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Synthesis and reactions of the first cyclopentadienyl isonitriles☆,☆☆

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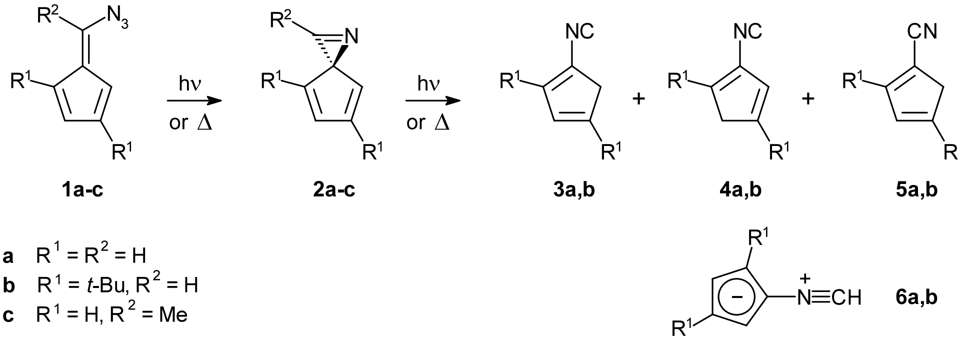
Dedicated to Professor Klaus Hafner on the occasion of his 75th birthday

Abstract—6-Azidofulvenes without a further substituent in the exocyclic position were transformed into new 1-isocyano- and 2-isocyanocyclopenta-1,3-dienes by photolysis in methanol. These novel functionalized cyclopentadienes are useful building blocks, e.g. as dienes in Diels–Alder reactions. © 2003 Elsevier Science Ltd. All rights reserved.

Cyclopentadiene and its derivatives prove to be very important building blocks in organic synthesis mainly because of their high reactivity in Diels–Alder reactions and because of the easiness of their deprotonation to form cyclopentadienylides. These compounds can be used in nucleophilic substitution or addition reactions as well as in the generation of metallocenes and other metal complexes. However, access to cyclopentadienes bearing a functional group directly bound to the five-membered ring is rather rare.[1] For example, isocyanocyclopentadienes are completely unknown to the best of our knowledge. We report here on the first synthesis of cyclopentadienyl isonitriles starting from 6-azidofulvenes **1a**,**b** (Scheme 1).

Recently, we thermolyzed or photolyzed solutions of **1a**–**c** to get excellent yields of the spirocyclic azirines **2a**–**c**, which showed a new type of homoconjugation termed azaspiroconjugation.[2] Whereas irradiation of **1a**[3,4] in several aprotic solvents at −40 to −60°C gave **2a** quantitatively without any successive reaction,[2] we have observed now that photolysis of **1a** in methanol at −50°C surprisingly led to a mixture of the isonitriles[5] **3a** (68% yield) and **4a** (29%). When the latter transformation was monitored by ^{1}H NMR spectroscopy, the signals of the heterocycle **2a** could not be detected. Heating diluted solutions of **1a** or **2a** in chloroform at 50°C furnished the same isonitriles in 44% or 87% yield, respectively. Flash vacuum pyrolysis[6] at 270°C was also a method to transform **1a** or **2a** into **3a**/**4a**. But the yield of the isonitriles was limited to 22–28% because the secondary rearrangement[7] to give the known nitrile **5a**[8] could not be suppressed. Flash vacuum pyrolysis of **1a**, **2a**, or **3a**/**4a** at higher temperatures (420–500°C) led only to **5a** (52–79% yield).



Scheme 1.

Keywords: azides; fulvenes; cyclopentadienes; isocyanides; Diels–Alder reactions.

☆ Part 15 of the series 'Reactions of Unsaturated Azides'. For Part 14, see Ref. 2.

