Synthesis and Oxidative Coupling of Bi-cyclononatetraenylide – Reaction of Bi-cyclononatetraenyl with Potassium**

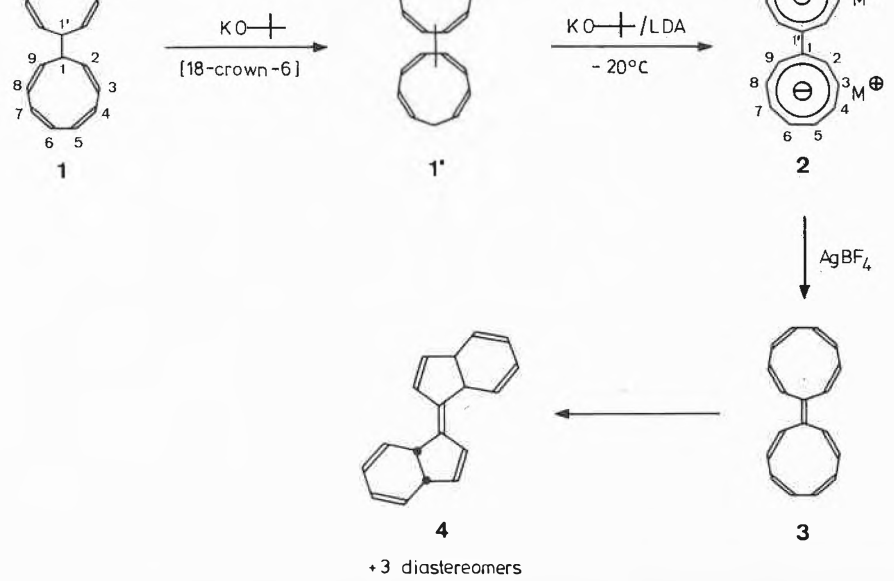
André Escher and Markus Neuenschwander*

Abstract: Contrary to literature reports, treatment of bi-cyclononatetraenyl (**1**) with potassium does not give bi-cyclononatetraenylide (**2**), but *ccct*-cyclononatetraenide (**6**) in a high yield. Twofold deprotonation of the ring assembly **1** takes place after equilibration $\mathbf{1} \rightleftharpoons \mathbf{1'}$ followed by treatment of **1'** with K-*tert*-butoxide/Li-diisopropylamide. The structure of **2** follows from its spectroscopic data as well as from the successful oxidative treatment of **2** with Ag$^\oplus$ to give thermally unstable nonafulvalene (**3**).

In 1975 *Hafner* et al. realized the first synthesis of bi-cyclononatetraenyl (**1**)[1] by application of the Doering procedure[2] to cyclononatetraenide[3]. The same authors reported that treatment of **1** with potassium leads to a twofold deprotonation of **1**. According to very reasonable NMR data[4], bi-cyclononatetraenylide (**2**) was postulated as reaction product: Key signal in the 60 MHz ^{1}H-NMR spectrum ([^{2}H$_8$]tetrahydrofuran (d_8-THF)) was a doublet of doublets at $\delta = 7.16$ with splittings of about 15 and 5 Hz, being assigned to protons H–C(2,2′,9,9′) of **2**, while a broad signal at $\delta = 6.61$ was assigned to the remaining ring protons. In the ^{13}C-NMR spectrum (d_8-THF) four lines of nearly equal intensity at $\delta = 110.4$, 110.6, 115.5, and 116.8 as well as a line of about 50% intensity at $\delta = 129.4$ seemed to be in accord with structure **2**. At this time the only surprising result was the observed slow fragmentation of the postulated bis-anion **2** in the presence of metallic potassium to give cyclononatetraenide (**7**)[1].

