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# The benzylidenefluorene dianion

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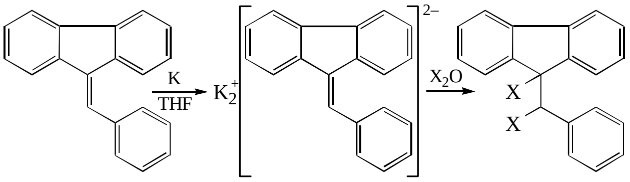
**The interaction of benzylidenefluorene with alkali metals in THF solutions results in the formation of the benzylidenefluorene dianion or the 1,2-bis(9-fluorenyl)-1,2-diphenylethane dianion depending on the nature of the alkali metal.**

Aryl-substituted olefins and polycyclic aromatic hydrocarbons undergo reduction to form dianions[1–3] or even tri- and tetra-anions.[2–5] The studies in this field were primarily concerned with symmetrically substituted olefins;[6–11] little information is availaible about unsymmetrically substituted vinylarenes.[12] Earlier, we have reported on the synthesis of organolanthanide complexes using hydrocarbon dianions as ligands.[13–15] To extend the range of dianions, we have examined the two-electron reduction of benzylidenefluorene, a trisubstituted vinylarene, which can be synthesised from fluorene and benzaldehyde.[16,17] However, the possibility of selective reduction of benzylidenefluorene to its dianion under the treatment with alkali metals is questionable because of the well-known ability of unsymmetrically substituted vinylarenes to form dimers under the action of alkali metals.[1] Moreover, Schlenk and Bergmann[18] found that the interaction of benzylidenefluorene with sodium in diethyl ether followed by hydrolysis of the reaction mixture leads to 1,2-bis-(9-fluorenyl)-1,2-diphenylethane. Therefore, the treatment of benzylidenefluorene by sodium in diethyl ether leads to dimerization of the benzylidenefluorene radical ion instead of formation of the dianion.

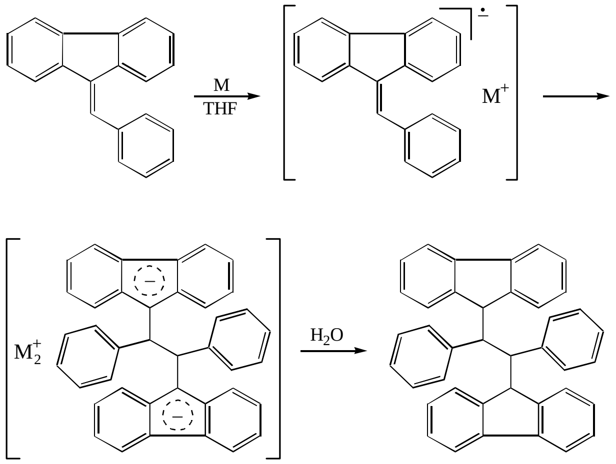
We report here on the reaction of benzylidenefluorene **1** with alkali metals in THF solutions resulting in formation of the benzylidenefluorene dianion or the 1,2-bis(9-fluorenyl)-1,2-diphenylethane dianion depending on the nature of the alkali metal. The behaviour of the benzylidenefluorene dianion in a THF solution was examined by NMR spectroscopy.

The reaction of **1** with potassium in a THF solution leads to the formation of the benzilydenefluorene dianion. A colourless solution of benzilydenefluorene placed in the Schlenk vessel† containing a potassium mirror immediately turned orange-brown ($\lambda_{max}$ = 428 nm). The keeping of the solution over the potassium surface at ambient temperature for 48 h with occasional stirring resulted in the quantitative formation of dipotassium benzylidenefluorene **2**.



**1** **2** **3** X = H
**4** X = D

The quenching of the dianion solution by $H_2O$ or $D_2O$ resulted in the formation of 9-benzylfluorene **3**[19] or 9,10-dideuterio-9-benzylfluorene **4**.‡ Therefore, the use of potassium/THF instead of sodium/diethyl ether allowed us to obtain the benzylidenefluorene dianion and to avoid dimerization of the initially formed radical ion. Nevertheless, the reduction of benzylidenefluorene by sodium or lithium metal in a THF solution (using a sodium mirror or a lithium suspension) led to another result. A slightly coloured precipitate and an intensely coloured solution were formed in both cases. The subsequent hydrolysis of the reaction mixture resulted in the formation of 1,2-bis(9-fluorenyl)-1,2-diphenylethane **5** in 86 (sodium) or 64% (lithium) isolated yield.§



M = Li, Na

**5**

The $^1$H NMR spectrum of **2** exhibits nine resonance signals due to aromatic protons (Figure 1).¶ The 2D $^1$H–$^1$H correlation and NOE between $H^{10}$–$H^{16}$ and $H^{10}$–$H^1$ allowed us to assign the $^1$H NMR signals. The $^3J_{HH}$ constants were calculated using the

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† All experiments were carried out in evacuated and sealed vessels like the Schlenk tubes. In the typical experiment, 1.053 g (4.14 mmol) of **1** was dissolved in 70 ml of absolute THF and allowed to react with a potassium mirror prepared from 0.500 g (12.8 mmol, 3-fold excess) of potassium. To prepare NMR samples, 7 mg scale experiments were performed in 0.5 ml of [$^2H_8$]THF.

