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Zinc(II) promoted conversion of aryltriazenes to aryl iodides and aryl nitriles

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Abstract—Aryltriazenes react with zinc perchlorate/zinc cyanide to produces arylnitriles and react with zinc iodide to produce aryliodides. The reaction mechanism involves aryl radicals that have been trapped by addition to propenenitriles in a good preparative Meerwein arylation process. © 2001 Elsevier Science Ltd. All rights reserved.

Aryltriazenes, 1-aryl-3,3-dialkyltriazenes, have a long history in both biological and chemical sciences.^{1,2} In chemistry, the aryltriazenes function as synthetic intermediates for the performance of aryldiazonium ion type reactions in non-aqueous media. The triazene function can be replaced by halogens, especially iodine, and by many other groups found in aqueous diazonium ion reactions.^{3–8} Following our studies reported in 1985 for replacement of the triazene function with a phenyl ring, we attempted without success to introduce a fluorine group.¹ In the course of these studies we conducted reactions between aryltriazines and zinc salts. We observed that the triazine function can be replaced by a cvano group through the use of zinc cvanide/zinc perchlorate and can be replaced by iodine through the use of zinc iodide. Our results provide some useful synthetic methodology as well as interesting mechanistic considerations and are the subject of this letter.

Aryltriazenes, 1-aryl-3,3-(pentanediyl)triazenes (1), reacted with a mixture of zinc perchlorate (1 equiv.) and zinc cyanide (1 equiv.) in acetonitrile at reflux for 3 h to give arylnitriles (2) (Eq. (1)). The yields of purified products are shown in Table 1.

| Table 1. | Conversion | of | aryltriazenes ^b | to | arylnitriles ^c | and |
|-------------|------------|----|----------------------------|----|---------------------------|-----|
| aryliodides | с | | | | | |

| R | % CN | % I |
|-------------------|------|-----|
| Н | 73 | 59 |
| 4-CH ₃ | 62 | 60 |
| 4-Et | 32 | 70 |
| 2-NO ₂ | 98 | 41 |
| $3-NO_2$ | 62 | 49 |
| 4-NO ₂ | 54 | 48 |
| 4- <i>n</i> -Bu | 55 | 70 |
| 4-OEt | 45 | 77 |
| 4-Cl | 80 | 57 |
| 4-Br | 75 | 37 |

^a Products were identified by comparison of physical properties with known physical properties.

^b Aryltriazenes were obtained from the aromatic amines as described in Ref. 1.

^c Yields of isolated products.

temperature over a period of 2 hours (Eq. (2)). The aryliodides (3) were easily isolated after filtration, evaporation and distillation. The yields are reported in Table 1.

$$R \xrightarrow{N=N-N} N \xrightarrow{Zn(CN)_2, Zn(ClO_4)_2} R \xrightarrow{2} CN$$
(1)

The reaction of aryltriazenes (1) with zinc iodide (3 equiv.) in acetonitrile solution occurred readily at room

conducted in the presence of excess propenenitriles

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 $[\]begin{array}{c} & \begin{array}{c} & \\ & \\ & \\ & \\ & \\ & \end{array} \end{array} \xrightarrow{\begin{subarray}{c} CH_3CN} & \begin{array}{c} & \\ & \\ & \\ & \\ & \\ & \\ \end{array} \end{array} \xrightarrow{\begin{subarray}{c} (2) \\ & \\ & \\ & \\ & \\ & \\ \end{array} \end{array}$

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Scheme 1.

(4a–c). Meerwein-type⁹ arylation adducts $5a–c^{10}$ were obtained in good yield (Eq. (3)). The observance of the iodinated adducts provides evidence for the presence of an aryl radical as an intermediate in these reactions. The relative reactivity of propenenitrile (1), 2-methyl-propenenitrile (2.7) and 2-butenenitrile (0.22) are also consistent with an aryl radical addition reaction.¹¹

The mechanism outlined in Scheme 1 accounts for the Meerwein arylation reaction that produces 5a-c. The aryltriazene produces an aryl free radical (A) on reaction with ZnI₂. The radical adds in 1,4-addition to produce the alkyl radical (B) that abstracts an iodine atom from ZnI₂. Our earlier work on triazene chemistry showed that diazonium salts are primary intermediates that decompose likely through aryl radicals.¹² This work lends further evidence to the involvement of aryl radicals and further demonstrates the value of aryltriazenes as non-aqueous synthetic equivalents of aryl diazonium ions.

Acknowledgements

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- 10. 5a: ¹H NMR (CDCl₃, TMS) δ 3.25 (1H, d, J=5 Hz, CH₂), 4.23 (2H, t, J=5 Hz, CH), 7.2–7.4 (5H, aromatic); 5b: δ 2.2 (3H, s, CH₃), 3.25 (1H, d, J=3 Hz, CH), 3.46 (1H, d, J=3 Hz, CH), 7.1–7.7 (5H, aromatic); 5c: δ 1.6 (3H, d, J=6 Hz, CH₃), 3.1 (1H, d of m, 3–H), 5.31 (1H, m, 2-H), 7.4–7.5 (5H, aromatic). All compounds gave satisfactory elemental analysis and mass spectral data.
- 11. Competitive rates were determined from the reaction of 1 with zinc iodide (1 equiv.) in acetonitrile solution with a 10-fold excess of propenenitrile and a 10-fold excess of a competing nitrile. The ratios of products were determined from integration of the peaks in the ¹H NMR spectra of the mixtures.
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