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Reaction of Triazene 1-Oxides: Novel Synthesis of Solid Arenediazonium Chlorides†

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Treatment of 1,3-diaryltriazene 1-oxides with oxalyl chloride in dry toluene at room temperature gives only solid arenediazonium chlorides; however, treatment with acetyl and benzoyl chlorides does not afford the corresponding diazonium chlorides.

In previous reports[1,2] we have shown that 1,3-diaryltriazene 1-oxides form stable charge-transfer complexes (1:1) with the electron-deficient tetracyanoethylene in different solvents.[1] The photolysis of these 1,3-dipoles in aromatic and non-aromatic solvents leads to their decomposition[2] giving 2-hydroxyazobenzene and mono- and di-substituted biaryls. These results prompted us to study the reactivity of these oxides towards different chemical reagents. Here we report the results of our investigations of the effect of acid chlorides on 1,3-diaryltriazene 1-oxides. It has been reported[3] that the analogous 1,3-dipoles, nitrones, rearranged to the isomeric amides on treatment with acetyl chloride. However the reaction of *N*-aryl nitrones with oxalyl chloride led to the introduction of the chlorooxalyl group at the *ortho* position of the *N*-aryl group.[4]

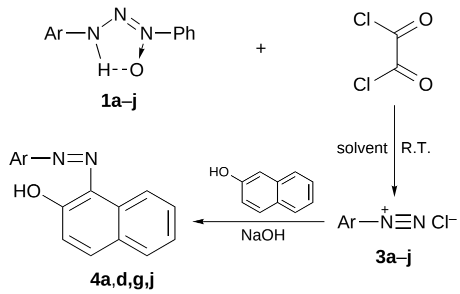
In the present work, the reaction of the 1,3-dipoles 1,3-diaryltriazene 1-oxides **1a–i** with acid chlorides behaved differently. Addition of oxalyl chloride to the 1,3-dipoles **1a–i** in dry toluene at room temperature gave only the arenediazonium chlorides in good yields (80–95%), Table 1.

The physical and spectral properties of the diazonium salts **3a–i** are summarised in Table 1. The well known instability of diazonium compounds is one of their outstanding characteristics, and they usually explode on heating above their melting points, a property which complicates both their analyses and mass spectral fragmentation. The IR spectra of **3a–i** in KBr disks showed a sharp absorption characteristic of the diazonium group $-^{+}N{\equiv}N$ at 2250–2280 cm^{-1}. Because of the instability of the diazonium salt, the ^{1}H NMR spectra could not be recorded. Chemical evidence for the diazonium salt structure was provided by coupling the salts **3a**,**d**,**g**,**i** with an ethanolic alkaline solution (NaOH) of 2-naphthol, which afforded the corresponding azo dyes[5,6] **4a**,**d**,**g**,**i** (Scheme 1). Chromatographic separation of the mother liquors did not give any pure compounds.

A rationale for the formation of the arenediazonium salts **3a–i** is presented in Scheme 2. It is expected from the dipolar nature of the triazene 1-oxides that the oxygen of the azoxy function will behave as a nucleophile and may attack the electron-deficient carbonyl carbon of the oxalyl chloride to form the dipoles **5a–i**. Proton shift followed by decomposition of **6a–i** may give rise to the diazonium salts **3a–i**, chlorooxalic acid **7** and nitrene **8**. In previous work[7] on the thermal characterization of triazene 1-oxides, we succeeded in capturing the nitrene species **8** which underwent dimerisation to form azobenzene in low yield (0.01%; GC–MS analysis). It was too difficult to separate the dimer by preparative TLC. However, the chloroxalic acid **7** could not be separated and although there are plenty of reports[8] on this acid, reference to explain the separation was not found.

Table 1 Physical and spectral data of diazonium chlorides **3a–i**

Compound 3	Yield (%)	Colour	Mp °C	ν_{max} (KBr)/cm^{-1}
a	93	White	59 (decomp.)	3000 (Ar–CH), 2280 ($-N^{+}{\equiv}N$)
b	80	Pink	71–72	3000 (Ar–CH), 2900 (aliph-CH), 2255 ($-N^{+}{\equiv}N$)
c	86	Buff	79–80	3030 (Ar–CH), 880 (aliph-CH), 2260 ($-N^{+}{\equiv}N$)
d	80	Brown	65	3030 (Ar–CH), 2850 (aliph-CH), 2250 ($-N^{+}{\equiv}N$)
e	87	White	60–61	3010 (Ar–CH), 2900 (aliph-CH), 2255 ($-N^{+}{\equiv}N$)
f	95	White	70–72	3030 (Ar–CH), 2885 (aliph-CH), 2265 ($-N^{+}{\equiv}N$)
g	90	Grey	74–75	3000 (Ar–CH), 2800 (aliph-CH), 2280 ($-N^{+}{\equiv}N$)
h	80	Orange	133–135	3000 (Ar–CH), 2265 ($-N^{+}{\equiv}N$), 775 (C–Cl)
i	83	Brown	75–77	3030 (Ar–CH), 2280 ($-N^{+}{\equiv}N$), 800 (C–Cl)
j	89	White	87–88	3030 (Ar–CH), 2260 ($-N^{+}{\equiv}N$), 780 (C–Cl)