‡ **3**: mp 130–131 °C (lit.,[19] 130–131 °C). $^1$H NMR (250 MHz, $CDCl_3$) $\delta$: 3.13 (d, 2H), 4.25 (t, 1H), 7.15–7.40 (mm, 11H), 7.75 (m, 2H).

**4**: mp 131–133 °C. $^1$H NMR (250 MHz, $CDCl_3$) $\delta$: 3.13 (br. s, 1H, $\nu_{1/2}$ 12 Hz), 7.15–7.40 (mm, 11H), 7.78 (m, 2H). $^{13}$C {$^1$H} NMR (75 MHz, $CDCl_3$) $\delta$: 39.7 (t), 48.7 (t), 119.9, 124.9, 126.4, 126.7, 127.2, 128.3, 129.6, 139.8, 140.9, 146.8. MS (EI, 70 eV, 250 °C) *m/z* (%): 259 (11) [M + 1], 258 (59) [M], 257 (44) [M – 1], 167 (47), 166 (100), 165 (70), 164 (17), 92 (42), 91 (8), 44 (18), 43 (68), 40 (30), 39 (11).

§ A solution of 0.226 g (0.89 mmol) of **1** in 20 ml of THF was stirred over a sodium mirror for 36 h. A reddish orange precipitate was formed. The precipitate was hydrolysed with 4 ml of degassed water. The reaction with lithium powder was carried out in a similar way. The standard procedure gave 0.196 g (86%) of **5**, mp 336–337 °C (lit.,[18] mp 321 °C). $^1$H NMR (500 MHz, $CD_2Cl_2$) $\delta$: 4.03 (br. s, 2H, $\nu_{1/2}$ 3.8 Hz), 4.66 (br. s, 2H, $\nu_{1/2}$ 3.8Hz), 6.88–6.975 (m, 10H), 7.21 (t, 2H), 7.28–7.38 (m, 6H), 7.40 (d, 2H), 7.47 (d, 2H), 7.70 (d, 2H), 7.87 (d, 2H). $^{13}$C {$^1$H} NMR (75.5 MHz, $CD_2Cl_2$) $\delta$: 50.0, 52.7, 119.7, 120.1, 124.7, 126.3, 126.6, 126.8, 127.0, 127.2, 127.5, 127.6, 138.2, 141.2, 142.5, 144.6, 147.2. MS (EI, 70 eV, 250 °C) *m/z* (%): 510 (1.4) [M$^+$], 345 (4), 331 (8), 330 (23), 253 (6), 180 (26), 179 (7), 178 (5), 167 (6), 166 (54), 165 (100), 164 (11), 163 (6), 115 (4), 91 (10), 57 (6).

¶ **2**: $^1$H NMR (500 MHz, [$^2H_8$]THF) $\delta$: 4.40 ($H^{10}$), 4.82 ($H^{14}$, $^3J_{H^{14}H^{15}}$ 7.1 Hz), 5.29 ($H^{12}$, $^3J_{H^{12}H^{13}}$ 7.9 Hz), 6.11 ($H^{15}$, $^3J_{H^{15}H^{16}}$ 8.1 Hz), 6.15 ($H^{16}$), 6.30 ($H^{13}$, $^3J_{H^{13}H^{14}}$ 7.1 Hz), 6.41 ($H^3$, $H^6$, $^3J_{H^3H^4}$ 7.4 Hz), 6.94 ($H^2$, $H^7$, $^3J_{H^2H^3}$ 7.2 Hz), 7.04 ($H^1$, $H^8$, $^3J_{H^1H^2}$ 8.1 Hz), 8.00 ($H^4$, $H^5$). $^{13}$C {$^1$H} NMR (100 MHz, [$^2H_8$]THF) $\delta$: 31.8 ($C^9$), 66.5 ($C^{10}$, $J_{C^{10}H^{10}}$ 142.8 Hz), 97.2 ($C^{14}$, $J_{C^{14}H^{14}}$ 158.4 Hz), 100.1 ($C^{quatern}$), 108.5 ($C^3$), 108.8 ($C^{12}$, $J_{C^{12}H^{12}}$ 149.7 Hz), 117.3 ($C^1$), 117.9 ($C^{15}$), 120.5 ($C^2$, $C^4$, $J_{C^4H^4}$ 149.1 Hz), 124.4 ($C^{quatern}$), 129.6 ($C^{16}$), 132.0 ($C^{13}$), 132.9 ($C^{quatern}$), 146.1 ($C^{quatern}$) (the assignments were made using DEPT and CW-decoupling experiments).

