Synthesis and Spectral Characterization of Azidoketenimines

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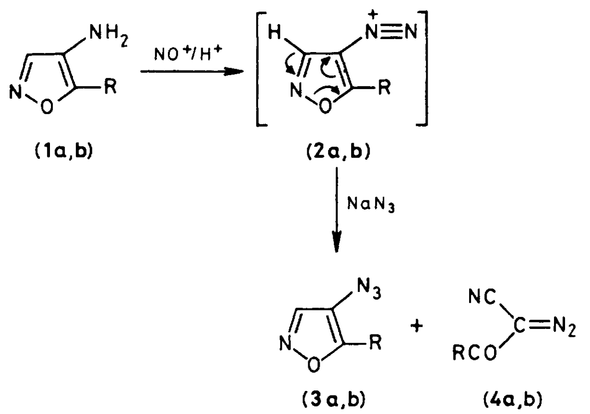
The first azidoketenimines (**6a,b**) have been generated from the 3-unsubstituted 4-azidoisoxazoles (**3a,b**) by successive quaternization and treatment with triethylamine at −90 °C.

An interesting method for synthesising ketenimines, developed by Woodward and co-workers,[1] involves the base-induced decomposition of 3-unsubstituted isoxazolium salts under mild conditions. In principle, this method may be suitable for the synthesis of the azidoketenimines (**6**) starting from the isoxazolium salts (**5**) which have an azide group in the 4-



Scheme 1. **a**, R = Me; **b**, R = CMe_3.

position. Azidoketenimines constitute a class of unknown compounds which are potential precursors of the azirinimines (**7**) by thermolysis. The latter are isoelectronic with the elusive azirinones,[2] and are theoretically of interest as 2π-Hückel aromatic systems.[3]

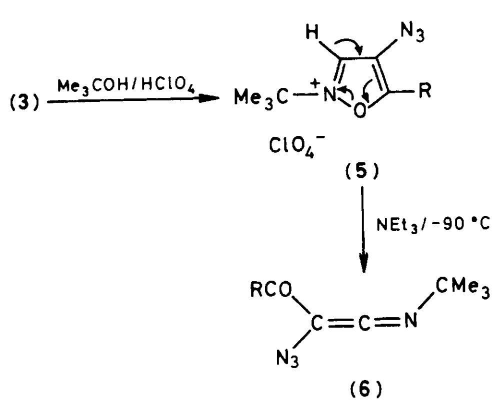
The 4-aminoisoxazoles (**1a,b**) were prepared from the corresponding 4-unsubstituted isoxazoles[4] by nitration in nitric–sulphuric acid, followed by reduction with amalgamated aluminium in moist ether.[5] They were isolated and stored as the hydrochlorides, and used as such for further reactions.

In order to prepare the azide (**3a**) by the classical procedure,[5] (**1a**) was treated with sodium nitrite in concentrated hydrochloric acid at 0—5 °C for 10 min, and then allowed to react with 1—3 equiv. of sodium azide. After work-up of the reaction mixture by extraction with ether, two products were isolated: the azide (**3a**) (8.5%, yellow liquid) and the α-cyanodiazoketone (**4a**) (72%, orange liquid). The product distribution was found to be dependent on the reaction conditions. For instance, when the reaction was carried out in methanol at −15 °C with 2—5 equiv. of hydrochloric acid and 1 equiv. of sodium azide, nearly equal amounts (12—15%) of (**3a**) and (**4a**) were obtained. The yield of (**3a**) increased to 26.5% by using a threefold excess of sodium azide.

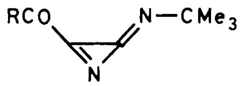
Mechanistically, the unexpected α-cyanodiazoketone (**4a**) is assumed to result from spontaneous deprotonation and ring cleavage of the diazonium salt (**2a**) (Scheme 1). This degradation may possibly be catalysed by protonation at the ring-nitrogen atom under the strong acidic conditions.

The usual procedure[5] cannot be used to prepare (**3b**) since (**2b**) had already decomposed after 10 min at 0—5 °C. Therefore, the diazotization of (**1b**) was carried out with nitrosyl sulphate in a mixture of acetic acid, propionic acid, and sulphuric acid at a temperature between −15 and −10 °C. After elimination of the excess of nitrosyl sulphate with urea, a threefold excess of sodium azide was added. This furnished, after work-up by column chromatography on silica gel, the azide (**3b**) as a pale-yellow liquid (30%) together with (**4b**) (20%). The ratio of the products (**3b**) and (**4b**), determined by ^1H n.m.r., spectroscopy was found to be 43 : 57.

The azidoisoxazoles (**3a,b**) were quaternized by the reported method of alkylation with t-butyl alcohol and perchloric acid at 0 °C.[6] Extensive decomposition of the azides occurred during this process. The isoxazolium perchlorates (**5a**) and (**5b**) crystallized from the reaction mixture upon addition of acetonitrile and ether (yields respectively 17 and 50%).



Scheme 2. **a**, R = Me; **b**, R = CMe_3.



(**7**)

When a dichloromethane solution of (**5a**) was treated with triethylamine (1 equiv.) in an i.r. cell at −90 °C, new absorptions were observed at 2030 (C=C=N) and 1630 cm^{-1} (CO) which are indicative of structure (**6a**) (Scheme 2). At −60 °C, the ketenimine absorption at 2030 cm^{-1} disappeared first and then only was followed by the disappearance of the azide absorption at 2100 cm^{-1}. The reaction was repeated in an n.m.r. tube (CD_2Cl_2) at −90 °C and showed a quantitative conversion of (**5a**) into (**6a**). In the ^1H n.m.r. spectrum, the t-butyl and acetyl singlets had shifted from, respectively, δ 1.78 and 2.56 in (**5a**) to δ 1.40 and 2.10 in (**6a**). The ^{13}C n.m.r. spectrum showed resonances at δ 25.6 (Me), 29.4 and 64.6 (Bu^t), 87.9 and 169.0 (C=C=N), and 192.6 p.p.m. (CO) (the assignment is deduced from the proton-coupled spectrum). It is noteworthy that the ketenimine central carbon atom in (**6a**) absorbs at much higher field (δ 169.0 p.p.m.) than that of stable ketenimines (δ 186—195 p.p.m.).[7] This is explained by the electron-donating effect of the azide function.

Compound (**5b**) was also converted into (**6b**) when treated with triethylamine in dichloromethane at −90 °C. The ^{13}C n.m.r. spectrum showed the expected resonances for the t-butyl groups (δ 26.9, 29.1, 42.7, and 64.1 p.p.m.) in addition to peaks at δ 85.0, 168.5 (C=C=N), and 200.5 p.p.m. (CO). Another absorption of lower intensity at δ 29.7 p.p.m. indicates that some decomposition to t-butyl isonitrile had already occurred.

So far azidoketenimines and the isoelectronic azidoketenes have only been postulated as intermediates,[2,8] and the success of the present method is based on three co-operative aspects. These are: (i) the presence of an electron-withdrawing acyl group which counter-balances the destabilizing effect of the electron-donating azide group, (ii) the presence of a bulky t-butyl group which shields the ketenimine from external attack, and (iii) the extremely mild reaction conditions of the last step.

The two azidoketenimines (**6a,b**) decomposed at −60 °C. An ^1H n.m.r. analysis of the decomposition products revealed that t-butyl isonitrile was formed in high yield, whereas the expected nitriles (RCOCN) were only present in small amounts together with several unidentified products. In view of our i.r. observation that the ketenimine group disappeared faster than the azide function, the azirinimine (**7**) cannot be considered as an intermediate of the decomposition.

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