Pyrolysis of N^1,N^3-Diaryltriazene 1-Oxides†

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Pyrolysis of the 1,3-dipole unsymmetrical diaryltriazene 1-oxides in acetonitrile and toluene shows that these compounds may serve as a source of aryl radicals.

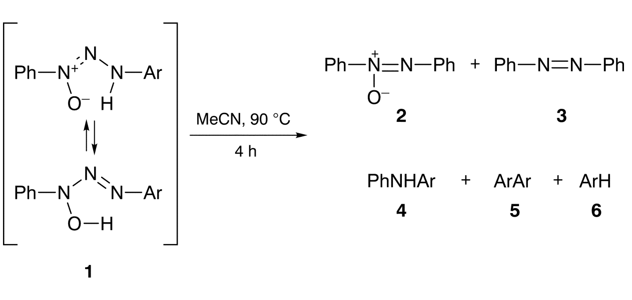
Previously, we have reported that unsymmetrical diaryltriazene 1-oxides did not undergo 1,3-dipolar cycloaddition reactions with tetracyanoethylene, instead charge-transfer complexes were formed.[1] On the other hand, photolysis of these oxides led to their decomposition. 2-Hydroxyazobenzene, mono- and di-substituted biaryls were produced.[2] Therefore, it seemed desirable to study the thermal effect on this 1,3-dipole system in organic solvents. This paper presents our results obtained from the pyrolysis of various N^1,N^3-diaryltriazene 1-oxides in acetonitrile and toluene.

Nitrogen was bubbled through solutions of 0.5 mmol of triazene 1-oxides **1** in dry acetonitrile to remove the oxygen, and the sealed ampoules were heated for 4 h (see Experimental section). The reaction mixtures were identified and quantified through gas chromatography coupled with mass spectrometry (GC-MS), by comparing the peak areas and fragmetation patterns of the products with those of authentic samples.

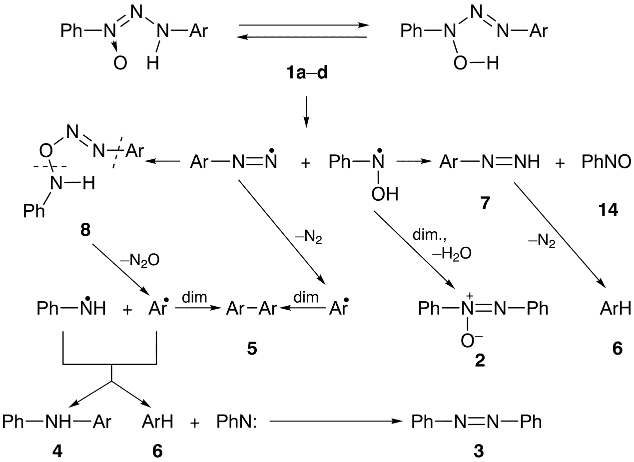
As shown in Scheme 1, pyrolysis of compounds **1** in acetonitrile led to the formation of azoxybenzene **2** (major product 10.3–36%), azobenzene **3**, diarylamines **4**, biaryls **5** and arenes **6**. In addition to these idenified compounds a multicomponent mixture is produced. The individual components of this mixture are characterized by higher retention times and therefore probably of higher molecular weight. None of these peaks has so far been identified.

Earlier Morgan and Walls[3] had proposed that pyrolysis of 1,3-di-*p*-tolyltriazene proceeds *via* fragmentation into *p*-polylaminyl radicals. In addition Hardie and Thomson[4] found that the tautomerism of asymmetric triazenes results in the production of two different aryl radicals and two arylaminyl radicals.

This partitioning phenomenon could not be observed by Morgan and Walls[3] because their triazenes were symmetrically substituted, and it will probably not occur in this investigation because an oxygen atom shift would not as easy as a (solvent mediated) hydrogen shift. In accordance with the literature results above, a rational formation of azoxybenzene **2**, azobenzene **3**, diarylamines **4**, biaryls **5** and arenes **6** is presented in Scheme 2 featuring radical pathways throughout.



