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ELECTRON-TRANSFER INDUCED VALENCE ISOMERIZATION OF 1,2-DISTYRYLBENZENE

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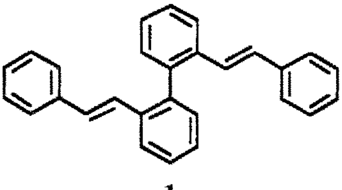
Abstract: Upon electron transfer 1,2-distyrylbenzene 2 undergoes a valence isomerization giving rise to an indane derivative. This process is controlled by the ion-pair structures of the anionic intermediates and differs from the photochemically induced rearrangement.

Electron-transfer (ET)-induced pericyclic reactions are of synthetic and mechanistic importance [1]. While a number of publications have pointed out the advantages of radical-cation catalyzed Diels-Alder cycloadditions of electron-rich dienophiles [1a,c,f], the scope of other ET-induced rearrangement reactions in comparison with the corresponding thermolytic or photolytic processes is widely unexplored. Recently we could demonstrate that the ET-induced valence isomerization of 2,2'-distyrylbiphenyl (1) shows a close analogy to the photochemical [2+2]cycloaddition observed in solution [2]. We now report on an ET-induced rearrangement of 1,2-distyrylbenzene (2) which differs drastically from the photolytic conversion of 2 in an isotropic phase [3]. The reaction is controlled by the ion-pair structures of the substrate anions formed during the reduction process and leads to the 1,2-disubstituted indane frame.



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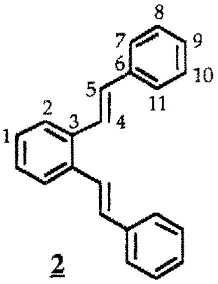

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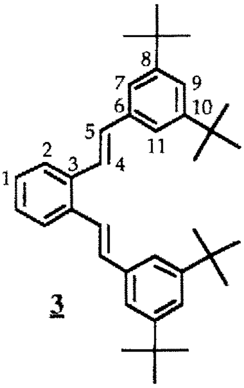

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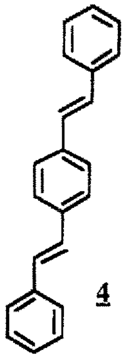

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The chemical reduction of 2 with lithium in THF at -80°C yields the dianion salt $2a^{2-}/2Li^+$ and the tetraanion salt $2a^{4-}/4Li^+$, which, according to their NMR spectroscopic characterization, possess the intact framework of the starting material (Table 1, 2a indicates a symmetric, 2b an asymmetric structure of the substrate anions). It can be deduced from a correlation of $^1H(^{13}C)$-NMR chemical shifts [4] and local charge densities that in the tetraanion the excess charge is delocalized over the entire molecule with the highest charge densities at the ethylenic bridges. The reduction of the isomeric 1,4-distyrylbenzene (4) only leads to a dianionic species [5]. The formation of a tetraanion in the case of the 'angular' isomer 2, unexpected from an electrostatic point of view, must be ascribed to stabilizing ion-pair effects, e.g. via lithium-bridged o-xylylidene substructures [6]. It is characteristic therefore, that upon warming to -20°C one observes a reversible equilibrium between the above species and an isomeric tetraanion less charged at the olefinic centers (Table 1). Both species, however, have a similar π-bond order for the olefinic C_7/C_8 (C_{15}/C_{16}) bond as deduced from the corresponding vicinal H,H-coupling constant. The number of ^{1}H-resonances found for the dianion **2a**$^{2-}$/2Li$^+$ also points towards a symmetrical structure with charge delocalization over the entire π-system.

Table 1: ^{1}H- and ^{13}C-NMR chemical shifts (δ_H, δ_C) of **2**, **3** and the corresponding anion salts $^{a)}$

