

Rearrangement of 4(5)-Azido- ν -triazolide to 5-(Diazomethyl)tetrazolide

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A literature finding with 4(5)-azido- ν -triazolide is reinterpreted as showing the occurrence of the title reaction; this constitutes a new kind of ν -triazole ring transformation.

Since Vilarrasa and his co-workers¹ have demonstrated that 5-azidotetrazolide (**1a**) is capable of undergoing degenerate rearrangements [e.g. (**1a**) \rightleftharpoons (**2a**)], we felt that under comparable conditions the related 4(5)-azido- ν -triazolide (**1b**) should (irreversibly) isomerise to 5-(diazomethyl)tetrazolide (**2b**). This led us to look more closely at a reported experiment with (**1b**) carried out by Elguero and his colleagues.²

These authors,² whose aim was to determine the position of a presumed (**1b**) \rightleftharpoons (**3b**) equilibrium, had observed that (**1b**), when generated in dimethyl sulphoxide (DMSO) solution from the corresponding ν -triazole by adding an excess of NaH, did not equilibrate with (**3b**). Instead, they had noticed that the spectroscopic peaks pertaining to (**1b**) (an i.r. band at 2120 cm^{-1} and a ^1H n.m.r. singlet at δ 6.97) gradually disappeared, while (remarkably) new absorptions developed at 2090 cm^{-1} and δ 5.63 (s).[†] To accommodate these data, the authors² thought of a degradation similar to that reported for 5-azido-1,4-diphenyl- ν -triazole,³ followed by a further decomposition step giving NaCN, to which the new i.r. band was attributed. However, according to our aforementioned supposition, we regarded the questionable data as pointing to a $-\text{CH}=\text{N}_2$ functionality [i.e. formation of (**2b**)]. This has now been established as follows.

(i) Brief heating of the tetrazole (**4**) with an excess of DBN (1,5-diazabicyclo[4.3.0]non-5-ene) in DMSO as solvent[‡] produced, *inter alia*, the same spectroscopic absorptions as quoted for 'decomposed' (**1b**). Parallel behaviour was also found in the electronic spectra, the visible part of which showed a low intensity band at approximately 480 nm (ϵ ca. 20).⁷ On addition of triphenylphosphine to either reaction mixture the singlet at δ 5.58 diminished, whilst a doublet at δ 8.38 ($^4J_{\text{HP}}$ 2 Hz) appeared, indicating the formation of the phosphazine (**6**) (in tetrazolide form) (*cf.* ref. 6).

(ii) In the ^{13}C n.m.r. spectrum of (**1b**) the initial resonances (a doublet at δ 118.9 and a singlet at δ 138.9) were gradually replaced by a doublet at δ 38.3 and a singlet at δ 150.5 [the high-field resonance at δ 38.3 is diagnostic for a diazo compound;⁷ *cf.* also ref. 6 for diazo carbon resonances of ring-substituted 5-(diazomethyl)tetrazoles].

(iii) Admixture of an excess of methyl iodide when (**1b**) was no longer detectable caused rapid disappearance of the singlet at δ 5.58 while giving rise to paired singlets (in 3:1 ratio, respectively) at (a) δ 3.87 and 6.42 and (b) δ 4.28 and 6.14 [singlets of pair (a) were slightly less intense than those of pair (b)]. As confirmed by comparison with authentic samples,⁶ these peaks are due to compounds (**7**) and (**8**).