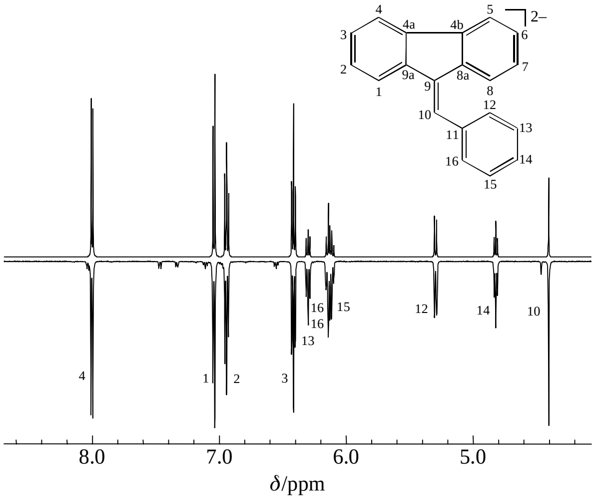

**Figure 1** Calculated (top) and experimental (bottom) $^1$H NMR (500 MHz) spectra of **2**.

CALM program. A comparison between the simulated and experimental spectra (Figure 1) confirm the rigidity of the dianion in a THF solution. Because all protons of the phenyl group in **2** are nonequivalent on the NMR time scale, we have to suppose that this phenomenon resulted from the inability of a phenyl ring to rotate at room temperature; thus, the *ortho*- and *meta*-protons are distinguishable.

The $^{13}$C NMR spectrum of **2**[¶] is also consistent with this hypothesis; there are 14 separated resonance signals in the spectrum. Six resonance signals correspond to the phenyl group.

A comparison of the $^{13}$C NMR data for **2**[¶] with the corresponding data for **1**[††] (all spectra were recorded in the same solvent to exclude the influence of specific solvatation on the chemical shifts) indicates that the most significant difference between the chemical shifts of the resonance signals of corresponding carbon atoms in **1** and **2** was observed for C-9 and C-10 carbon atoms. This observation allowed us to suppose that an excessive electron density is significantly localised at the 'former double bond' carbon atoms that is rather common for the dianions of vinylarenes.[1,2] A significant difference in the chemical shifts of *ortho*-, *meta*- and *para*-carbons and protons of the phenyl group should be mentioned. At the same time, the chemical shifts of protons of the fluorenyl moiety of the dianion are in a good agreement with those found for fluorenyl derivatives of alkali metals.[20,21] The strong upfield shift of C(H)-14 in both $^{13}$C and $^1$H NMR spectra is of most interest. A significant impact of a quinoid resonance structure of the benzyl fragment of the dianion can be an explanation for this phenomenon.

This speculation is also consistent with the absence of free rotation of the phenyl ring and with a considerable difference in the $^{13}$C chemical shifts of C-9 and C-10 carbons. The latter is downfield shifted by more than 30 ppm in comparison with the C-9 signal; this can be interpreted as the consequence of a significant impact of the quinoid resonance structure.

To investigate the dynamics of this system, we performed high-temperature NMR experiments. Suprisingly, no changes in the $^1$H NMR spectrum of **2** were found up to 333 K. This fact indicates that the rigid structure of **2** in a $[^2H_8]$THF solution remains unchanged even at elevated temperatures; therefore, no rotation of the phenyl ring can be observed. This observation is inconsistent with the behaviour of the more sterically hindered tetraphenylethylene dianion in solution, where equivalent phenyl protons were detected even at room temperature.[15] Similar phenomena were observed earlier in dilithium 1-phenyl-1,2,2-tris(trimethylsilyl)ethylene, where the rotation of phenyl group was also frozen at room temperature.[12] Unfortunately, high-temperature NMR spectra were not measured for this compound.

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[††] **1**: $^1$H NMR (300 MHz, $[^2H_8]$THF) $\delta$: 7.09 (t, 1H), 7.20–7.55 (mm, 6H), 7.65 (m, 3H), 7.82 (m, 3H), 7.91 (d, 1H). $^{13}$C {$^1$H} NMR (75 MHz, $[^2H_8]$THF) $\delta$: 120.2, 120.4, 121.1, 125.1, 127.3, 127.7, 128.09, 128.11, 128.8, 128.9, 129.3, 130.0, 137.4, 137.5, 138.1, 140.2, 140.5, 142.3.