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SYNTHESIS AND PROPERTIES OF TEN-MEMBERED CYCLODIYNES WITH ONE OR TWO HETERO ATOMS

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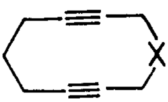
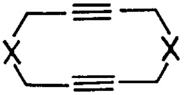
The synthesis of the heterocyclic decadiynes 1 and 2 via a cyclization sequence and the subsequent CpCo-induced oligomerization of 1a as well as its acyclic analogues 3c and 9 are reported.

In the course of our investigations on the properties of medium sized cyclic diynes[1-4] the reactions of the heterocyclic congeners 1 and 2 came into focus. Although the preparation of 2a and 2b have been described, the yields left much to be desired. A one step synthesis of 2a from 1,4-dichlorobutyne and $(NH_4)_2S$ yielding 28% of raw material[5] has been reported. We found that after purification there remains at most 7-10% of the pure product. The yield of 2b from the dimagnesium bromide of acetylene and α,α'-dichlorodimethyl ether (DCDME) was reported to be 2%.[6]



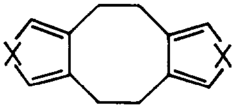
1a X=S
1b X=O



2a X=S
2b X=O

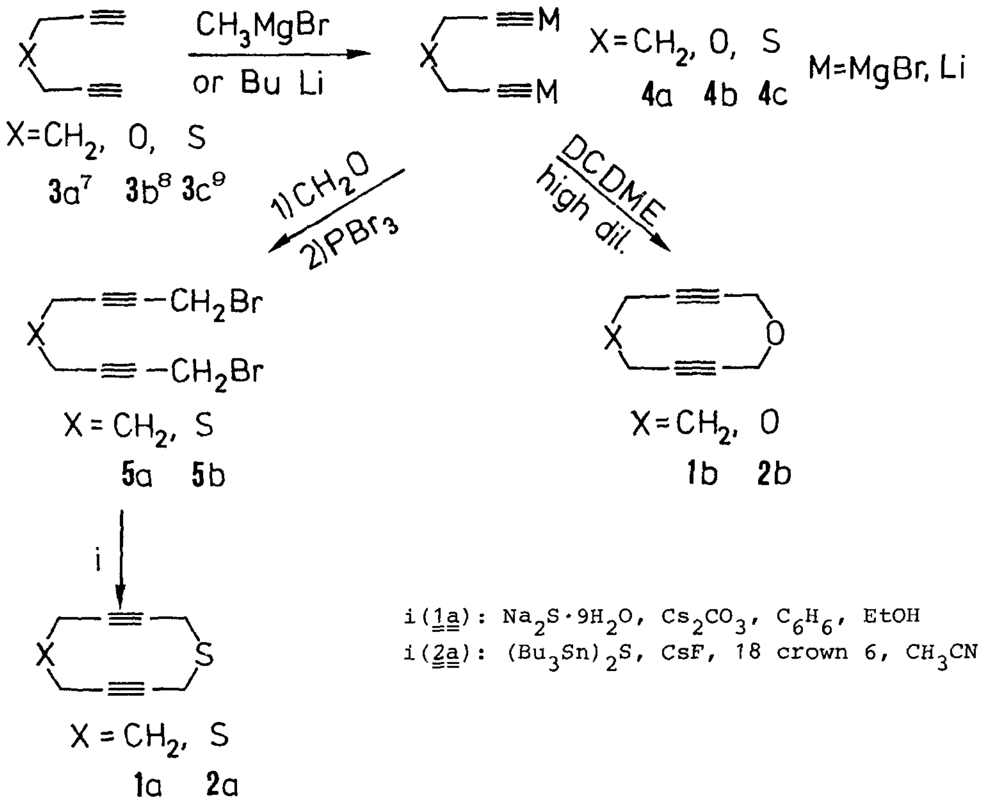
Our approach to 1 and 2 is summarized in **Scheme 1**. By dividing the one step ringclosing procedure of Lespieau[6] into two parts and using high dilution conditions 1b and 2b could be obtained in 5% yield.

Making proper use of the "cesium effect"[10] and using $(Bu_3Sn)_2S$ for thiacyclization[11] the yield of pure 2a could be improved considerably (36%). Similarly cyclization of 5a with $Na_2S \cdot 9H_2O$ in the presence of Cs_2CO_3[10] yielded 38% of 2. In the metallation step of the synthesis of 2a and 2b we isolated 6 and 7 as side products.[12]