Taking into account the recent results of a detailed NMR-analysis of nonafulvenes[5], some spectral features of the reaction product of **1** with potassium seem to be quite surprising: First of all vicinal H,H coupling constants over formal double bonds of nonafulvenes of type **3** are in the range of 12.6 ± 0.6 Hz. Furthermore allylic couplings of type $J_{2,4} = J_{7,9}$ are very small for nonafulvenes (about 1.4 Hz) and are in most cases invisible due to further long-range couplings. Considering the fact that the splitting pattern of H–C(2)/H–C(9) of nonafulvenes does not significantly change with increasing cyclononatetraenide character of the nine-membered ring[5], protons H–C(2)/H–C(9) of the bis-anion **2** are expected to show splitting into a broad doublet (with $J \approx 12.5$ Hz) and not into a doublet of doublets with $J \approx 15$ and 5 Hz. – In the ^{13}C-NMR spectrum, the considerable intensity of the signal at $\delta = 129.4$ being assigned to C(1)/C(1′) of **2** is surprising under routine conditions. – Furthermore, the attempted oxidative treatment of the postulated bis-anion **2** with Ag$^\oplus$ did not give the expected nonafulvalene **3** but **1**, although an equivalent amount of silver was deposited.

Scheme 1



According to these spectral and preparative discrepances we decided to prepare bis-anion **2** by treatment of **1** with strong bases and to reinvestigate the structure of the product formed by reaction of **1** with potassium.

1. Synthesis and Oxidative Treatment of Bi-cyclononatetraenylide (2)

According to Scheme 1, the bis-anion **2** should be easily available by treatment of the neutral ring assembly **1** with strong bases. However, one has to bear in mind that deprotonation of sterically hindered cyclononatetraenes is extremely difficult[6]. With several strong bases only one proton of **1** is removed so that oxidative coupling of two mono-anions gives tetrameric products. Fortunately, a deprotonation/protonation equilibrium $\mathbf{1} \rightleftharpoons \mathbf{1'}$ is obtained with potassium *tert*-butoxide/18-crown-6 so that the sp^3-C-atoms are shifted to the periphery of the rings. Following this, potassium *tert*-butoxide/lithium diisopropylamide (LDA) is strong enough for twofold deprotonation to take place giving the bis-anion **2**.

The structure of bi-cyclononatetraenylide (**2**) is supported by it's NMR spectra as well as by the successful transformation **2**→**3**→**4**. In the 400 MHz ^{1}H-NMR spectrum (d_8-THF; Fig. 1, bottom) the expected broad doublet of H–C(2,2′,9,9′) appears at $\delta = 7.78$ with a splitting of 12.5 Hz, while the other ring protons are absorbing in the range between $\delta = 7.1$ and 6.9, a range being very typical for cyclononatetraenides of type **7**. In the ^{13}C-NMR spectrum (Fig. 2, below) the high-field shift

---

* *Correspondence:* Prof. Dr. M. Neuenschwander
Institut für Organische Chemie
Universität Bern
Freiestrasse 3, CH-3012 Bern

** Financial support of this work by Ciba-Geigy AG as well as by the Swiss National Science Foundation (Project No. 2.003-0.86) is gratefully acknowledged.

of C(2,2′)–C(9,9′) compared with nonafulvenes[5] is compatible with a cyclononatetraenide as well. The three resonances of C(3,3′)–C(8,8′) at $\delta = 108.7$, 107.8, and 107.4 nearly coincide, and the signal of C(2,2′)/C(9,9′) appears at 114.7, while the expected low-field signal of the quaternary C(1,1′), being expected to absorb around $\delta = 140$, is not localized due to a considerable noise.

Oxidative coupling of the bis-anion **2** proceeds readily in the presence of $Ag^{\oplus}$ even at −75 °C to yield nonafulvalene **3**, which is thermally much more unstable than pentafulvalene[2, 7] or nonapentafulvalene[8]. Even at −50 °C valence isomerization proceeds to give a mixture of four diastereomeric tetrahydro-dibenzopentafulvalenes **4**[9]. Because of this fast process, direct spectroscopic evidence for **3** is so far incomplete, whereas the structure of the predominant (*E*)-*anti*-isomer **4** has been proved both by spectroscopic methods and a X-ray analysis[9].

