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

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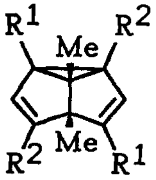
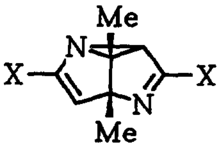
Abstract: Reductive dehalogenation of dichloride 5b with magnesium affords the new stable diazacyclooctatetraene (1,5-diazocine) 7. There is strong evidence for the intermediate formation of a 2,6-diaza-4,8-dicyanosemibullvalene 6.

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 models[4], 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]

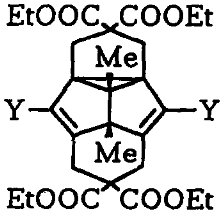


1a: $R^1, R^2 = H$

1b: $R^1 = H, R^2 = CN$



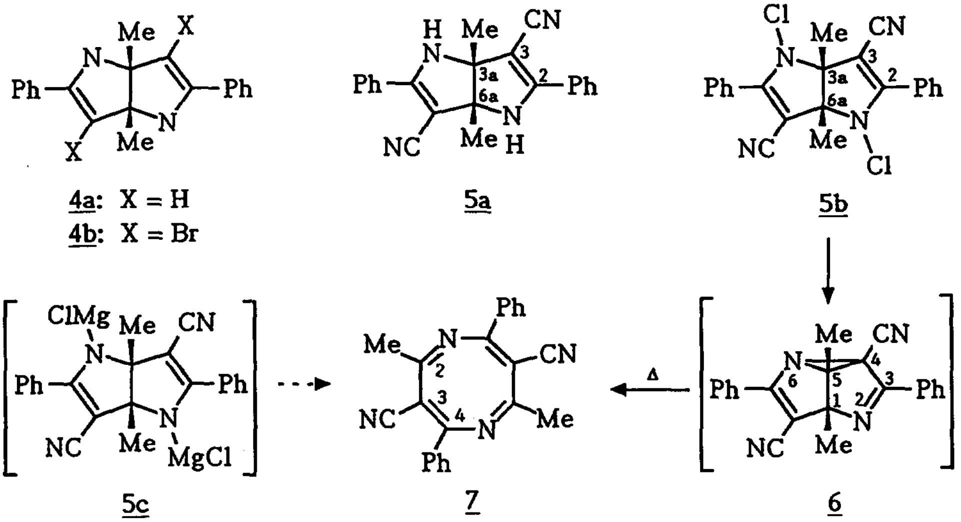
2a: X = Ph



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 enaminonitrile 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}


4a: X = H
4b: X = Br
5a
5b
5c
7
6

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 ^{13}C-NMR spectrum shows two signals at low field with δ_C = 161 and 172 ppm, and another high-field resonance at δ_C = 92 ppm. These extreme differences in ^{13}C-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 δ_H = 2.5 and δ_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-diazocines'[14] 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 (δ_H = 1.62 ppm) and phenyl resonances (δ_H = 7.2 to 8.0 ppm) appear, while signals of the starting compound **5b**, such as the methyl absorption at δ_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 δ_H = 2.5 ppm with concommitant 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 enaminonitrile **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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10 Compound **5a**: colourless crystals. Yield: 52%, **m.p.:** 250° C under decomposition. **^{1}H-NMR (200 MHz, CDCl$_3$, ppm):** 1.68 (s, 6H, CH$_3$); 4.95 (s, 2H, NH); 7.40 - 7.52 (m, 6H, H-m, p); 7.69 - 7.75 (m, 4H, H-o). **^{13}C-NMR (50 MHz, DMSO-d$_6$, 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).

11 Compound **5b**: colourless crystals. Yield: 68%, **m.p.:** 175° C. **^{1}H-NMR (200 MHz, THF-d$_8$, ppm):** 1.79 (s, 6H, CH$_3$); 7.50 - 8.30 (m, 10H, arom. H). **^{13}C-NMR (50 MHz, THF-d$_8$, 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]$^+$).

12 Compound **7:** yellow crystals. Yield: 40% (based on **5b**), **m.p.:** 151° C. **^{1}H-NMR (200 MHz, CDCl$_3$, ppm):** 2.48 (s,6H, CH$_3$); 7.38 - 7.55 (m, 6H, m-,p-phenyl-H); 7.78 - 7.87 (m, 4H, o-phenyl-H). **^{13}C- NMR (50 MHz, CDCl$_3$, ppm):** 21.3 (CH$_3$); 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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