Fragmentation of *N*-Chlorotriazoles

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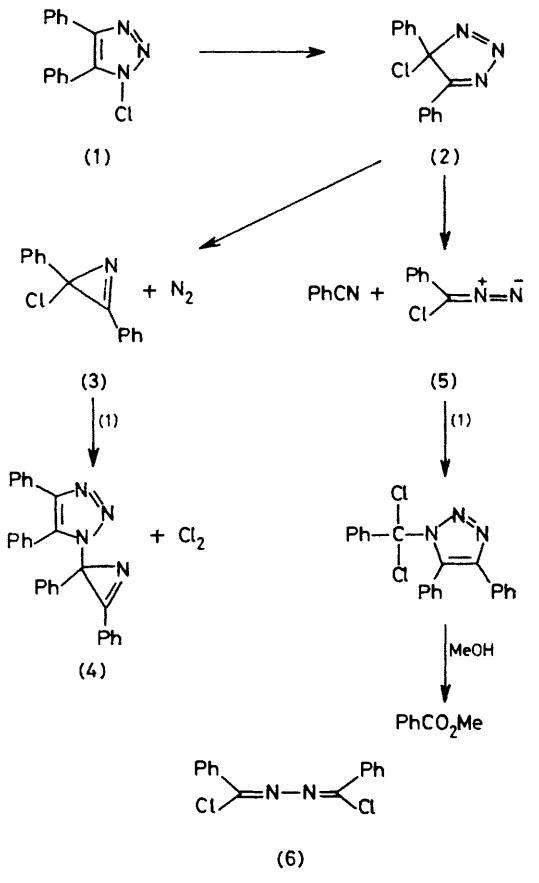
Summary The triazole ring in *N*-chloro-4,5-diphenyltriazole (**1**) undergoes exceptionally mild fragmentation, most likely *via* the non-aromatic *C*-chloro isomer (**2**), to give the azirine (**3**) and hence (**4**); a second mode of fragmentation leading to PhCN competes.

1-CHLOROBENZOTRIAZOLE has found considerable use as an oxidant and chlorinating agent.[1] Unfused *N*-chlorotriazoles, where substituents attached directly to the triazole ring should have a profound effect on reactivity, are therefore of interest.

As expected, *N*-chloro-4,5-diphenyltriazole (**1**),† m.p. 86—88 °C, obtained by treatment of diphenyltriazole in aqueous acetic acid with sodium hypochlorite has typically positive halogen character and like 1-chlorobenzotriazole adds readily to reactive alkenes. More surprisingly, it undergoes an exceptionally mild degradation of the aromatic triazole ring.[2] Thus, on prolonged standing or heating under reflux in acetonitrile the triazolylazirine (**4**),‡ m.p. 190—192 °C, is formed (53%) together with a number of minor products including benzonitrile (13%). We rationalise formation of the azirine (**4**) by rearrangement of the *N*-chloro- to the non-aromatic *C*-chloro-triazole (**2**) which loses nitrogen to give the chloroazirine (**3**). This reactive halide (*cf.* cyclopropenyl halides) reacts with the *N*-chlorotriazole (**1**) to give chlorine and triazolylazirine.[3] The chloroazirine (**3**) prepared independently from α-chlorostilbene by addition of chlorine azide, elimination of HCl, and thermolysis of the resulting vinyl azide, does indeed react rapidly with the *N*-chlorotriazole to give (**4**). It is possible that the chloroazirine (**3**) could have arisen *via* rearrangement of the antiaromatic *N*-chloro-1*H*-azirine formed by direct loss of nitrogen from (**1**) but this seems unlikely at these low temperatures.[4]

The formation of benzonitrile reveals a second mode of cleavage of the triazole ring which again reasonably involves the *C*-chloro-isomer (**2**). 1,3-Dipolar cycloreversion would give chlorophenyldiazomethane (**5**) as the other fragment and some evidence for this comes from decomposition of the *N*-chlorotriazole in methanol. This gives mainly diphenyltriazole from (**1**) acting as oxidant, but in addition benzonitrile and methyl benzoate are formed in equimolar amounts (30%). The latter is the expected product from the diazo-compound, chlorotriazole, and methanol[3] (Scheme).§

Surprisingly no products derived from the chloroazirine are observed in methanol. Formation of benzonitrile and the diazo compound (**5**) could be explained by an alternative fragmentation of the triazole system *via* the 2-(*N*)-chloro-isomer. This would give *N*-chlorobenzonitrilimine as the immediate precursor to (**5**) but this seems unlikely in view of the general stability of 2-substituted triazoles.



SCHEME

N-Chloro-4,5-dimethyltriazole can be obtained similarly but decomposes rapidly in the solid state or in concentrated solution.¶ Nitrogen is evolved and acetonitrile and biacetyl are detected in the products suggesting that both fragmentation pathways found with (**1**) occur in this case also. Methyl acetate is formed from decomposition in methanol. In contrast *N*-chlorodibenzoyltriazole is quite stable and shows no tendency towards ring fragmentation.

† The mass spectrum of this *N*-chloro compound shows a large $M - 28$ peak consistent with the 1-chloro structure (**1**). The symmetry of the 220 MHz ^{1}H n.m.r. spectrum ($CDCl_3$), however, suggests that the chlorine is rapidly equilibrating between N-1 and N-3 or that the chlorine is on N-2.

‡ ν_{max} 1745 cm^{-1} (azirine C=N), λ_{max} (EtOH) 248 nm (log ϵ 4·47) consistent with 1-substituted triazole, hydrolysis gave diphenyltriazole and benzil.

§ Control experiments demonstrate that neither (**3**) nor (**4**) account for the formation of benzonitrile and methyl benzoate.

¶ The only previous attempt to obtain *N*-chloro-1,2,3-triazoles also reported this compound as an unstable species, R. Huttel and G. Welzel, *Annalen*, 1955, **593**, 207.

The benzoyl groups, as expected, enhance the positive halogen character making this *N*-chloro-compound considerably more reactive than (**1**) in additions to alkenes. Fragmentation coupled with chlorine migration also occurs with tetrazoles. Thus *N*-chloro-5-phenyltetrazole undergoes decomposition in benzene to give *inter alia* the azine (**6**). Although this chlorine migration to carbon probably precedes fragmentation, decomposition *via* the 2-chlorotetrazole and *N*-chlorobenzonitrilimine cannot yet be discounted.

Finally we urge that these *N*-chloro-compounds should be handled with extreme caution. Decomposition of *N*-chlorodimethyltriazole can be vigorous and on one occasion the chlorotetrazole exploded violently.

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