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Transannular Additions to 1,6-Cyclodecadiyne

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The reaction of 1,6-cyclodecadiyne (**1b**) with $(SCN)_2$, BrCN and CCl_4 yields mainly to 2- or 2,7-substituted bicyclo[4.4.0]deca-1,6-diene derivatives. © 1997 Elsevier Science Ltd. All rights reserved.

Recently we found that 1,6-diazacyclodeca-3,8-diyne (**1a**) yielded the biradical intermediate **2a** upon heating in unpolar solvents.[1] An investigation of the parent system (**1b**) in the gas phase gave further details of the activation parameters of this reaction.[2] In order to trap the intermediately formed biradical **2a** we reacted **1a** with different hydrogen donors such as 1,4-cyclohexadiene or 9,10-dihydroanthracene.[1] We also investigated the reaction of **1a** with CH_3OH, HCl and H_2SO_4.[3] In continuation of this work we reacted **1b** with $(SCN)_2$, BrCN and CCl_4. The reaction with halogens has recently been reported by others.[4]

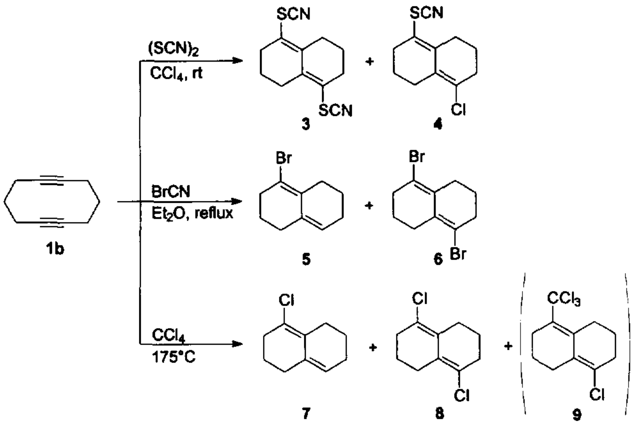
Scheme 1

X = NR, CH2

1 **a, b** **2**

The reaction of **1b** with $(SCN)_2$, prepared in situ from $Pb(SCN)_2$ and bromine in CCl_4 as solvent[5] formed a 1:1 mixture of the 2,7-diisothiocyanato- and the 2-chloro-7-thiocyanato-bicyclo[4.4.0]deca-1,6-diene compounds **3** and **4**[6], respectively, in an overall yield of 80% (GC) (isolated **3**: 8%, **4**: 6%). We assume that the chlorine in **4** stems from the solvent (CCl_4) used. Application of halogen-free solvents did neither yield **3** nor **4**. The reaction of **1b** with BrCN in diethylether under reflux yielded the bromo-derivatives **5** and **6**[6] in the ratio of 4:1 in 50% overall yield (GC) (isolated **5**: 11%). The anticipated cyano-derivative could not be detected. By heating **1b** in CCl_4 at 175 °C we isolated the mono- and dichloro-products **7** and **8**[6] in the ratio of 1:3 in an overall yield of ca. 50% (GC) (isolated 25%). In traces we could detect (GC/MS) **9**. Attempts to generate **8** by chlorination of **1b**

Scheme 2



failed. The results shown in Scheme 2 can be rationalized by assuming a radical mechanism.

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[1] Gleiter, R.; Ritter, J. *Angew. Chem.* **1994**, *106*, 2550-2552; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2470-2472.

[2] Roth, W. R.; Wasser, T.; Gleiter, R., Weigl. H. *Liebigs Ann.* in preparation.

[3] Ritter, J.; Gleiter, R. *Liebigs Ann.* in print.

[4] Gu, X.; Sponsler, M. B. *Tetrahedron Lett.* **1996**, *37*, 1571-1574.

[5] Anderson, Jr., A. G.; McDonald, R. N. *J. Am. Chem. Soc.* **1959**, *81*, 5669-5674.

[6] Spectroscopic data of **3** - **8**. **3**: ^{1}H NMR (200 MHz, C_6D_6) δ: 2.03 (4H, t, J = 5.8 Hz), 1.65 - 1.58 (4H, m), 1.04 (4H, t, J = 6.5 Hz). ^{13}C NMR (50.3 MHz, C_6D_6) δ: 135.5, 121.9, 108.9, 31.5, 27.1, 22.0. **4**:[7] (200 MHz, $CDCl_3$) δ: 2.51 - 2.40 (8H, m), 1.86 - 1.74 (4H, m). ^{13}C NMR (50.3 MHz, $CDCl_3$) δ: 137.8, 133.3, 129.8, 117.8, 109.9, 34.3, 32.1, 27.7, 26.5, 22.6, 22.4. **5**:[7] ^{1}H NMR (200 MHz, C_6D_6) δ: 5.25 (1H, t, J = 4.2 Hz), 2.51 - 2.43 (4H, m), 2.05 - 1.97 (2H, m), 1.84 - 1.78 (2H, m), 1.50 - 1.34 (4H, m). ^{13}C NMR (50.3 MHz, C_6D_6) δ: 133.9, 133.3, 124.1, 122.3, 37.7, 31.1, 30.7, 26.1, 24.7, 22.9. **6**: ^{1}H NMR (200 MHz, C_6D_6) δ: 2.55 (4H, t, J = 6.1 Hz), 2.46 - 2.38 (4H, m), 1.69 (4H, q, J = 6.2 Hz). ^{13}C NMR (50.3 MHz, C_6D_6) δ: 132.3, 123.2, 37.5, 30.1, 23.6. **7**:[7] ^{1}H NMR (200 MHz, $CDCl_3$) δ: 5.42 (1H, t, J = 4.4 Hz), 2.40 - 2.34 (4H, m), 2.17 - 2.12 (2H, m), 2.03 - 1.97 (2H, m), 1.75 - 1.65 (4H, m). ^{13}C NMR (50.3 MHz, $CDCl_3$) δ: 133.4, 130.4, 126.1, 123.5, 34.7, 30.7, 27.0, 25.6, 23.7, 22.4. **8**: ^{1}H NMR (200 MHz, $CDCl_3$) δ: = 2.44 (8H, t, J = 6.2 Hz), 1.81 - 1.69 (4H, m). ^{13}C NMR (50.3 MHz, $CDCl_3$) δ: = 129.6, 129.2, 34.4, 26.5, 22.6.

[7] The spectroscopic data of **4**, **5** and **7** do not allow a differentiation between the bicyclo[4.4.0]-deca-1,6-diene and a bicyclo[5.3.0]decadiene structure.

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