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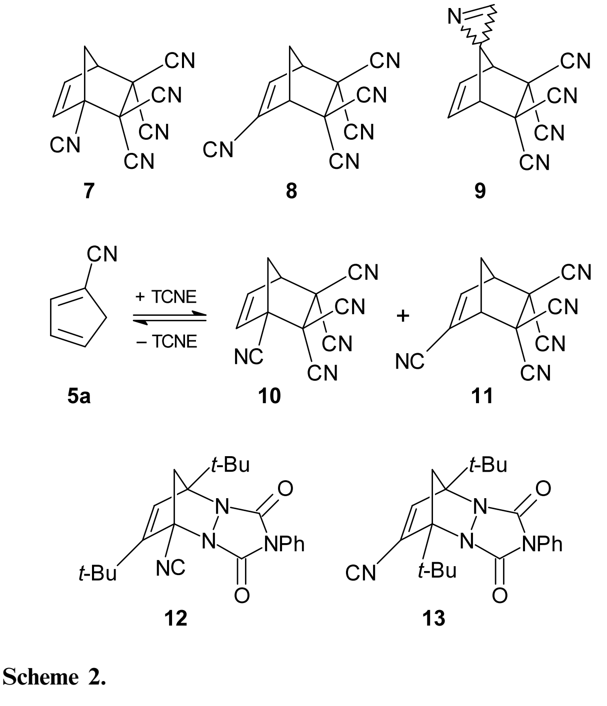
After photolysis of **1b** in methanol at −50°C and flash chromatography (SiO_2, Et_2O/hexane, 1:10) we obtained a 1:1 mixture of **3b** and **4b** as a yellow oil (49% yield)[9] and **5b** as yellow crystals (22%, mp 103°C). Prolonged irradiation of **1b** in chloroform produced also **3b**, **4b**, and **5b**, but the yields were lower. On the other hand, thermolysis of **1b** in chloroform (66°C, 4 h) or flash vacuum pyrolysis of **3b**/**4b** at 420°C resulted only in **5b** formed with 44% or 61% yield, respectively. In all cases of photolyses and thermolyses of **1b**, the intermediate **2b** could be observed when the transformations were monitored by ^1H NMR spectroscopy.

The rearrangement of **2a**,**b** to give **3a**,**b** and **4a**,**b** can be explained by ring opening to nitrile ylides **6a**,**b** followed by tautomerism. Thus, photolysis or thermolysis of **2c** did not afford any isonitrile. Thermal ring cleavage of 2*H*-azirines to generate nitrile ylides is rare, however, the negative charge is highly stabilized by the aromatic cyclopentadienylide in the case of **6a**,**b**.

We assume a rapid equilibration of **3a** and **4a**, and thus we were not able to separate both compounds. Although these isonitriles can only be handled in solution, treatment with an excess of tetracyanoethylene (TCNE) in acetone at −25 to 20°C yielded quantitatively the Diels–Alder products **7** and **8** (Scheme 2). The analogous reaction of **2a** led to the relative stable cycloadduct **9**.[10] Treatment of **5a** with TCNE at −25°C gave quantitatively a 7:1 mixture of **10** and **11**, whereas the same reaction at 20°C resulted in a 1:1 mixture of **10** and **11**. On heating these mixtures to 50°C, **11** and regenerated **5a** were the only products observed. Thus, the Diels–Alder reaction of **5a** and TCNE is reversible already at low temperature favoring the thermodynamically more stable product **11**. The latter is formed from TCNE and 2-cyanocyclopentadiene generated in a small concentration by equilibration with **5a**. Due to this equilibration, retro-Diels–Alder reaction of **11** performed by sublimation at 150°C/10^{-3} torr gave only TCNE and **5a** instead of 2-cyanocyclopentadiene. Because of steric hindrance, we observed no reaction of **3b** or **4b** with TCNE. However, the Diels–Alder products **12** and **13** were obtained in 73% yield on treatment with the more reactive dienophile 4-phenyl-1,2,4-triazolinedione.



Scheme 2.

At present, we are continuing the investigations of other transformations starting with isocyanocyclopentadienes.

