Tetrahedron Letters No. 29, pp 2711 - 2714, 1973. Pergamon Press. Printed in Great Britain.

REACTION OF OPEN-CHAIN CONJUGATED NITRONES WITH LEAD TETRAACETATE AND ACETIC ANHYDRIDE

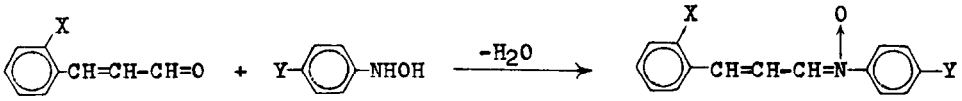
Nazar Singh and Kewal Krishan

Department of Chemistry, Punjabi University, Patiala-147002, India.

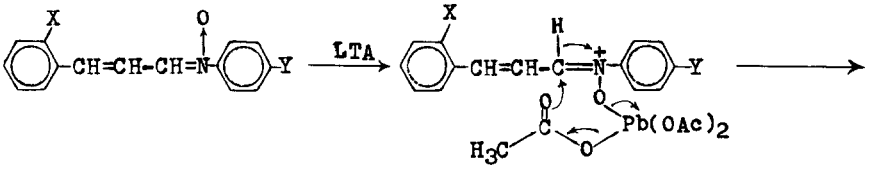
(Received in UK 30 May 1973; accepted for publication 7 June 1973)

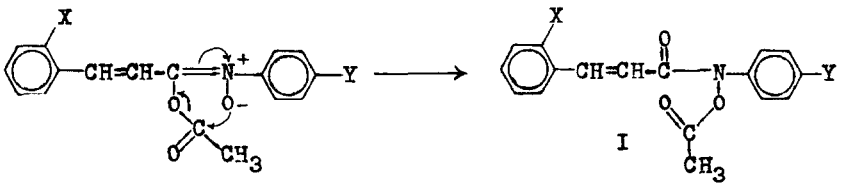
Some aromatic heterocyclic amine N-oxides are oxidized by lead tetra-acetate[1] (LTA) to the corresponding N-hydroxy derivatives. Quinoline N-oxide for example, on heating with LTA in benzene or chloroform gives N-acetoxycarbostyril which, when allowed to stand in air or when hydrolysed with dilute hydrochloric acid yields 1-hydroxycarbostyril in satisfactory yield. This type of reaction fails with pyridine N-oxide and 4-nitroquinoline N-oxide. C,N-Diphenylnitrone[2] gives only N-acetoxy-N-benzoylaniline in quantitative yield, on treatment with LTA. Aldonitrones rearrange to the isomeric amides[3] on treatment with phosphorus pentachloride, phosphorus trichloride, phosphorus oxy-trichloride, thionyl chloride, sulphur dioxide, acetic anhydride (Polonovski rearrangement), acetyl chloride, ethanolic alkali solutions etc.

Similar reactions have not been reported so far with open-chain conjugated nitrones. Nitrones[4], with or without a conjugated nitro group have been synthesized by condensing o-nitrocinnamaldehyde and cinnamaldehyde with arylhydroxylamines.



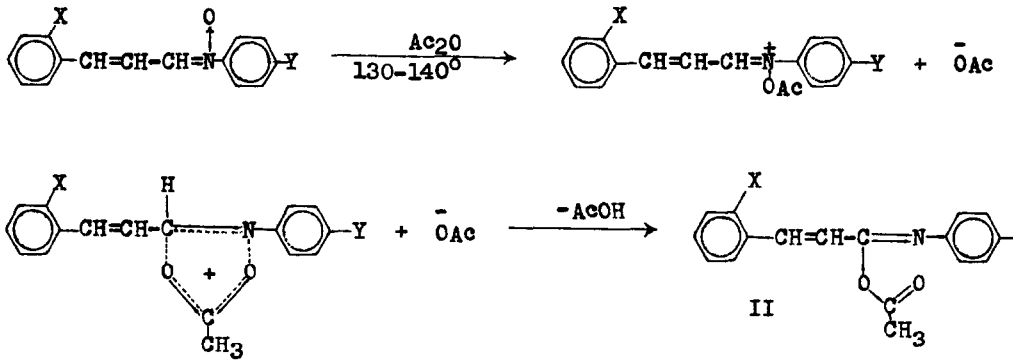
These nitrones on reaction with LTA in benzene or methylene dichloride, are oxidized exclusively to the corresponding, highly stable N-acetoxy drivatives in good yields.