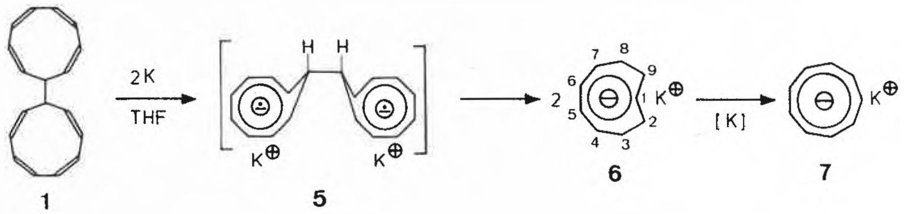
2. *Reaction of* **1** *with potassium*

According to the different spectroscopic as well as reactive behavior of bis-anion **2** compared with the reaction product of **1** with potassium[1], it was challenging to look for a revised structure of the latter product. We felt that there was a close similarity between the NMR data of *Hafner*'s product and those of *ccct*-$CNT^{\ominus}$[3], having been prepared[10] and thoroughly investigated[11] by *Boche* et al., although slight changes in chemical shifts had to be expected depending on the nature of the counter-ion, the solvent, temperature and concentration. The only difference was the missing ^{1}H-NMR triplet at $\delta \approx -3.3$ in *Hafner*'s paper[1] and spectra[4] which could have been overlooked in a routine NMR investigation.

This idea was easily confirmed by comparison of the ^{1}H-NMR spectra of freshly prepared solutions of the anions. According to Fig. 1 the ^{1}H-NMR spectra of *ccct*-CNT-Na[11] as well as of the product obtained by reaction of bi-cyclononatetraenyl **1** with potassium[1] show similar chemical shifts (including a triplet at ca. −3.25 ppm with splittings of 14.8 Hz for H-C(1) of **6**) and the same splitting pattern of all the multiplets[12]. This result as well as the significantly different pattern of the ^{1}H-NMR spectrum of **2** obtained by twofold deprotonation of **1** definitely proves that, in contrary to literature reports[1], the reaction of **1** with potassium gives *ccct*-$CNT^{\ominus}$ (**6**).

The ^{13}C-NMR spectrum of the product obtained by reaction of **1** with potassium[1] (Fig. 2, above) is in good agreement with the results reported in the literature[1]. However, off-resonance decouplings and DEPT-experiments immediately show that the low-field signal at $\delta = 130$ belongs to a CH-group and not to a quaternary C-atom. So bis-anion **2** has to be ruled out by ^{13}C-NMR arguments as well, while chemi-