X=O, S
6 7

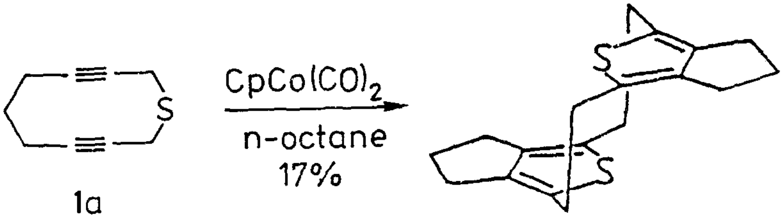
Scheme 1



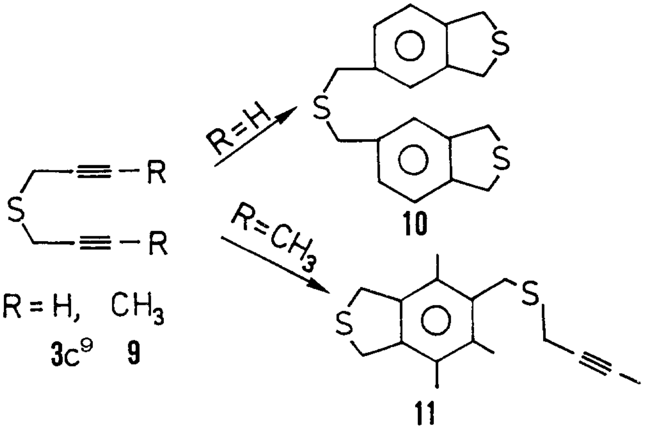
i(1a): $Na_2S \cdot 9H_2O$, Cs_2CO_3, C_6H_6, EtOH
i(2a): $(Bu_3Sn)_2S$, CsF, 18 crown 6, CH_3CN

Oligomerization experiments of 1a with catalytic as well as stoichiometric amounts of $CpCo(CO)_2$ in n-octane under reflux yielded in analogy to 2a[2] the [2.2](2,5)thiophenophane derivative 8. The reaction time in the case of 1a(4h) is considerably shorter compared to that of 2a (20h).

The acyclic thiadiynes 3c and 9 lead to the anticipated [2+2+2]cycloaddition products[13] 10 and 11. 3c reacts by trimerization and 9 by dimerization leaving one unreacted triple bond.



8



R = H, CH$_3$

3c[9] 9

10

11

All operations with organometallic reagents were carried out in purified solvents[14] under inert gas atmosphere. All new compounds gave correct elemental analysis. The most relevant data are collected in the **Table.** The extension of the cyclization sequence to other hetero atoms and the chemistry of the new products are currently under investigation.

Acknowledgment

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Table Most Relevant Analytic Data of the New Compounds.

5a: ^{1}**H NMR** (CDCl$_3$, 200 MHz) δ: 3.9 (4H,t), 2.34 (4H, tt), 1.69 (2H,q); ^{13}**C NMR** (CDCl$_3$, 50.32 MHz) δ: 86.7(s), 76.0(s), 27.1(t), 25.4(t), 18.0(t).

5b: ^{1}**H NMR** (CDCl$_3$, 200 MHz) δ: 3.95 (4H,t), 3.45 (4H,t).

1a: mp 94°C; ^{1}**H NMR** (CDCl$_3$, 200 MHz) δ: 3.48 (4H,t), 2.37 (4H,tt), 1.75 (2H,q); ^{13}**C NMR** (CDCl$_3$, 50.32 MHz) δ: 85.5(s), 77.9(s), 25.4(t) 22.6(t), 19.7(t); **IR** (KBr) $\tilde{\nu}$: 2270(w), 2223(m) cm^{-1}.

1b: mp 59.5°C; ^{1}**H NMR** (CDCl$_3$, 300 MHz) δ: 4.15 (4H,t), 2.4 (4H,tt), 1.8 (2H,q); ^{13}**C NMR** (CDCl$_3$, 75.46 MHz) δ: 90.1(s), 80.4(s), 60.6(t), 24.4(t), 19.8(t); **IR** (KBr) $\tilde{\nu}$: 2260(m), 2200(m) cm^{-1}.

8: mp>230°C(decomp.); ^{1}**H NMR** (**CDCl$_3$**, 200 MHz) δ: 2.2-2.6 (12H,m), 2.65-

3.10(8H,AA'BB'); ^{13}**C NMR** (CDCl$_3$, 50.32 MHz) δ: 149.0(s), 137.8(s), 31.0(t), 27.7(t), 27.0(t). **UV** (n-pentane) λ_{max} (log ε): 253 (3.26), 287 (3.15)nm.

9: ^{1}**H NMR** (CDCl$_3$, 90 MHz) δ: 3.35 (4H, q), 1.8 (6H, t).

10: mp 144°C; ^{1}**H NMR**(CDCl$_3$, 200 MHz) δ: 7.12 (6H,m), 4.22 (8H,s), 3.58(4H,s); ^{13}**C NMR** (CDCl$_3$, 50.32 MHz) δ: 140.9(s), 139.3(s), 136.8(s), 127.6(d), 125.1(d), 124.5(d), 37.8(t), 37.7(t), 35.5(t).

11: mp: 134°C; ^{1}**H NMR** (CDCl$_3$, 200 MHz) δ: 4.22 (4H,s), 3.93 (2H,s), 3.25(2H,q), 2.32 (6H,s), 2.17(3H,s), 1.85(3H,t); ^{13}**C NMR** (CDCl$_3$, 50.32 MHz) δ: 138.4(s), 137.1(s), 134.6(s), 132.5(s), 130.4(s), 130.2(s), 78.3(s), 75.2(s), 38.5(t), 38.3(t), 31.3(t), 20.4(t), 17.0(q), 16.4(q), 15.6(q), 3.6(q).

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