position	δ_H (**2**)	δ_H (**2a**$^{4-}$/4Li$^+$)	δ_H (**2a**$^{4-}$/4Li$^+$)	δ_H (**2a**$^{4-}$/4Li$^+$)	δ_C (**3**)	δ_C (**3**$^{4-}$/4Li$^+$)
	RT	-80°C	-60°C	-20°C	RT	-70°C
1	7.45, m (AA'BB')	5.35, bs	5.39, b	5.39, b	126.8 (126.1)	101.9
2	7.45, m (AA'BB')	4.72, bs	4.35, b	4.55, b	126.1 (126.8)	86.0
3					136.3	123.2
4	7.62, d (AB), J=16.0Hz	3.38, d (AB), J=10.5Hz	3.41, d (AB), J=10.5Hz	3.41, bd (AB)	132.4 (127.8)	60.6
5	7.06, d (AB), J=16.0Hz	2.72, d (AB), J=10.5Hz	3.05, d (AB), J=10.5Hz	2.83, bd (AB)	127.8 (132.4)	54.0
6					137.1	142.6
7	7.32, m	5.20, d, J=8.5Hz	5.08, b	5.22, b	121.1	104.9
8	7.58, s	5.73, m	5.88, m	5.88, m	151.2	146.4
9	7.32, m	4.54, t, J=6.0Hz	4.58, t, J=6.0Hz	4.72, t, J=6.0Hz	122.5	93.4
10	7.58, s	6.17, t, J=8.5Hz	6.23, t, J=8.5Hz	6.23, t, J=8.5Hz	151.2	150.1
11	7.32, m	5.73, m	5.88, m	5.88, m	121.1	112.2

a) δ_H (200 MHz, THF-d_8); δ_C (50 MHz, THF-d_8; b) The dianion salt **2a**$^{2-}$/2Li$^+$ exhibits ^{1}H-resonances at δ_H = 4.32 (d), 5.08 (t), 5.26, 5.58 (d), 5.81 (d), 6.34 (t) and 6.53. These signals suffer from line broadening and are partly covered by tetraanion absorptions so that a reliable assignment is not possible. The number of absorptions observed, however, strongly suggests a symmetric structure which is in analogy to **2a**$^{4-}$/4Li$^+$ and contrasts to **2b**$^{2-}$/2K$^+$.

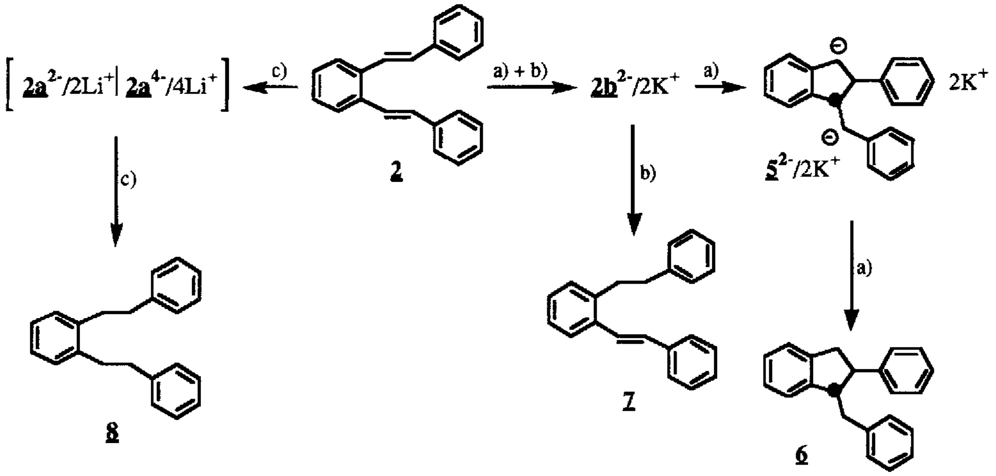
Reduction of **2** with potassium produces only a dianion salt. The number and shifts of the ^{13}C-NMR signals provide convincing evidence for an unsymmetric species **2b**$^{2-}$/2K$^+$ in which the excess charge is essentially located on one stilbene unit and the uncharged styryl moiety is strongly twisted with respect to the molecular plane [7]. At temperatures above -60°C the dianion **2b**$^{2-}$/2K$^+$ is converted into follow-up products (see below), while the lithium salts **2a**$^{2-}$/2Li$^+$ and **2a**$^{4-}$/4Li$^+$ are stable even at 0°C.

The reactivity of anionic species derived from **2** can also be demonstrated by cyclovoltammetric measurements (dimethylformamide, tetrabutylammonium hexafluorophosphate, 0°C, v = 100 mV/s), although a direct comparison with the chemical reduction is impossible in view of the different ion pairing: while **2** can be charged reversibly under formation of the radical monoanion at a potential of -2.19V (vs. Ag/AgCl), the transfer of a second electron at E° = -2.43V is clearly irreversible and produces a follow-up product with slightly higher reoxidation potential.