Acknowledgements

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References

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2. Banert, K.; Köhler, F.; Kowski, K.; Meier, B.; Müller, B.; Rademacher, P. *Chem. Eur. J.* **2002**, *8*, 5089–5093.
3. For the synthesis of **1a**, see: Hafner, K.; Bauer, W.; Schultz, G. *Angew. Chem.* **1968**, *88*, 800–801; *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 806–807.
4. Caution should be exercised during isolation of azides which may be explosive.
5. Mixture **3a**/**4a**: IR (CCl_4): $\tilde{\nu}$ 2117 cm^{-1} (NC). GC–MS *m*/*z* (%): 91 (100) [M^+], 64 (91), 63 (40), 39 (45), 38 (33). Compound **3a**: ^1H NMR ($CDCl_3$): δ 3.04 (q, $J=1.5$ Hz, 2H, H-5), 6.10 (ddt, $^3J=5.7$ Hz, $^4J=1.5$ Hz, $^3J=1.5$ Hz, 1H, H-4), 6.23 (ddt, $^3J=5.7$ Hz, $^3J=2.3$ Hz, $^4J=1.5$ Hz, 1H, H-3), 6.46 (m, 1H, H-2). ^{13}C NMR ($CDCl_3$): δ 42.78 (t, $^1J_{(C,H)}=130.0$ Hz), 116.80 (s), 130.99 (d, $^1J_{(C,H)}=169.7$ Hz), 131.62 (2C, 2×d, $^1J_{(C,H)}=174.1$ Hz), 166.82 (t, $^1J_{(C,^{14}N)}=5.9$ Hz, NC). Compound **4a**: ^1H NMR ($CDCl_3$): δ 2.93 (q, $J=1.5$ Hz, 2H, H-5), 6.23 (m, 1H, H-3), 6.32 (ddt, $^3J=5.4$ Hz, $^4J=2.4$ Hz, $^3J=1.5$ Hz, 1H, H-4), 6.36 (m, 1H, H-1). ^{13}C NMR ($CDCl_3$): δ 40.09 (t, $^1J_{(C,H)}=128.5$ Hz), 123.35 (s), 129.68 (d, $^1J_{(C,H)}=176.4$ Hz), 130.14 (d, $^1J_{(C,H)}=176.6$ Hz), 135.20 (d, $^1J_{(C,H)}=172.9$ Hz), 164.74 (t, $^1J_{(C,^{14}N)}=6.6$ Hz, NC). Assignments of the ^1H NMR signals of **3a** and **4a** are based on double resonance, NOE, and LIS experiments.
6. For experimental details of flash vacuum pyrolyses, see: Banert, K.; Hagedorn, M.; Müller, A. *Eur. J. Org. Chem.* **2001**, 1089–1103.
7. For the thermal rearrangement of isonitriles to nitriles, see: Rüchardt, C.; Schmittel, M.; Wolber, E. K. A. *Chem. Ber.* **1992**, *125*, 525–531.
8. Chou, C.-H.; Wu, C.-C.; Chen, W.-K. *Tetrahedron Lett.* **1995**, *36*, 5065–5068 and references cited therein.
9. Mixture of **3b**/**4b**: IR (CCl_4): $\tilde{\nu}$ 2113 cm^{-1} (NC). GC–MS *m*/*z* (%): 203 (9) [M^+], 188 (12), 147 (11), 133 (9), 132

(77), 117 (10), 77 (12), 57 (100), 41 (48), 39 (19). Compound **3b**: ^{1}H NMR (CDCl$_3$): δ 1.134 (s, 9H), 1.279 (s, 9H), 3.16 (d, $^{4}J=1.1$ Hz, 2H, H-5), 6.02 (t, $^{4}J=1.1$ Hz, 1H, H-3). ^{13}C NMR (CDCl$_3$): δ 29.15 (q), 30.42 (q), 33.07 (s), 33.42 (s), 42.98 (t, C-5), 116.97 (t, $^{1}J_{(C,^{14}N)}=14$ Hz, C-1), 123.66 (d, C-3), 151.87 (s), 156.62 (s), 167.83 (t, $^{1}J_{(C,^{14}N)}=5$ Hz, NC). Compound **4b**: ^{1}H NMR (CDCl$_3$): δ 1.131 (s, 9H), 1.275 (s, 9H), 2.98 (d, $^{4}J=1.1$ Hz, 2H, H-5), 5.89 (t, $^{4}J=1.1$ Hz, 1H, H-3). ^{13}C NMR (CDCl$_3$): δ 29.47 (q), 30.37 (q), 33.11 (s), 33.48 (s), 39.45 (t, C-5), 120.26 (t, $^{1}J_{(C,^{14}N)}=12$ Hz, C-2), 122.74 (d, C-3), 150.02 (s), 156.23 (s), 166.32 (t, $^{1}J_{(C,^{14}N)}=5$ Hz, NC). Assignments of the ^{1}H NMR signals of **3b** and **4b** are based on NOE difference spectra.

10. Surprisingly, we were not able to get **9** by photolysis of the Diels–Alder product easily available from **1a** and TCNE.