Novel reaction of [bis(acyloxy)iodo]arenes

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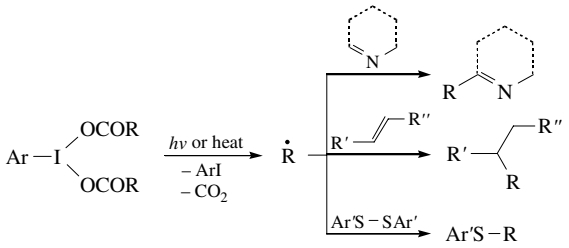
The reaction of [(diacetoxy)iodo]benzene with furazan dicarboxylic acid was accompanied by a novel decarboxylative ring-cleavage reaction; the cyanogen *N*-oxide, reactive intermediate generated in the process, was dimerised or trapped by a dipolarophile.

The chemistry of [bis(acyloxy)iodo]arenes, $ArI(OCOR)_2$, is of considerable interest and excellent reviews on both the synthesis and the reactivity of these compounds were published.[1–6] It is well known[7] that upon irradiation or heating $ArI(OCOAlk)_2$ undergo decarboxylative decomposition generating alkyl radicals, which can be effectively trapped with various heteroaromatic bases, electron-deficient alkenes or disulfides (Scheme 1).



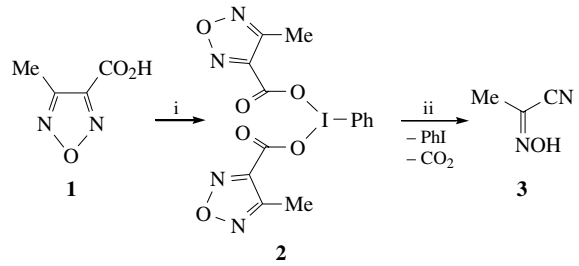
Scheme 1

The chemistry of $ArI(OCOR)_2$, which incorporate a heterocyclic ring as a key structural component R, has never been published.

We are interested in the chemistry of azoles since the presence of heteroatoms in such molecules can provide a wider range of ring opening and rearrangement reactions.[8,9] An intriguing possibility is the use of azolylcarboxylic acids in the synthesis of respective [bis(azoloyloxy)iodo]arenes whose reactivity is based on main heterocycle transformations rather than usual radical reactions. Here, we report on the novel reaction of [bis(acyloxy)iodo]benzenes derived from furazan carboxylic acids.

A variety of [bis(acyloxy)iodo]arenes are usually synthesised by ligand exchange of commercially available [(diacetoxy)iodo]benzene (DIB) or [bis(trifluoroacetoxy)iodo]benzene (BTI) with corresponding acids.[1] When 3-methylfurazan-4-carboxylic acid **1** was treated with DIB in warm chlorobenzene, target compound **2**† was prepared in a moderate yield of 74% (Scheme 2). When the reaction was repeated using BTI, compound **2** was obtained in high yield (87%). The decarboxylation experiment was performed by heating compound **2** in toluene at 100–110 °C until finishing carbon dioxide evolution. α-Hydroxyimino nitrile **3** was isolated by chromatography in 65–70% yield.

In attempting to prepare carboxylate **5** starting with dicarboxylic acid **4**, we encountered the evolution of carbon dioxide and the formation of 3,4-dicyanofuroxan **7**[10] (GLPC yield was 84%) and iodobenzene (GLPC yield was 96%) (Scheme 3).



Scheme 2 *Reagents and conditions*: i, DIB or BTI, chlorobenzene or CH_2Cl_2, 40–50 °C; ii, toluene, 100–110 °C.

The net result of this process corresponds to a formal breaking of five bonds (as indicated in Scheme 3) with concomitant generation and dimerization of cyanogen oxide **6**. Note that, previously, nitrile oxide **6** was only generated (i) from α-chloro-α-cyanoformoxime by base treatment[11–13] and (ii) from 3-aminofurazan carboxylic acid by diazotization.[10] 1,3-Dipolar cycloaddition[14] of nitrile oxide **6** generated from carboxylate **5** was examined with styrene, cyclopentene, cyclohexene, 2,5-dihydrofurane, and phenylacetylene. The reactions were run by simply heating a mixture of furazan dicarboxylic acid **4**, 5–10 equiv. of a dipolarophile and DIB in chlorobenzene.‡ The crude products were isolated from these reactions by chromatography. While a *ca.* 70% yield of isoxazolines **8**–**11**§ was obtained from the olefins, phenylacetylene reacted poorly even at a high concentration to furnish at best a 16% isolated yield of izoxazole **12**; a complex product mixture was obtained, and the isolation of target product **12** was difficult to perform. Probably, DIB was also consumed in side-reactions with phenylacetylene; reactions of iodine(III) compounds with terminal acetylenes are well documented.[15]

Another goal was to obtain 1,2,4-oxadiazoles by the reactions of nitrile oxide **6** with nitriles.[14] However, slightly heating furazan dicarboxylic acid **4** with DIB in an excess of a nitrile [MeCN, CCl_3CN, $C(NO_2)_3CN$, or PhCN] afforded only intractable product mixtures.