Scheme 2



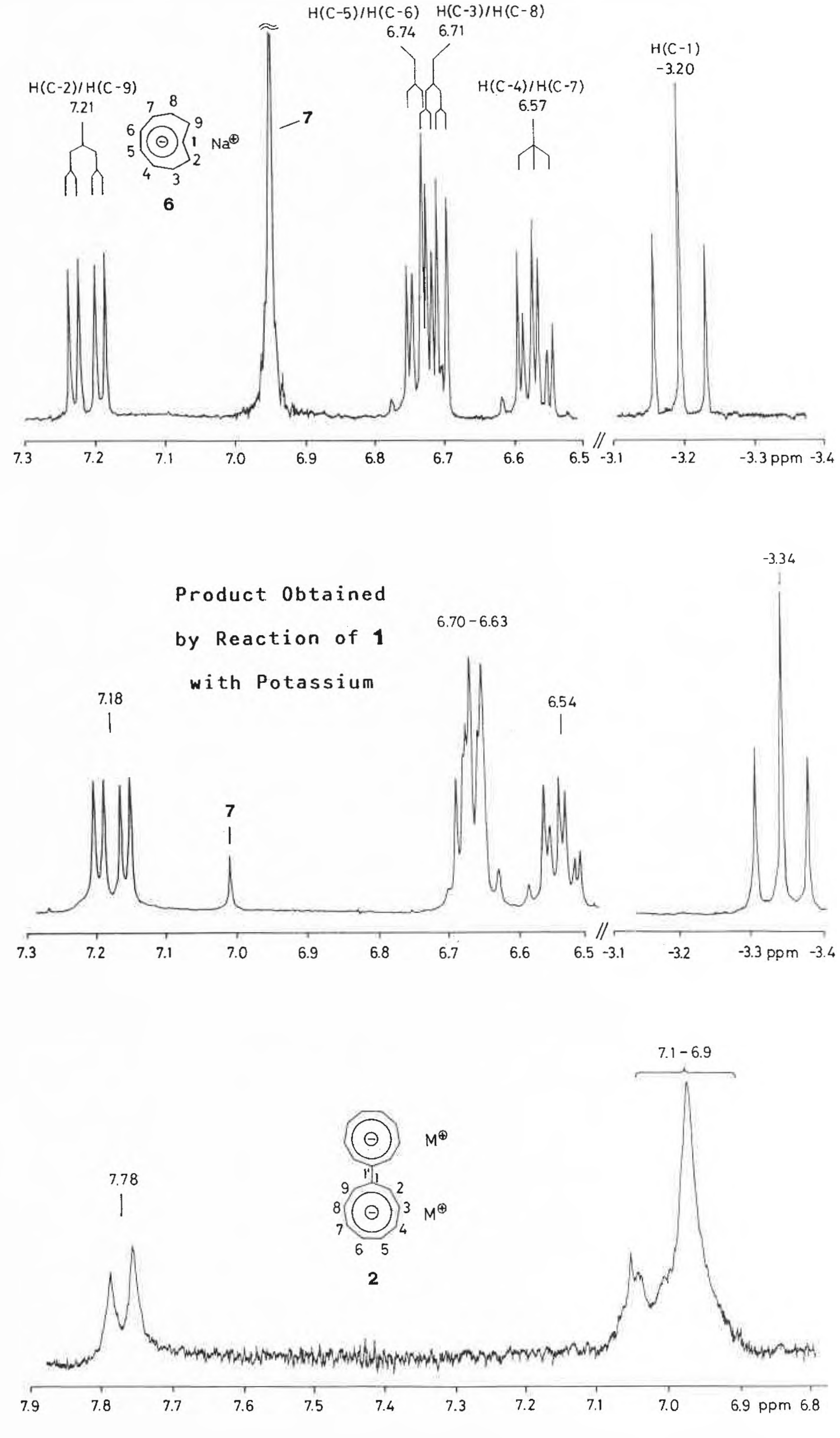


Fig. 1. 400 MHz ^{1}H-NMR spectra (d_8-THF, 34 °C) of Na-**6**, *of the product obtained by reaction of* **1** *with potassium, as well as of* **2** *(from top to bottom)*[12].

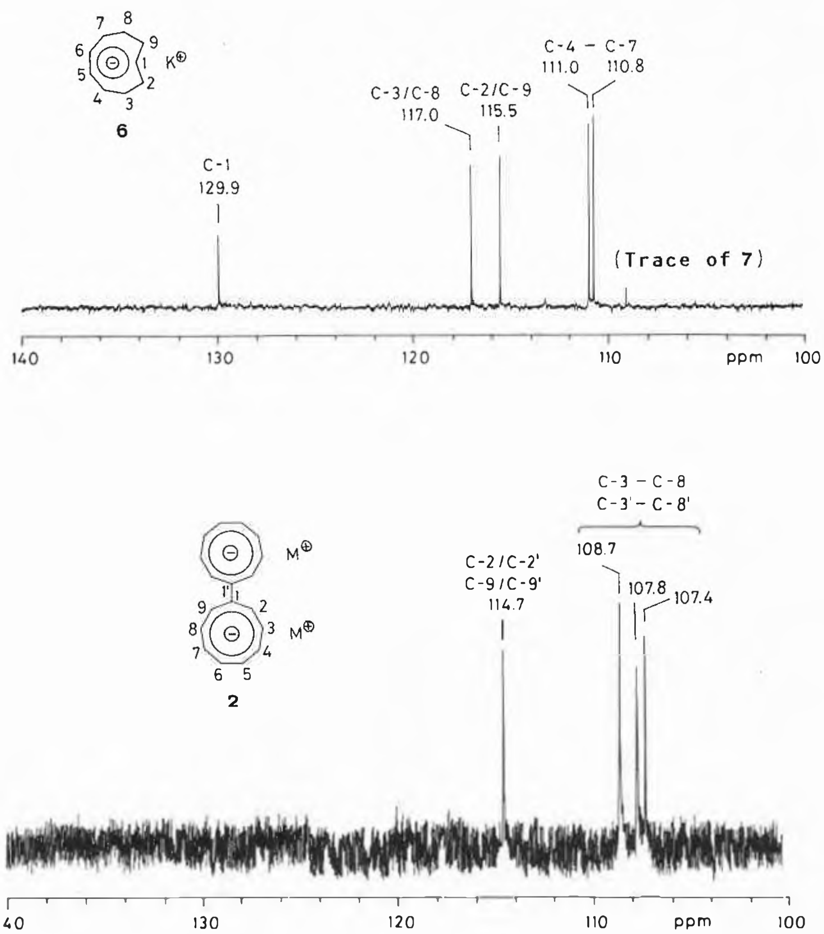


Fig. 2. 100 MHz ^{13}C-NMR spectra (d_8-THF, 34°C) of the product obtained by reaction of **1** *with potassium, as well as of* **2**.

cal shifts and off-resonance splittings are in agreement with structure **6**[13].

