Interception of a Metallo-intermediate in the Oxidation of a Bis-hydrazone: Reactions of Benzil (Toluene-*p*-sulphonyl)hydrazones with Lead(IV) and Mercury(II) Acetates

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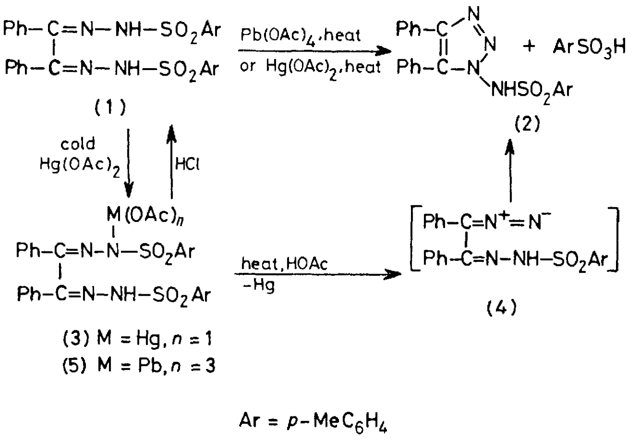
Summary Oxidation of benzil bis(toluene-*p*-sulphonyl)-hydrazone with mercuric acetate or lead tetra-acetate gave 4,5-diphenyl-1,2,3-triazol-1-yl-toluene-*p*-sulphonamide; an unstable hydrazono–mercury acetate intermediate was isolated from the oxidation and comparative evidence for a subsequent diazo intermediate is presented.

Bis-hydrazones[1] and osazones[2] have been oxidised with a range of metal-containing oxidising agents. Few mechanistic data have been reported on these reactions and metallo-intermediates have not been detected for either bis- or mono-hydrazone oxidations. We have, for the first time, intercepted a metallo-intermediate in the oxidation of a bis-hydrazone system.

When benzil bis(toluene-*p*-sulphonyl)hydrazone (**1**) (1mM) was heated under reflux in acetic acid containing an equimolar quantity of mercuric acetate, the cyclised product (**2**)† (92%), m.p. 222—224 °C from $CHCl_3$), was obtained. The triazole (**2**) (72%) was also obtained by heating compound (**1**) with $Pb(OAc)_4$ in acetic acid at 60 °C for 6 h. Toluene-*p*- sulphonic acid was encountered in both reactions. When the reaction with mercuric acetate was carried out in cold acetic acid, the unstable mercurio-intermediate (**3**)† (80%), m.p. 173—175 °C, was isolated. Separate heating of compound (**3**) in acetic acid gave the triazole (**2**) (70%) along with mercury globules and some gums containing toluene-*p*-sulphonic acid.



The conversion of the metallo-intermediate into the triazole may involve a fragmentation to a diazo intermediate (**4**) which undergoes internal cyclisation more rapidly than external solvent attack. Thus treatment of benzil mono(toluene-*p*-sulphonyl)hydrazone with $Pb(OAc)_4$ in acetic acid at 60 °C for 1·5 h gave PhCH(OAc)·COPh (80%) and toluene-*p*-sulphonic acid, in a reaction typical of attack by acetic acid on a diazo intermediate.[3] The presence of a diazo intermediate in this reaction was proved by using as solvent dichloromethane, containing sufficient triethylamine to remove the acetic acid expected to be formed. Treatment of the hydrazone in this solvent at ambient temperature gave a deep red solution, which, after washing with water and evaporation of the solvent, gave an oily residue showing intense i.r. absorptions at

2080 and 1750 cm^{-1} assigned to $Ph{\cdot}CO{-}C(Ph){=}N^{+}{=}N^{-}$. This residue, when warmed separately in acetic acid, gave $PhCH(OAc){\cdot}COPh$. The toluenesulphonic acid may arise from hydrolysis, during work-up, of a species such as $AcOSO_2C_6H_4Me$ formed in the fragmentation of the metallo-intermediate.

The hydrazono–lead triacetate intermediate (**5**) could not be detected and careful reactions in cold acetic acid gave mixtures of compounds (**1**) and (**2**) only. When benzil mono(toluene-*p*-sulphonylhydrazone) was treated with mercuric acetate, the intermediate corresponding to (**3**) reacted intermolecularly, before it could be isolated, giving a bis-hydrazono-mercury compound, $[Ph{\cdot}CO{\cdot}C(Ph){=}N{-}N{\cdot}SO_2Ar]_2Hg$, m.p. 183—185 °C.†

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† Structural assignments were confirmed by microanalysis, i.r., and ^1H and ^{13}C n.m.r. data, and by chemical conversions. Characterization data were made available to the referees.

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