Scheme 1 **a** Ar = Ph; **b** Ar = *p*-MeC$_6$H$_4$; **c** Ar = *p*-MeOC$_6$H$_4$; **d** Ar = *p*-ClC$_6$H$_4$



Scheme 2 **a** Ar = Ph; **b** Ar = *p*-MeC$_6$H$_4$; **c** Ar = *p*-MeOC$_6$H$_4$; **d** Ar = *p*-ClC$_6$H$_4$

Pyrolysis of triazenes 1-oxides **1a**–**d** may lead to cleavage into the corresponding hydroxyphenylaminyl and aryldiazenyl radicals. The latter may undergo loss of nirogen to form an aryl radical and/or to react with hydroxyphenyl aminyl radical to form either compound **8** or nitrosobenzene with the aryldiimine **7**. It has been reported that triazene 1-oxides may exist in a tautomeric mixture with their hydroxytriazene form.[5] The N—OH tautomer of **1** may be envisaged as the 1 : 1 adduct of aryldiazine **7** and nitrosobenzene, since it had earlier also been demonstrated that α-azoalcohols may be generated by addition of diazenes to aldehydes[7–9] (but not to ketones), and nitrosobenzene may well be regarded as aza-analogous to benzaldehyde. Ketone-derived α-hydroxydiazenes have been reported by Schulz *et al.*,[10] and the proposed fragmentation pattern for **1** is well in accord with the suggested fragmentation of α-hydroperoxy diazenes[11] and α-hydroxydiazenes,[12] which have been demonstrated as a source of alkyldiazenes. Diimines **7** may either form the ayldiazenyl radicals or lose nitrogen to produce the arenes **6**; loss of nitrogen from the aryldiazenyl radical leaves an aryl radical which may dimerise to form the biaryls **5**. On the other hand, loss of dinitrogen oxide (N$_2$O) from compound **8** generates phenylaminyl and aryl radicals. The latter can dimerise into the biayls **5** or couple with phenylaminyl radical to form the penylarylamines **4**. Alternatively, phenylaminyl may react with any aryl to form phenylnitrene and the corresponding arenes **6**; dimerisation of the pheylnitrene results in formation of azobenzene **3**. It should be noted that phenyldiazene may give dinitrogen and hydrazobenzene in a bimolecular process.[13] Moreover, hydrazobenzene could be converted into **3** by dehydrogenation.

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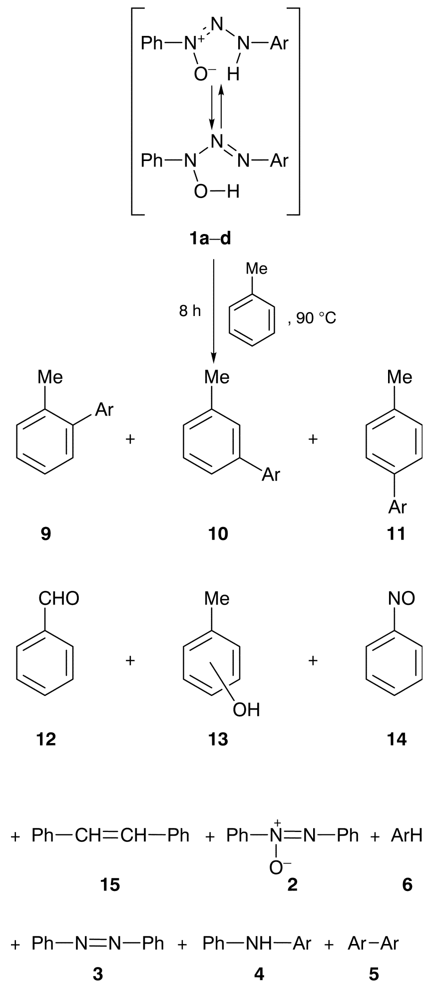
†This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1998, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.



