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[n.n]CYCLOPROPENYLIOPHANES

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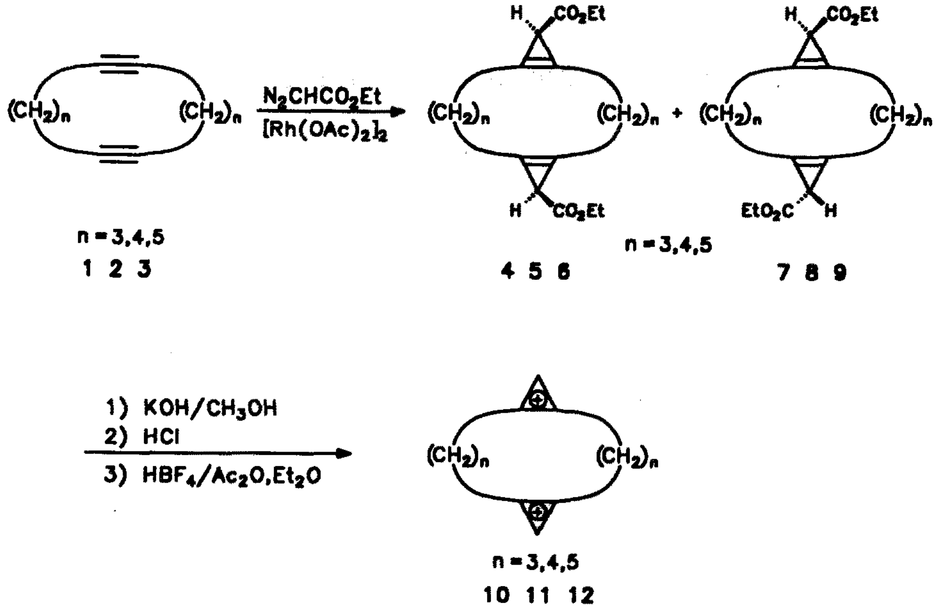
Abstract: *Reactions of cyclic diacetylenes with ethyl diazoacetate lead to bis-cyclopropenes which can be transformed into bis-cyclopropenylium ions. By this method [n.n]cyclopropenyliophanes with n = 3,4,5 have been prepared.*

Two conjugated π-systems which are connected by two alkyl chains containing m and n methylene groups are called [m.n]phanes. The best known representative of this type is [2.2]paracyclophane; [n.n]phanes of the tropyliumcation, 6π-heterocycles and higher benzenoid and non-benzenoid ring systems are known[1]. Phanes in which two cyclopropenylium rings are connected by two bridges have not been reported so far. Now we are able to present some examples of this new species.

[n.n]Cyclopropenyliophanes with three, four and five methylene groups in each bridge can be prepared from cyclic diacetylenes by addition of substituted carbenes and transformation of the obtained bis-cyclopropenes into bis-cyclopropenylium ions. Reactions of the cyclic diacetylenes[2] 1,6-cyclodecadiyne **1**, 1,7-cyclododecadiyne **2** and 1,8-cyclotetradecadiyne **3** lead to the tricyclic bis-cyclopropenes **4-9** in about 55% yield (Scheme 1).

Scheme 1



The assignment of **4**-**6** to the syn- and **7**-**9** to the anti-configurations is based on ^{1}H NMR data (see Table) under the assumption that the multiplets of the diastereotopic hydrogens at the central carbon of the bridges in **4** and **6** are more complex than the corresponding enantiotopic hydrogens in **7** and **9**. To discriminate between **5** and **8**, the ^{1}H NMR signals of the allylic hydrogens are suitable. The results were confirmed by double resonance experiments on **4** and **6**.

Refluxing **4**-**9** with KOH[4] in methanol and subsequent treatment with HCl gives the diacids in 90% yield. Further treatment with HBF_4[5] and acetic acid anhydride results in the [n.n]cyclopropenyliophanes **10**-**12**. Their tetrafluoroborate salts form colourless short needles, which can be stored for weeks at -30°C. On heating they decompose rapidly, changing colour to dark brown.

The most characteristic spectroscopic features of these new compounds are the small number of signals in their ^{13}C NMR spectra caused by their high symmetry, and the anticipated downfield shifts of the NMR signals compared to the cyclopropenes, which are due to the cyclopropenylium cations. In the ^{13}C-NMR spectra the corresponding signals are found at δ= 170-185. These values agree with those reported in the literature[7]. In the ^{1}H NMR spectra the singlet of the protons at the three-membered rings are observed at $\delta \approx$ 10.4-10.5 (see Table). These values are similar to those reported for other cyclopropenylium compounds[7].

Further investigations concerning structure and reactivity of cyclopropenyliophanes are in progress.

Table 1. Selected physical data of **4**-**12**.

4: m.p. 68°C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ=4.10 (q,^{3}J=7.13 Hz, 4H), 2.73 (m, 4H), 2.38 (m, 4H), 2.02 (s, 2H), 1.94 (m, 4H), 1,24 (t,^{3}J= 7.13, Hz, 6H);

5: m.p. 83°C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ=4.10 (q,^{3}J=7.13, 4H), 2.50 (m, 8H), 1.98 (s, 2H), 1.85 (m, 8H), 1.23 (t,^{3}J=7.13 Hz, 6H);.

6: m.p. 63°C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ=4.09 (q, ^{3}J=7.12 Hz, 4H), 2.43 (m, 8H), 1.93 (s, 2H), 1.55 (m, 8H), 1.23 (t, ^{3}J=7.12 Hz, 6H), 1.14 (m, 4H);.

7: ^{1}H-NMR (300 MHz, $CDCl_3$): δ= 4.09 (q,^{3}J=7.13 Hz, 4H), 2.54 (m, 8 H), 2.07 (s, 2H), 1.98 (m, 4H), 1.22 (t, ^{3}J=7.13 Hz, 6H);.

8: m.p. 125°C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ= 4.11 (q, ^{3}J=7.13 Hz, 4H), 2.50 (m, 8H), 1.99 (s, 2H), 1.84 (m, 8H), 1.24 (t, ^{3}J=7.13 Hz, 6H).

9: m.p. 34°C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ=4.07 (q, ^{3}J=7.14 Hz, 4H), 2.43 (m, 8H), 2.00 (s, 2H), 1.57 (m, 8H), 1.20 (t, ^{3}J=7.14 Hz, 6H), 1.14 (m, 4H).

10: ^{1}H-NMR (300 MHz, CD_3CN): δ=10.45 (s, 2H), 3.49 (m, 8H), 2.75 (m, 4H); ^{13}C-NMR (75.47, CD_3CN): δ=182.82, 172.79, 29.92, 22.66.

11: ^{1}H-NMR (300 MHz, CD_3CN): δ=10.37 (s, 2H), 3.35 (m, 8H), 1.93 (m, 8H); ^{13}C-NMR (75.47 MHz, CD_3CN): δ= 183.71, 172.88, 29.10, 26.09.

12: ^{1}H-NMR (300 MHz, CD_3CN): δ= 10.47 (s, 2H), 3.30 (m, 8H), 1.94 (m, 8H), 1.24 (m, 4H); ^{13}C-NMR (75.47 MHz, CD_3CN): δ=184.49, 172.42, 29.81, 28.77, 25.84.

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