# An Exceptionally Simple and Unexpected 'One-pot' Synthesis of New 4,6-Diazasemibullvalenes

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An exceptionally simple and unexpected 'one-pot' synthesis of the hitherto unknown 4,6-diazasemibullvalene derivatives (**5**) is achieved by reaction of the chloro-2-aza-1,3-dienes (**2**) with tetracyanoethylene; the structure of one of the products (**5**) has been determined by *X*-ray crystallography.

Despite their potential utility and theoretical importance,† the aza-,[1] and, especially, the diaza-derivatives[2] of semibullvalenes are an almost unknown type of system. In fact, only recently has the first two-step synthesis of a 2,6-diazasemibullvalene[2c] starting from a 2,6-diazabicyclo[3.3.0]octa-2,6-diene and its utility in the synthesis of 1,5-diazocines[2d] been described. We report here the first 'one-pot' synthesis of 4,6-diazasemibullvallene derivatives, starting from 2-aza-1,3-diene derivatives and tetracyanoethylene.

Our interest in the study of the reactivity of unactivated 2-aza-1,3-dienes led us to the development of a simple and multigram synthesis[3a] of this type of system (**1**) and its monochloro-derivatives (**2**),[3b] easily obtained by reaction of (**1**) with NCS (1 equiv.) and isolated as a mixture of two

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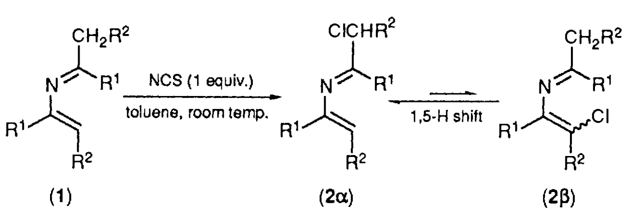
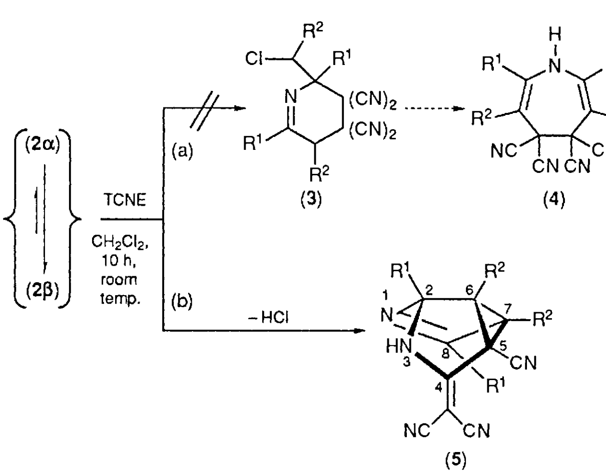
† For example, the 2,6-diaza-derivatives have been predicted to have very low barriers to tautomerization, and the 2,3-diaza-derivatives are also potential precursors to reactive intermediates.



Scheme 1



Scheme 2. a; $R^1 = Ph$, $R^2 = Me$, yield (**5a**) 80%
b; $R^1 = p\text{-}MeC_6H_4$, $R^2 = Me$, yield (**5b**) 70%
c; $R^1 = Ph$, $R^2 = Pr^n$, yield (**5c**) 85%

tautomers (**2α**) and (**2β**) (see Scheme 1).‡ Their reactivity in Diels–Alder reactions[3,4] and in other types of processes[5] was also shown.

Tetracyanoethylene (TCNE)[6] is a widely used reagent in addition and cycloaddition reactions, and in this context, we have recently reported[4a] a Diels–Alder reaction of (**1**) with TCNE. We thought it might be useful to extend this reaction to the monochloro-derivatives (**2**) because they might be a good model, firstly, for testing the face selectivity of the Diels–Alder reaction,[7] and secondly, because the resulting products offer good possibilities for further manipulations. With this purpose in mind we studied the reaction between (**2**) and TCNE.

However, we found that the process, which takes place under mild conditions [$CH_2Cl_2$, room temperature; 10 h; ratio (**2**) : TCNE 1 : 1] and with high yields did not lead to the expected Diels–Alder adducts (**3**), nor to other compounds, *e.g.* (**4**), that could be derived therefrom (see Scheme 2, route a).

Surprisingly, other compounds, which did not contain chlorine, identified as the 4,6-diazasemibullvalene derivatives (**5**)‡ were isolated instead, as colourless crystals, after crystallization [hot methanol–diethyl ether (2 : 7) or ethanol], of the brown powder obtained by washing the crude product with diethyl ether (see Scheme 2, route b).

