A New Reaction of Aryl Isocyanates with Nitrite Ion

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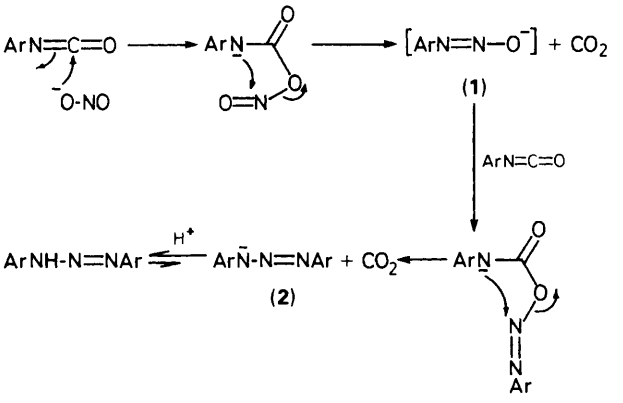
Reaction of nitrite ion with excess aryl isocyanate in organic solvents at 0 °C rapidly produces 1,3-diaryltriazenes in good yields *via* an aryldiazotate ion intermediate reacting with a second molecule of the aryl isocyanate.

Isocyanates are very susceptible to nucleophilic attack[1] and some of these reactions (*e.g.* with alcohols) have been extensively studied in connection with polymer production.[2] Reactions with acetate ion are well-known,[1] despite its relatively low nucleophilicity [$pK_A(HOAc) = 4.75$]. On comparing acidities [$pK_A(HNO_2) = 3.4$], a reaction with nitrite ion is expected but has not been reported hitherto.

Treatment of arylisocyanates in an organic solvent (*e.g.* MeCN) at 0 °C with tetraethylammonium nitrite (TEAN) gives an instantaneous deep purple colouration. After aqueous work-up and flash chromatography on neutral alumina, 1,3-diaryltriazenes are obtained in good yields (Table 1). Formation of 1,3-diaryltriazenes proceeds successfully under a variety of reaction conditions and with a range of reactant concentrations; for example, in toluene using $NaNO_2$ with 18-crown-6 ether, in MeCN using $NaNO_2$ in dimethyl sulphoxide (DMSO), and in tetrahydrofuran (THF) using TEAN, at temperatures from 0—37 °C with a 2- to 50-fold excess of aryl isocyanate. The best yields of 1,3-diaryl isocyanates were obtained, however, under the conditions of Table 1. This implies that low temperature, homogeneous reaction conditions, and a relatively large excess of arylisocyanate over nitrite ion are important.

A plausible mechanism for the formation of 1,3-diaryltriazenes is outlined in Scheme 1. This involves an initial reaction of nitrite ion with the arylisocyanate, followed by an intramolecular rearrangement and loss of CO_2 to give an aryldiazotate ion intermediate (**1**). Reaction of (**1**) with a



Scheme 1

Table 1. Yields of 1,3-diaryltriazenes for 4-substituted arylisocyanates with TEAN in MeCN at 0 °C: initial [TEAN] 2—5 mM.

XC_6H_4NCO	$[XC_6H_4NCO]/[TEAN]$	$XC_6H_4N{=}N{-}NHC_6H_4X$ Yield (%)[a]
$X = NO_2$	10	85
$X = CF_3$	10	63
X = Cl	20	65
X = H	30	90
X = Me	30	60
X = MeO	50	20

[a] Relative to [TEAN].

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Table 2. Yield of 1,3-bis(4-nitrophenyl)triazene from 4-nitrophenyldiazotate ion and 4-nitrophenylisocyanate in MeCN at 0 °C: initial [$O_2NC_6H_4N_2O^-$] 2.5 mM.

[$O_2NC_6H_4NCO$]/[$O_2NC_6H_4N_2O^-$]	$O_2NC_6H_4N{=}N{-}NHC_6H_4NO_2$ Yield (%)[a]
5	40
10	70
20	85
30	80

[a] Relative to 4-nitrophenyldiazotate ion.

second molecule of arylisocyanate followed by analogous intramolecular rearrangement and loss of CO_2 gives the 1,3-diaryltriazene anion (**2**). The validity of this mechanism was established by the following experiments. Formation of the aryldiazotate ion intermediate (**1**) was demonstrated for 4-nitrophenylisocyanate using excess TEAN in MeCN at 0 °C. The 4-nitrophenyldiazotate ion was trapped by quenching the reaction solution in aqueous 0.1 M borax buffer (pH 9) containing excess 2-naphthol-3,6-disulphonic acid (*R* salt). This gave an orange azo dye which was quantified by visible spectrophotometry (λ_{max} = 490 nm). The maximum yield of azo dye (90%) was obtained with a 50-fold excess of TEAN over 4-nitrophenylisocyanate. Also, independent reactions of authentic 4-nitrophenyldiazotate ion with excess 4-nitrophenylisocyanate in MeCN at 0 °C gave substantial amounts of 1,3-bis-4-nitrophenyltriazene (Table 2). Further, the yields of 1,3-diaryltriazenes in Table 1 imply that stability of the corresponding aryldiazotate ion is important, and formation of CO_2 was apparent (lime-water) on sparging the reaction solutions containing TEAN and arylisocyanates.

These findings are relevant to the formation of *N*-nitrosamines from secondary amines and nitrite ion in the presence of carbonyl compounds.[3] It is clear that electron deficient C=N compounds are able to convert nitrite ion into an efficient nitrosating agent.

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