In the ^{13}C-NMR spectrum of the bis-anion **2** all the CH-groups show the expected high-field shift due to the anionic character of the species. C(2,2')/C(9,9') may be assigned to the signal at $\delta = 114.7$. Once more the spectra of *ccct*-CNT-K (**6**) prepared according to ref.[1] and those of **2** are clearly different.

Summarizing our results, we have shown that **1** reacts with potassium to give *ccct*-CNT-K (**6**) in a highly stereoselective way and not bis-anion **2**, as reported earlier[1]. Mechanistically the sequence **1**→**6** may tentatively be rationalized by an electron transfer from potassium to each nine-membered ring to give the bis-radicalanion **5** which obviously undergoes cleavage of the central CC-bond to give **6** in a highly stereoselective way. The formation[11] and the steric course of the cleavage of C(1)–X bonds[11, 14] of radical anions of type **2** (with one nine-membered ring) has been discussed. – Finally, in the light of these findings, the surprising fragmentation **2**→**7**[1] is easily explained in terms of the well-known isomerization of *ccct*-CNT$^{\ominus}$ (**6**) to CNT$^{\ominus}$ (**7**) which has been shown to be catalyzed by an excess of alkali metals[15].

Received: January 7, 1987 [FC 94]

---

[1] K. Hafner, S. Braun, T. Nakazawa, H. Tappe, *Tetrahedron Lett. 16* (1975) 3507.

[2] W. von E. Doering, Kekulé Symposium, London (1958); E. Matzner, Ph. D. thesis, Yale University (1958).

[3] In the following CNT$^{\ominus}$ stands for all-*cis*-cyclononatetraenide (**7**) while *ccct*-CNT$^{\ominus}$ stands for *cis,cis,cis,trans*-cyclononatetraenide (**6**).

[4] We are grateful to Prof. *K. Hafner* for sending us the procedure as well as the ^{1}H- and ^{13}C-NMR spectrum of the reaction product of **1** with potassium in another context (personal communication, December 22, 1983).

[5] A. Otter, M. Neuenschwander, H. P. Kellerhals, *Magn. Reson. Chem. 24* (1986) 353; A. Otter, G. Sabbioni, M. Neuenschwander, H. P. Kellerhals, *Helv. Chim. Acta 69* (1986) 124.

[6] G. Sabbioni, M. Neuenschwander, *Helv. Chim. Acta 68* (1985) 623.

[7] A. Escher, W. Rutsch, M. Neuenschwander, *Helv. Chim. Acta 69* (1986) 1644.

[8] A. Escher, M. Neuenschwander, *Angew. Chem. 96* (1984) 983; *Angew. Chem. Int. Ed. Engl. 23* (1984) 973; *Helv. Chim. Acta 70* (1987) 49.

[9] A. Escher, M. Neuenschwander, P. Engel, *Helv. Chim. Acta*, in preparation.

[10] G. Boche, D. Martens, W. Danzer, *Angew. Chem. 81* (1969) 1003; *Angew. Chem. Int. Ed. Engl. 8* (1969) 984.

[11] G. Boche, H. Weber, D. Martens, A. Bieberbach, *Chem. Ber. 111* (1978) 2480.

[12] Due to the high-order type of the spectra, it is not allowed to derive the coupling constants from the observed splittings without computer-simulation and iteration of highly resolved spectra.

[13] The ^{13}C-NMR spectrum of *ccct*-CNT-Na shows the same pattern (signals at $\delta = 126.8$, 117.0, 114.3, 110.0, and 109.9), although some differences in chemical shifts are observed compared with *ccct*-CNT-K due to different counter-ions.

[14] N. L. Bauld, J. Cessac, *J. Am. Chem. Soc. 99* (1977) 23.

[15] G. Boche, A. Bieberbach, *Tetrahedron Lett. 17* (1976) 1021; Chem. Ber. *111* (1978) 2850.