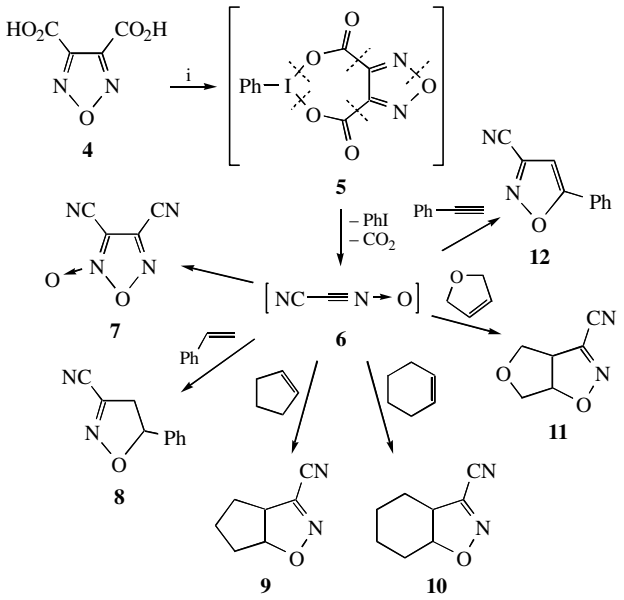
In contrast, acid **4** was recovered from boiling chlorobenzene. However, the decarboxylation of acid **4** can be carried out in boiling dichlorobenzene under air atmosphere.¶ Interestingly, the reaction of acid **4** with styrene under the above conditions gave a mixture of products that contained cyanoformaldoxime **13** (47%), isoxazoline **8** (14%), addition products **12** (3%) and 3,7-diphenyl-5-cyano-1-aza-2,8-dioxabicyclo[3.3.0]octane **14** (3%)

† *Synthesis of [bis(3-methylfurazan-4-oyloxy)iodo]benzene* **2**. A mixture of 3-methylfurazan carboxylic acid (1.28 g, 10 mmol) and DIB (1.61 g, 5 mmol) in chlorobenzene (15 ml) was stirred on a rotary evaporator at 45 °C under reduced pressure (~10 Torr) for 30 min. The reaction mixture was cooled to ambient temperature and diluted with hexane (10 ml). The precipitate was filtered off and washed with $CHCl_3$ to give 1.69 g (74%) of **2** as a colourless powder, mp 171–173.5 °C. ^{1}H NMR ([$^2H_6$]DMSO) δ: 2.42 (s, 6H, Me), 7.51 (3H, Ph), 8.12 (2H, Ph). ^{13}C NMR ([$^2H_6$]DMSO) δ: 8.96 (Me), 125.1 (*i*-Ph), 130.8 (*m*-Ph), 131.4 (*p*-Ph), 133.5 (*o*-Ph), 149.1 (C–CO_2), 152.2 (C–Me), 160.5 (C=O). IR (ν/cm^{-1}): 3090, 1670, 1614, 1480, 1405, 1395, 1358, 1303, 1180, 1142, 1018, 996, 920, 835. Found (%): C, 36.72; H, 2.43; N, 12.17; I, 27.68. Calc. for $C_{14}H_{11}IN_4O_6$ (458.17) (%): C, 36.70; H, 2.42; N, 12.23; I, 27.70.

‡ *General procedure for the generation and trapping of cyanogen oxide* **6**. To a suspension of furazan dicarboxylic acid **4** (0.02 mol) in a mixture of chlorobenzene (10 ml) and an olefin (0.1–0.2 mol) at 40–50 °C DIB (0.011 mol) was added in small portions with stirring. The reaction mixture was vigorously stirred at the specified temperature until the complete generation of iodobenzene (according to GLPC). The resulting solution was cooled, concentrated under reduced pressure, and separated by silica gel chromatography.

§ All spectroscopic and analytical data were consistent with the structures assigned. Compounds **7**,[10] **8**,[11,12] **9**,[12] **10**,[12] **11**,[13] **12**[11] and **14**[18] corresponded to materials described previously.

¶ Note that decarboxylation of acid **4** was observed at 170 °C/25 Torr.[16] The decomposition produced *syn*-cyanoformaldoxime **13**.[16,17]



Scheme 3 *Reagents and conditions*: i, DIB, chlorobenzene, 40–50 °C.

(Scheme 4). Compound **14** is known to result from the reaction of intermediate furoxan **7** with styrene.[18]

In conclusion, the ability of [(furazan-4-oyloxy)iodo]benzene to undergo decarboxylation with simultaneous furazan ring cleavage is a novel type of [bis(acyloxy)iodo]arene transformations. This difference in the reactivity of [bis(acyloxy)iodo]-arenes and [bis(azoloyloxy)iodo]arenes indicates that the presence of heteroatoms in acyloxy moieties play a crucial role in determining the overall pathway of the degradation process.

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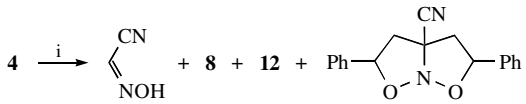

Scheme 4 *Reagents and conditions*: i, *o*-dichlorobenzene, 180 °C.

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