I

These nitrones when treated with freshly redistilled acetic anhydride at 130-140°, yield highly stable C-acetoxy conjugated imino intermediates in excellent yields. These derivatives may be hydrolysed to the corresponding amides on treatment with hydrochloric acid.



II

TABLE

S.No.	X=	Y=	I		II	
			M.P.* °C	Yield %	M.P.* °C	Yield %
1.	NO_2	H	101	70	99	85
2.	-do-	CH_3	122	75	149	80
3.	-do-	Cl	111	80	134	80
4.	H	H	152	50	135	100
5.	-do-	Cl	172(d)	40	136-137	90

*All the melting points are uncorrected.

These products have been characterized by their elemental analysis and the study of their Infrared, Nuclear Magnetic Resonance and Mass spectra.

The infrared spectrum of N-acetoxy-N-(o-nitro)-cinnamoylaniline shows strong absorption bands at 1795 cm^{-1} (C=O, ester); 1672, 1630 cm^{-1} (C=O, conjugated keto group); 1528-1515, 1370-1340 cm^{-1} (nitro group) and 996, 970 cm^{-1} (CH=CH, trans group). The Nuclear Magnetic Resonance spectrum of this compound shows a doublet signal equivalent to one proton at τ 1.83 (C<u>H</u>=CH), a multiplet equivalent to one proton at τ 3.60 (CH=C<u>H</u>), a singlet equivalent to three methyl protons at τ 7.76 in addition to a multiplet for aromatic protons. The High Resolution Mass spectrum of this product gives the molecular ion peak at m/e 326. Prominent ion peaks are obtained by the fission of the bonds α to the carbonyl and nitrogen functions.

The infrared spectrum of C-acetoxy-C-(o-nitro)-styryl-N-phenyl imine showed the presence of characteristic strong bands at 1708-1692 cm^{-1} (C=O, ester) and 1628, 1616 cm^{-1} (C=N, conjugated) in addition to the usual bands for nitro and CH=CH trans groups. The Nuclear Magnetic Resonance spectrum of C-acetoxy-C-(o-nitro)-styryl-N-(o-tolyl)-imine showed a doublet signal for one proton at τ 1.70-2.10(C<u>H</u>=CH), a doublet signal for one proton at τ 3.10-3.50 (CH=C<u>H</u>), a singlet signal for six methyl protons at τ 7.60 in addition to a multiplet for aromatic protons. The mass spectra of C-acetoxy-C-(o-nitro)-styryl-N-phenyl imine and C-acetoxy-C-(o-nitro)-styryl-N-(p-Chloro)-phenyl imine give the molecular ion peaks at m/e 310 and 345 respectively.

Structures assigned to other derivatives are also similarly supported by their elemental and spectral analysis.

Acknowledgement:

The authors are thankful to the University Grants Commission, New Delhi, for financial assistance (to K.K.).

References:

1. E.Ochai and A. Ohta, Chem. Pharm. Bull. (Tokyo), 10 , 1260(1962).

2. S. Tamagaki and S. Oae, Bull. Chem. Soc. Jap., 43(5) , 1573 (1970).

3. J. Hamer and A. Macaluso, Chem. Rev., 64 , 473 (1964).

4. Kewal Krishan, Ph.D. Thesis, Punjabi University, Patiala, 1972.