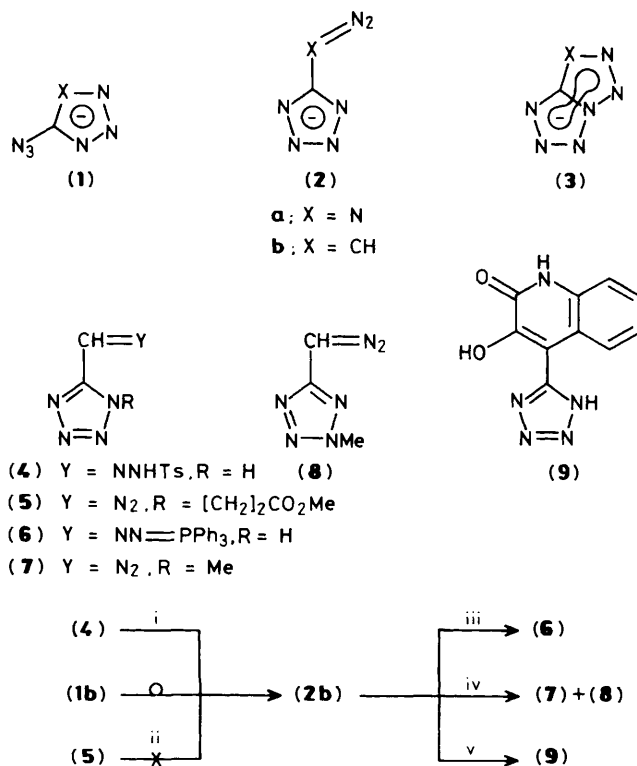
[†] In repeating this experiment, we measured ν_{max} 2120 cm^{-1} , δ 6.93 and ν_{max} 2080 cm^{-1} , δ 5.58, respectively.

[‡] *Procedure.* The tetrazole (**4**) [60 mg; m.p. 190–192 °C (decomp.); prepared from dimeric tetrazole-5-carbaldehyde⁴] in Me_2SO or $(\text{CD}_3)_2\text{SO}$ (1 ml) was heated to 90–95 °C for 1 min, after 5–6 drops of DBN had been added [by this method a 50% conversion of (**4**) could be effected; NaH in place of DBN proved less efficient].

An attempt to generate (**2b**) by DBN-induced removal (*cf.* ref. 5) of the *N*-substituent from (**5**) [yellow oil; obtained by amine diazotisation (*cf.* ref. 6)] failed because the reagent preferentially attacked the $-\text{CH}=\text{N}_2$ group of the precursor.

(iv) Addition of isatin (*cf.* ref. 6) to a solution as used for methylation, followed by acidification, afforded the quinolone (**9**) [m.p. 317 °C (decomp.) (from AcOH); satisfactory C,H,N analysis; ferric test, i.r. and ^1H n.m.r. as expected; m/z (70 eV; 200 °C) 229 (M^+ , 55%), 173 (69), and 117 (100)]. The same material was obtained, albeit in low yield, by heating a mixture of (**4**), DBN, and isatin.

In comparison with the conversion of (**1a**), the rearrangement of (**1b**) turned out to be much faster [at 32 °C, $k_{\text{obs}} = 9.20 \times 10^{-5} \text{ s}^{-1}$, $r = -0.998$ (monitored up to >90% of conversion)]. Moreover, as the reaction has the advantage of giving fairly pure and reasonably stable solutions of (**2b**) [some (**2b**) was detectable even after one week], it seems especially suited for further studies of this particular diazo compound. As regards the mechanism, we believe that (**1b**) is transformed through (**3b**), for the reasons that suggested¹ the intermediacy of (**3a**) in the (**1a**) \rightleftharpoons (**2a**) interconversion.[§] The alternative



Scheme 1. Reagents and conditions: i, DBN/heat; ii, DBN/room temp.; iii, PPh_3 (product in tetrazolide form only); iv, MeI; v, isatin (then H_2O and HCl); DMSO as solvent throughout.

[§] The existence of direct evidence for the presence of (**3b**) seems open to discussion. When the reaction (**1b**) \rightarrow (**2b**) had reached at least 50% conversion, a very weak ^1H n.m.r. singlet at δ 7.86 [intensity ca. 1/25th that of the singlet of (**2b**)] was observed. After completion of the reaction, two further small singlets became visible between δ 8 and 9. All these three minor peaks disappeared on addition of methyl iodide. In the ^{13}C n.m.r. spectrum there was no extra signal.

pathway *via* a discrete α -diazo imine (in its anionic form) is considered less likely, since this species should be much higher in energy than (3b) (*cf.* ref. 1). The reaction (1b) \rightarrow (2b) thus differs in type from the recently described⁸ rearrangement of 1-aryl-5-azido-4-methoxycarbonyl- ν -triazoles where α -diazo imines are obvious intermediates.

Since the new ν -triazole ring transformation described here is expected to apply to derivatives (1) having (for X) a variety of CR groups, work is in hand to reveal the scope of the reaction.

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