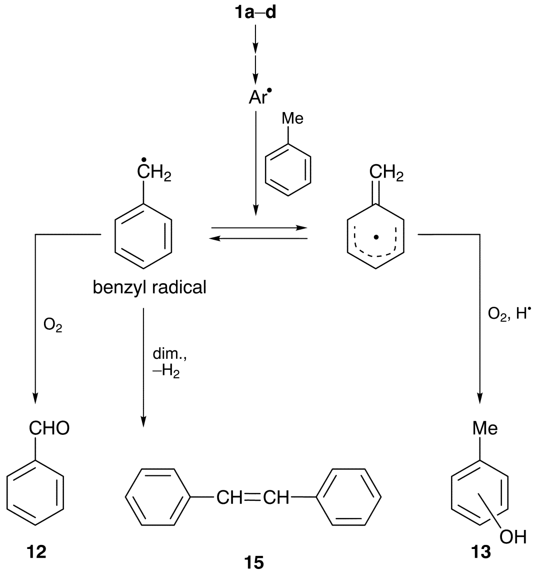
Scheme 3 **a** Ar = Ph; **b** Ar = p-MeC$_6$H$_4$; **c** Ar = p-MeOC$_6$H$_4$; **d** Ar = p-ClC$_6$H$_4$

The pyrolysis of triazene 1-oxides **1** in toluene was investigated qualitatively. As expected, arylation of toluene to form the three isomers **9**–**11**, as well as formation of benzaldehyde **12**, cresols **13** and nitrosobenzene **14**, 1,2-diphenylethene **15** besides **2**–**6** were observed. The reaction products were identified by GC-MS as in the case of acetonitrile, as solvent. The product pattern was rationalised in the same manner as in the case of acetonitrile, assuming radical processes throughout. Formation of benzaldehyde **12** and cresols **13** in this case may be attributed to toluene acting as a hydrogen source and consequently giving rise to benzyl radicals which have to react with some oxygen source (H$_2$O). 1,2-Diphenylethene **15** may be formed by combination of benzyl radicals with **12**.

These results generally show that diaryltriazene 1-oxides **1** may serve as a source of aryl radicals. One has, however, to accept accompanying formation of arylamino and arylhydroxyamino radicals with their own follow-up reactions.

Experimental

Melting points were taken with a microscope/Reichert Thermovar and Griffin apparatus and uncorrected. The triazene 1-oxides **1a**–**d** (**1a**: mp 127 °C, lit., 127 °C. **1b**: mp 130–131 °C, lit., 131 °C. **1c**: mp 113–114 °C, lit., 114 °C. **1d**: mp 146–147 °C, lit., 146 °C)[14] were prepared according to the literature.[15] Acetonitrile and toluene were purified following Vogel,[16] dried and distilled. GC-MS spectra were recorded using a HP5890 series II Gas chomatograph and HP5971 mass-selective detector (Hewlett-Packard) using SE-54 on Chromosorb as a column packing material (polysiloxane with 94% methyl, 1% vinyl, and 5% phenyl). The column length was 25 m, inner diameter 0.25 mm and outer diameter 0.38 mm.



Scheme 4 **a** Ar = Ph; **b** Ar = p-MeC$_6$H$_4$; **c** Ar = p-MeOC$_6$H$_4$; **d** Ar = p-ClC$_6$H$_4$

General method.—Solutions of 0.5 mmol of each unsymmetrically substituted triazene 1-oxide **1** in 1 ml of the dry reactant solvent (either acetonitrile or toluene) were placed in sealed ampoules and kept for 8 h at 90 °C. Single ampoules were then withdrawn for GC-MS analysis. Available authentic samples were used for the identification and quantification of the products; the other compounds were identified by comparison of spectral and physical data with those of reported samples.

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