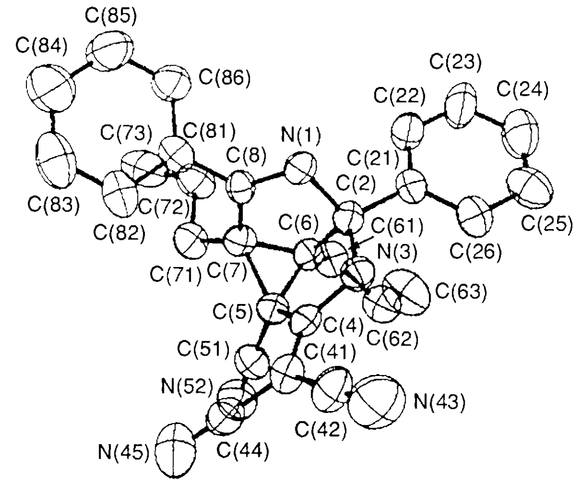
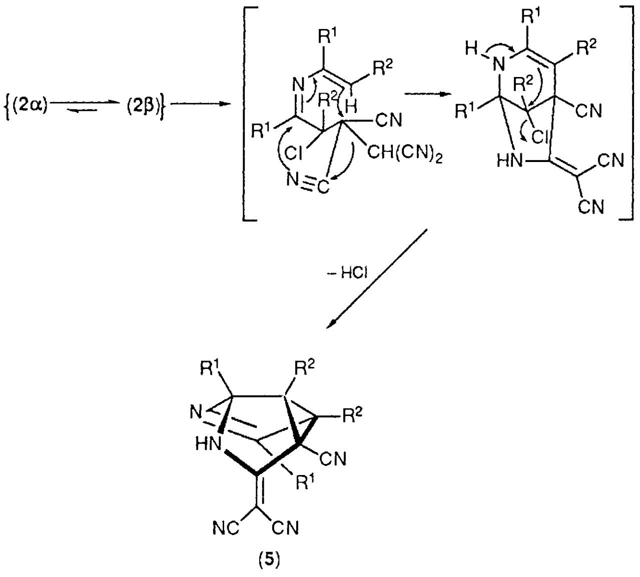


Figure 1



Scheme 3

The $^1H$ and $^{13}C$ NMR spectra of the compounds (**5**) obtained did not clearly reveal their structure [*e.g.* for (**5a**) there are only two $^1H$ NMR singlets at δ 1.0 (3H) and 1.6 (3H) in the δ 0—5 region, and a broad singlet at δ 8.7 (NH) readily exchangeable with $D_2O$, and only three $^{13}C$ NMR signals corresponding to three cyano groups at δ 111.42, 113.52, and 113.81] and so the structure of (**5c**) was determined by *X*-ray crystallography, which showed that it had the semibullvalene structure indicated (Figure 1).§

The thermal stability of compounds (**5**) was tested by heating in refluxing toluene, for several days, in presence or

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‡ All products were unequivocally characterized on the basis of their spectroscopic and mass spectral data and showed satisfactory microanalysis; *e.g.* (**2a**; $R^1 = Ph$, $R^2 = Me$): $^1H$ NMR ($CDCl_3$; 300 MHz): 0.8 (t, 3H), 2.2 (s, 3H), 2.6 (q, 2H), and 6.8—7.9 (m, 10H); $^{13}C$ NMR ($CDCl_3$; 20 MHz); δ 172.45 (s), 143.82 (s), 138.09 (s), 131.09—124.73 (m), 110.73 (s), 24.18 (t), 21.64 (q), and 10.18 (q); *m/z* 283 ($M^+$); yield: 2.55 g [90% from (**1**)].

(**5c**) m.p. 243—246 (decomp.); IR (KBr) $\nu_{max.}$ 3460 (NH) and 2224 (CN) $cm^{-1}$; $^1H$ NMR ($CDCl_3$; 300 MHz): δ 0.5 (t, 3H), 0.7 (t, 3H), 1.0 (m, 2H), 1.4 (m, 2H), 1.6 (m, 2H), 2.4 (m, 2H), 6.9—7.8 (m, 10H), and 9.1 (br. s, 1H, NH exchangeable with $D_2O$); $^{13}C$ NMR ($CD_3SOCD_3$; 75 MHz): δ 172.92, 165.26, 132.12, 131.91, 129.57—126.27, 113.96, 111.85, 110.77, 99.76, 68.05, 65.92, 56.06, 41.53, 28.67, 26.71, 19.58, 18.09, 13.93, and 13.83; *m/z* 431 ($M^+$); yield; 1.83 g [85% from (**2**)]

§ *Crystal data* for (**5c**) $M_r = 431.54$, monoclinic, $a = 17.218(3)$, $b = 10.624(2)$, $c = 13.357(3)$ Å, $\beta = 99.22(2)°$, $V = 2412(1)$ Å$^3$, space group $P2_1/n$, $D_c = 1.188\ g\ cm^{-3}$, $Z = 4$, $F(000) = 912.0$, $\lambda$ (Mo-$K_\alpha$) = 0.71069 Å, $\mu$(Mo-$K_\alpha$) = 0.78 $cm^{-1}$, 298 K. Final $R = 0.051$. The structure was solved by direct methods, using MULTAN. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

absence of a Lewis acid, and in all cases the unaltered starting materials were recovered.

Taking into account the simplicity of the starting materials and the complexity of the structure (**5**), a simple mechanism for the formation of these compounds is difficult to rationalise. Despite this, formation of the 4,6-diazasemibullvalene derivatives (**5**) could be understood by assuming a four-step mechanism (see Scheme 3), in which the initial Michael addition of (**2**) to TCNE is followed by intramolecular cyclizations with migration of the dicyanomethyl group[8] and the loss of HCl. Further mechanistic studies are in progress.

In conclusion, we report here an efficient and simple 'one-pot' synthesis of new 4,6-diazaemibullvalene derivatives (**5**). The simplicity of the reaction and the accessibility of the starting materials provides a good route to these compounds.

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