

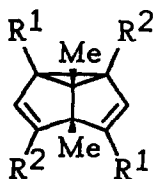
2,6-Diaza-4,8-dicyanosemibullvalene. A short lived Intermediate?

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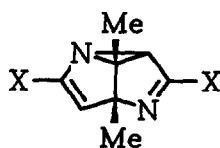
Abstract: Reductive dehalogenation of dichloride **5b** with magnesium affords the new stable diazacyclooctatetraene (1,5-diazocine) **7**. There is strong evidence for the intermediate formation of a 2,6-diaza-4,8-dicyanosemibullvalene **6**.

We have recently reported that the activation barrier of the degenerate Cope rearrangement of semibullvalene **1a** can be significantly lowered by incorporating nitrogen atoms, as in the 2,6-diazasemibullvalene **2a**², and by introducing bridging groups, as in the polycycle **2b**.³ The former effect is of electronic origin and has been rationalized by MO models⁴, while the latter can be ascribed readily to the increasing molecular strain which should decrease in the transition state of the Cope rearrangement.^{3,5}

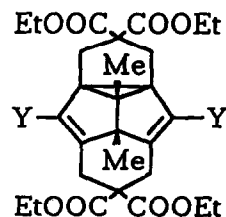


1a: R¹, R² = H

1b: R¹ = H, R² = CN



2a: X = Ph

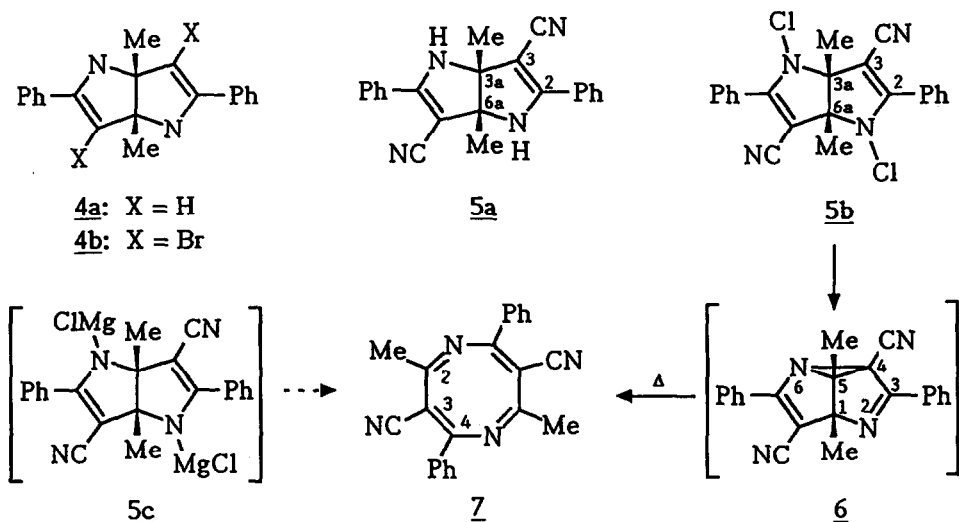


2b: Y = Cl

Replacing hydrocarbon **1a** with the diaza-analogue **2a** appears to have similar consequences on the behaviour of the parent hydrocarbon as the substitution of hydrogens by cyano groups, which leads e.g. to **1b**.⁶⁻⁸ It

is therefore straightforward to combine the aza and cyano group effect in a semibullvalene molecule such as 6.⁵ Additional motivation comes from the possibility of a stabilizing donor/acceptor interaction. Herein we report on the extremely unstable compound 2,6-diaza-3,7-diphenyl-1,5-dimethyl-4,8-dicyanosemibullvalene 6.

The known 4,8-diazabicyclo[3.3.0]octa-2,6-diene (4a)⁹ can be subjected readily to bromination with N-bromosuccinimide, giving rise to the dibromo derivative 4b. Nucleophilic substitution of 4b with sodium cyanide at 60° C provides the enamionitrile 5a. The use of dimethyl sulfoxide as solvent is crucial for the successful conversion. It is noteworthy that in the course of the Kolbe-nitrile synthesis, the diazabicyclo[3.3.0]octadiene frame tautomerizes under formation of 5a, whose N-H functions are nicely documented by its IR spectrum.¹⁰



Treatment of 5a with *tert.*-butyl hypochlorite produces the crystalline N,N'-dichloro-2,5-diphenyl-3a,6a-dimethyl-3,6-dicyanodihydropyrrolo[3,2b]pyrrole (5b).¹¹ Dichloride 5b serves as a possible semibullvalene precursor after reductive dehalogenation. Towards that end, 5b is subjected to an ultrasound promoted reaction with magnesium. Contacting a degassed tetrahydrofuran solution of 5b with magnesium turnings (30 min at -50° C, 10 h at -25° C), followed by purification of the product via filtration over a short column (silica gel, n-hexane/dichloromethane 1:1) affords a new crystalline compound in 40% yield based on 5b.

