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THE TRIAZOLE RING AS A NEIGHBOURING GROUP IN LEAD TETRAACETATE REACTIONS

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While the oxidation of hydrazone systems with lead tetraacetate (LTA) has received considerable study (1), there are very little quantitative data available in the literature to substantiate the mechanisms proposed. In fact, only in one paper (2) has there been reported a body of kinetic data and these pertain to the oxidation of certain ketonic hydrazones alone. We now report the first kinetic studies of such oxidations using arylidene hydrazones, the system we used being p-substituted arylidene -5(3-phenyl)-1,2,4-triazolylhydrazones (I). In the reactions we studied, the triazole ring proved a powerful neighbouring group competitor for the reaction intermediate formed.

We examined the kinetics of oxidation of compounds (I) with LTA, by following the disappearance of the hydrazone absorptions, in the 310 mμ region in the u.v., using glacial acetic acid as solvent. The reactions followed second order kinetics being first order each in hydrazone and LTA. The relevant second order rate constants are assembled in Table 1. From these data a Hammett ρ of -0.60 ($r = 0.995$) was calculated.

Before correlating this kinetic pattern with a mechanistic scheme the products of the reaction must be considered. The product runs (Table 2) were performed by reacting hydrazones (I) with equivalent quantities of LTA in acetic acid for 3-4 hours at ambient temperatures. Work-up (3) revealed a competitive behaviour of the LTA towards the hydrazones, the reactions observed being oxidative cyclisation of (I) to 3-aryl-6-phenyl-s-triazolo (4,3-b) -s-triazoles (II) and acetoxylation of (I) to yield the N-acetyl hydrazides (III), Figure 1. (Several benzylidene triazolylhydrazones have been reacted with LTA in benzene (4) and acetic acid (5) previously, compounds (II) being again formed in high yields with no report of compounds (III)). While the bicyclic systems (II) could arise by attack at the triazolyl 1-,2-, or 4- ring positions, we demonstrated by unambiguous syntheses (6) that the products corresponded to attack at the 1- position alone. This result agrees with the earlier work of Gehlen and Röbisch (7)

Table 1

Kinetics of LTA oxidation of compounds I (acetic acid solution, 35°)

Substrate (I), Ar =	Substrate m.p. °C	k_2 (1.mole^{-1}sec.$^{-1}$)^a
4-$CH_3O.C_6H_4$	205	792 (±16)
4-$CH_3C_6H_4$	236	587 (±10)
4-$(CH_3)_2CH.C_6H_4$	217	585 (±10)
C_6H_5	237	458 (± 8)
4-$Cl.C_6H_4$	258	357 (± 3)
4-$Br.C_6H_4$	257	343 (± 6)
3-$NO_2.C_6H_4$	260	182 (± 3)
4-$NO_2.C_6H_4$	273	167 (± 3)

a. Values quoted are the means of at least three measurements.

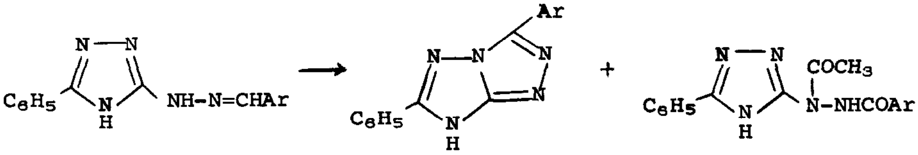
Table 2

Product runs - LTA oxidation of compounds (I)

Substrate (I)	Triazolotriazoles (II)		N-Acetyl hydrazides (III)	
Ar =	Yield %,	m.p. °C	Yield %,	m.p. °C
4- $CH_3O.C_6H_4$	91	267	-	-
4- $CH_3.C_6H_4$	88	288	1.5	228-229
4- $(CH_3)_2CH.C_6H_4$	80	233	8	238
C_6H_5	84	266	2	225-226
4- $Cl.C_6H_4$	82	326	9	242
4- $Br.C_6H_4$	76	327	11	261
4- $NO_2.C_6H_4$	76	>358	9	268

who found that cyclisation of compound I, Ar = C_6H_5, occurred at the 1-triazolyl position. Compounds (III) we prepared independently by reaction of the corresponding triazolyl hydrazides with acetyl chloride in acetic acid.

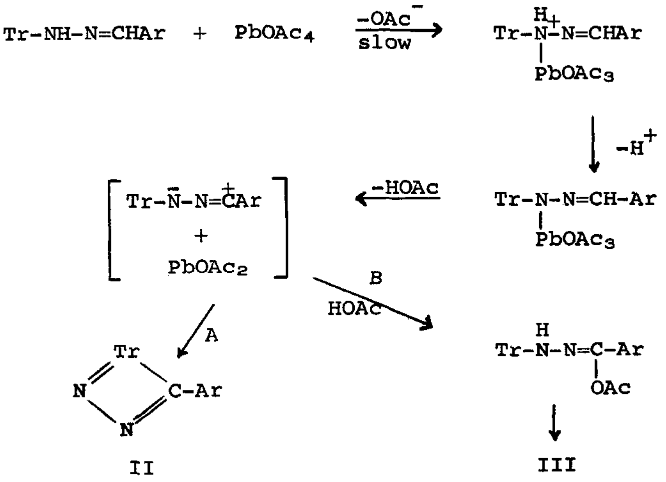
We interpret our kinetic results, in line with Norman's interpretation (2), as a rate-determining S_N2 displacement on lead (IV), (Figure 2), followed by several product-determining steps, namely, triazolyl neighbouring group participation (A) or acetate ion attack (B). In line with that scheme is our negative ρ. Norman (2) obtained a ρ of -1.95 for the effect of N-aryl variation in his LTA reactions with ketonic hydrazones. Taking the hydrazone system as a whole, ArC = N – NHAr′, and combining Norman's



I II III

Figure 1.

result and ours, this gives an N-aryl-ρ/C-aryl-ρ ratio of 3.25. We have found (8) that a very similar ratio (ca. 3.5) applies for attack on hydrazone systems by electrophiles such as diazonium ion and bromine where methine attack is rate-determining. In our present work, therefore, the kinetic data are equally compatible with N- or C- attack.



Tr = 3-phenyl -1,2,4-triazol-5-yl

Figure 2.

Norman and co-workers (9) have recently suggested that nitrilimines (Ar$\overset{+}{C}$ = N-$\bar{N}$Ar′) are intermediates in such LTA reactions with arylidene hydrazones. We attempted to trap such species in our reactions by running an LTA reaction with compound I, Ar = C_6H_5, in acrylonitrile as solvent.

While the reaction was not clean-cut and requires further study, no trapped products were detected, cyclisation (II) instead occurring in 70% yield. Thus, whatever the nature of the steps after the initial lead attack, these steps making the methine carbon more electrophilic, then the nearby triazole ring remains a powerful nucleophilic competitor for the electrophilic centre, with acetate ion attack, either intra-or inter- molecularly, being a poor alternative.

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