1,3,4a Ar = Ph
b Ar = 2-MeC$_6$H$_4$
c Ar = 3-MeC$_6$H$_4$
d Ar = 4-MeC$_6$H$_4$
e Ar = 2-MeOC$_6$H$_4$
f Ar = 3-MeOC$_6$H$_4$
g Ar = 4-MeOC$_6$H$_4$
h Ar = 2-ClC$_6$H$_4$
i Ar = 3-ClC$_6$H$_4$
j Ar = 4-ClC$_6$H$_4$

Scheme 1

In contrast to the oxalyl chloride reaction, treatment of triazene 1-oxides **1a–i** with acetyl chloride and benzoyl chloride did not give the corresponding arenediazonium salts but instead gave resins. Chromatographic separation gave decomposed compounds in small quantities, which could not be isolated in a pure form.

Experimental

All melting points were recorded on a Galenkamp melting point apparatus and are uncorrected. Oxalyl chloride, benzoyl chloride and acetyl chloride were obtained from Aldrich. Toluene was distilled and dried following the method of Vogel.[9] Triazene 1-oxides **1a–i** were prepared according to literature methods.[10] IR spectra

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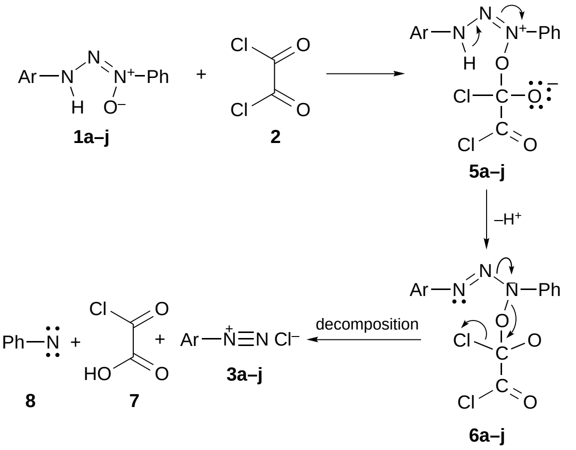

Scheme 2

were recorded on Shimadzu 470 and Perkin Elmer 283 spectrophotometers (KBr disk).

Synthesis of Solid Diazonium Chlorides **3a–i**.—To a clear stirred solution of the unsymmetrical triazene 1-oxides **1a–i** (1 mmol) in dry toluene (10 ml), oxalyl chloride **2** (1 mmol) in dry toluene (5 ml) was added dropwise. The reaction mixture became turbid and after 10 min at room temperature the solid diazonium chloride products precipitated. The diazonium chlorides **3a–i** were separated by filtration in 80–95% yield.

Reaction of Triazene 1-*Oxides* **1a–i** *with Acetyl Chloride and Benzoyl Chloride*.—To a stirred solid cold (−10 °C) solution of triazene 1-oxide (1 mmol) in dry toluene (10 ml), acid chloride (1 mmol) in dry toluene (5 ml) was added dropwise over 10 min. The reaction mixture was allowed to warm to room temperature and gradually became darker giving an oily viscous material. Separation of these resins by preparative TLC afforded multi-decomposed compounds in small quantities which could not be isolated in pure solid form.

Preparation of the Azo Dyes **4a**,**d**,**g**,**i**.—Addition of a solution of the solid diazonium salt **3a**,**d**,**g**,**i** (1 mmol) in cold water (5 ml) to an ethanolic alkaline solution (10% NaOH) of 2-naphthol (1 mmol) at 0–5 °C gave a red precipitate. The reaction mixture was then allowed to stand at room temperature for 10 min and then filtered. The solid obtained was dried and then recrystallized from an appropriate solvent. The melting points of the product dyes were compared with those of authentic samples.[5,6] **4a**: scarlet red (93%), mp 132 °C (lit.,[5] 132–133 °C). **4d**: deeply red (96%), mp 133 °C (lit.,[6] 133–134 °C). **4g**: red dye (87%), 140 °C (lit.,[6] 139–140 °C). **4i**: bright red (94%), mp 156 °C (lit.,[6] 155–157 °C).

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