

OXIDATIVE FRAGMENTATION OF 3-ARYL-1-(TETRAZOL-5'-YL)TRIAZENES:
A NEW ROUTE TO ARYL DIAZOCYANIDES.

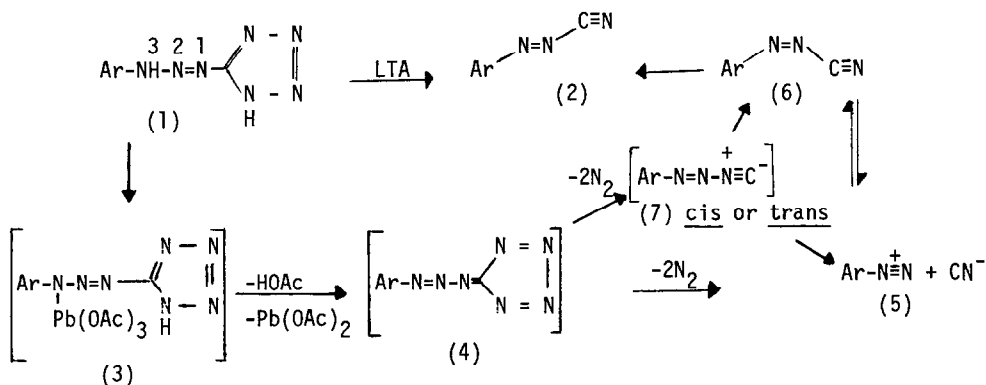
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Summary: Oxidation of 3-Aryl-1-(tetrazol-5'-yl)triazenes with $\text{Pb}(\text{OAc})_4$ resulted in a fragmentation and gave aryl diazocyanides.

Our interest in the oxidations of nitrogen systems¹ led us to examine the reactions of some electrophilic reagents with the new² 3-aryl-1-(tetrazol-5-yl)triazenes (1). Treatment³ of the compounds (1) with lead-acetate (LTA) at ambient temperatures in solvents such as dichloromethane, chloroform or pyridine resulted in an interesting new route to trans-diazocyanides (2) (Table). The products were identified from i.r. ¹H and ¹³C n.m.r. spectra and they were identical with samples prepared by direct coupling of aryl diazonium salts with cyanide ion.^{4,5} When the oxidations were carried out at 0°C in CDCl_3 and the ¹³C n.m.r. spectrum of the products measured immediately at 0°C it was found that the initial detectable products of the reaction were the cis-diazocyanides (6)⁵ which quickly rearranged to the trans-forms at ambient temperatures.

The reaction probably involved the sequence shown in Scheme 1. Oxidative dehydrogenation of the compounds (1) may occur through an N-metallo species.¹ (With $\text{Hg}(\text{OAc})_2$ polymeric triazenyl mercury derivatives containing a 3-N-Hg bond were formed). A redox in this would lead to an unstable tetrazafulvene intermediate (4). Such intermediates have been postulated in previous oxidation reactions of the 5-aminotetrazole moiety and they appear to fragment to isocyanides^{6,7}. Thus it has recently been reported⁶ that 5-aminotetrazoles, RNHCN_4H , on oxidation with LTA gave stable isocyanides $\text{R-N}^+\equiv\text{C}^-$. Such isocyanides could be precursors to the diazocyanides, although trans-diazoisocyanides have been reported⁸ to be stable. (We cannot confirm this report. Attempts by us, and by others⁹ to obtain the reported stable N-formyltriazene precursors of the diazoisocyanides failed). In the present case a direct fragmentation of the species (4) to a diazonium ion and cyanide ion could be the route to diazocyanides. The presence of aryl diazonium ion in the system was confirmed by introduction of 2-naphthol to the reaction shortly after the oxidizing agent was added when an azo dye was obtained in high yield. Attempts to trap isocyanide intermediates were not successful but they are not precluded by the presence of diazonium ion which can also arise from the cis-products(6). The initial formation of the diazocyanides in the cis-configuration is consistent with their generation intermolecularly from a diazonium ion.

TABLE		(carbon shifts (δ))						
Product	Yield %	M.p.	ν_{\max} -C \equiv N	CN	C-1'	C-2'	C-3'	C-4'
(2a)	70	102-103 ⁰	2187cm ⁻¹	115.4	151.5	125.9	130.6	143.6
(2b)	73	130-131	2184	115.4	151.6	125.8	133.5	124.5
(2c)	76	84-85	2186	114.8	154.9	125.3	125.3	150.7
(6b)	73	40-42	2146	110.7	154.6	123.6	133.05	130.2



Scheme 1 Ar=(a)4-ClC₆H₄; (b)4-BrC₆H₄; (c)4-NO₂C₆H₄

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3. General Method: A solution of the compound (1)(2 m.mole) and LTA (2m.mole) in CH₂CL₂ (20 ml.) was stirred at ambient temperatures for 18h, or at 0⁰C for 250h, after which insoluble salts were removed and the solution was washed with water and evaporated to give the products (2) (Table) which were recrystallised from n-pentane.
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