Its ¹³C-NMR spectrum shows two signals at low field with $\delta_c = 161$ and 172 ppm, and another high-field resonance at $\delta_c = 92$ ppm. These extreme differences in ¹³C-chemical shift values of olefinic double bonds are

characteristic for the influence of electronegative nitrogen atoms in 1,5-diazocines.^{13,14} In contrast to the known methyl phenyl substituted 1,5-diazacyclooctatetraenes, the compound isolated shows only one kind of ^1H - or ^{13}C -methyl resonance with $\delta_{\text{H}} = 2.5$ and $\delta_{\text{C}} = 21.3$ ppm. We conclude that there is only one double-bond isomer. A structural elucidation by comparing of the new compound's spectroscopic data with the already known 1,5-diazocines¹⁴ suggests the existence of the isomer in which the phenyl groups are positioned in conjugation with the nitrile groups as depicted by formula 7.¹²

The formation of the 3,7-dicyano-2,6-dimethyl-4,8-diphenyl-1,5-diazocine 7 from dichloride 5b seems to occur via diazasemibullvalene 6 (see Scheme). Indeed, when the dehalogenation of 5b is monitored by ^1H -NMR spectroscopy, an intermediate species can be detected. After 30 minutes at -50°C , new methyl ($\delta_{\text{H}} = 1.62$ ppm) and phenyl resonances ($\delta_{\text{H}} = 7.2$ to 8.0 ppm) appear, while signals of the starting compound 5b, such as the methyl absorption at $\delta_{\text{H}} = 1.82$ ppm, disappear. It is characteristic that the new methyl resonance is shifted upfield by 0.2 ppm, which can be ascribed to the shielding effect of the aziridine ring in 6. Supporting evidence for the formation of compound 6 is obtained when the NMR tube is allowed to stand at -25°C for several hours without metal contact. NMR spectroscopic control shows an increasing intensity of an allylic methyl signal at $\delta_{\text{H}} = 2.5$ ppm with concomitant reduction of the intensity of the aziridine methyl absorption.

One thus concludes that the primarily formed semibullvalene system 6 isomerizes into the new diazocine even at low temperatures. The dicyano-diazasemibullvalene 6 has a much higher thermal lability than the related diazasemibullvalene 2a, for which rearrangement to the related diazocine requires temperatures over 80°C .^{13, 14} A similar destabilization has been reported by Gompper et al. in the course of an attempted synthesis of a tetraazasemibullvalene which only gave rise to a 1,3,5,7-tetrazocine.¹⁵ Even when the 1,5-positions of the bicyclooctane frame were bridged by a hydrocarbon chain, formation of the eight-membered ring could not be suppressed and there was no indication for tetraazasemibullvalene formation.¹⁶

Compound 6 shows an extreme chemical instability: prolonged metal contact with magnesium gives rise to decomposition even at -50°C ; attempted quenching with methyl iodide, water or methanol only produces non-identified polymeric products. On the other hand, the quenching experiments fail to give evidence for the formation of enamionitrile 5a. Thus, an intermediate organometallic species such as 5c (see Scheme),

which could also give rise to a methyl resonance at higher field, can be excluded.

It appears from the above example that attempts to increase the rate of the Cope rearrangement of a semibullvalene by suitable substitution also increase the tendency for cyclooctatetraene formation.

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- 11 Compound **5a**: colourless crystals. Yield: 52%, m.p.: 250° C under decomposition. ¹H-NMR (200 MHz, CDCl₃, ppm): 1.68 (s, 6H, CH₃); 4.95 (s, 2H, NH); 7.40 - 7.52 (m, 6H, H-m, p); 7.69 - 7.75 (m, 4H, H-o). ¹³C-NMR (50 MHz, DMSO-d₆, ppm): 20.17 (C-3a'/6a'); 75.7 (C-3/6); 81.0 (C-3a/6a); 120.2 (CN); 127.2, 128.6, 128.8 (phenyl-C); 131.1 (ipso-C); 159.9 (C-2/5). MS (EI, 70 eV, 200° C): m/z 338 (M⁺), 235 ([M-PhCN]⁺). IR (KBr): ν 2200 cm⁻¹ (CN).
- 12 Compound **5b**: colourless crystals. Yield: 68%, m.p.: 175° C. ¹H-NMR (200 MHz, THF-d₈, ppm): 1.79 (s, 6H, CH₃); 7.50 - 8.30 (m, 10H, arom. H). ¹³C-NMR (50 MHz, THF-d₈, ppm): 17.5 (C-3a'/6a'); 67.4 (C-3/6); 88.3 (C-3a/6a); 114.7 (CN); 129.5, 129.7, 130.0, (arom. C); 133.8 (ipso-C); 165.7 (C3/7). MS (EI, 70 eV, 150° C): m/z 406, 408, 410 (M⁺); 371, 373 ([M-Cl]⁺).
- 13 Compound **7**: yellow crystals. Yield: 40% (based on **5b**), m.p.: 151° C. ¹H-NMR (200 MHz, CDCl₃, ppm): 2.48 (s, 6H, CH₃); 7.38 - 7.55 (m, 6H, m-, p-phenyl-H); 7.78 - 7.87 (m, 4H, o-phenyl-H). ¹³C-NMR (50 MHz, CDCl₃, ppm): 21.3 (CH₃); 92.0 (C-3/7); 115.6 (CN); 128.9, 129.3, 132.9, (arom. C); 133.5 (ipso-C); 160.7 (C-4/8), 172.3 (C-2/6). MS (EI, 70 eV, 150° C): m/z 336 (M⁺).
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