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‡ Satisfactory C, H, and N analyses have been obtained for all new compounds described.

ether (VIIIa). In no instance did oxidation of benzaldehyde *p*-nitrophenylhydrazone give products of the type (I), but with lead tetra-acetate in methanol both the methoxy-compounds (VIIIb) (13·5%) and (IXb) (47·5%) could be isolated: compounds of the type (VIII) have been prepared by other methods.[8] Several *NN'*-diacyl derivatives (III) of phenyl and *p*-nitrophenylhydrazine were oxidised to azodiacylates (IV), mostly in good yield, but oxidation of these hydrazines in alcohols did not lead to ethers of the type (IX).

Further oxidations have also been carried out in acrylonitrile. Benzaldehyde *p*-nitrophenylhydrazone gave 1-*p*-nitrophenyl-3-phenylpyrazole-5-carbonitrile (VIb) (60%) which was also obtained from the *p*-nitrophenylhydrazones of benzoin (57%) and benzil (22%); in the last two cases, the nitrilimine is evidently formed by loss of the cations $PhCH(OH)^+$ and $PhCO^+$ respectively. Propanal *p*-nitrophenylhydrazone gave 3-ethyl-1-*p*-nitrophenylpyrazole-5-carbonitrile (26%). These experiments illustrate this convenient method for the generation of nitrilimines and thus for the preparation of the products obtainable from them.

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