The reduction of 1,2-distyrylbenzene (**2**) with potassium (2.2 equiv.) in THF/NH$_3$ 1:1 (-80°C —> -20°C) on a preparative scale yields 78% of the indane derivative **6**. Surprisingly enough, performing the same experiment in boiling ammonia at -33°C leads, after complete protonation of the anionic precursors by the solvent, to 78% of 2-(β-phenylethyl)stilbene (**7**); additionally, 22% of **2** are recovered.

With lithium as reducing agent and liquid ammonia/THF as solvent a quantitative transformation of the substrate into 1,2-bis(β-phenylethyl)benzene (**8**) is observed [8].

Reduction of **2** with lithium (-25°C; heterogeneous ET) or dilithiostilbenediide (2 equiv.; -25°C; homogeneous ET, one electron is transferred from each stilbene molecule) under aprotic conditions (THF) provides mixtures of **2**, **7** and **8**. Their composition depends on the quenching conditions (reoxidation of the anions formed with CdCl$_2$ resp. iodine or protonation with MeOH) and the number of charge equivalents transferred; the formation of **6**, however, is never observed [9].



a) 2.2 equiv. potassium, THF/NH$_3$, -80°C/-20°C; b) 2.2 equiv. potassium, THF/NH$_3$, -33°C;
c) 2 equiv. lithium, THF/NH$_3$, -33°C

The sensitive dependence of the product distribution on the reaction conditions can be readily explained by the geometry of the ion-pair structures **2a**$^{2-}$/2Li$^+$, **2a**$^{4-}$/4Li$^+$ and **2b**$^{2-}$/2K$^+$: the non-planar geometry of **2b**$^{2-}$/2K$^+$ and the high rotational mobility of the uncharged styryl moiety at temperatures above -50°C allow for an effective interaction between the neighbouring olefinic centers under formation of an anionic rearrangement product which is then protonated to the thermodynamically most stable indane derivative **6**. If the reduction is performed at higher temperatures (-33°C), the slower rearrangement can no longer compete with the rapid protonation of the primarily formed substrate anions by the ammonia. Due to geometric and electrostatic reasons the symmetric, nearly planar anions **2a**$^{2-}$/2Li$^+$ and **2a**$^{4-}$/4Li$^+$, resulting from the reduction with lithium or dilithiostilbenediide, do not undergo any intramolecular valence isomerizations and, instead, are protonated to **7** and **8**, respectively, or reoxidized to **2**.

The intramolecular formation of **6** upon electron transfer to 1,2-distyrylbenzene (**2**) differs significantly from the photolytic transformation of **2** in solution, which provides a complex dimeric structure containing two cyclobutane moieties.

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[4] The ^{13}C-NMR spectra were recorded for the tert.-butyl substituted reference compound **3** which exhibits a higher solubility than **2**. The reductive behavior of **2** and **3**, however, is completely analogous.

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[7] **2b**$^{2-}$/2K^{+}: ^{1}H-NMR (200 MHz, THF-d_8, -60°C): δ = 6.52 (m, 5H), 6.21 (m, 2H), 6.03 (m, 3H), 5.82 (bs, 2H), 5.66 (d, J = 12.0 Hz, 1H, olef.), 5.29 (m, 3H), 4.83 (t, J = 6.0 Hz, 1H), 4.54 (d, J = 12.0 Hz, 1H, olef.); ^{13}C-NMR (50 MHz, THF-d_8, -70°C): δ = 150.2, 147.3, 144.0, 134.8, 132.6, 128.0, 125.2, 121.7, 121.5, 121.3, 120.9, 116.8, 115.0, 113.8, 111.9, 109.1, 95.8, 88.3.

[8] Some spectroscopic data: **6**: ^{1}H-NMR (200 MHz, CDCl$_3$, rt): δ = 7.70-7.00 (m, 14H, arom.), 3.74 (m, 1H), 3.38 (m, 2H), 3.06 (m, 3H); ^{13}C-NMR (50 MHz, CDCl$_3$, rt): δ = 145.9, 145.5, 142.7, 140.3, 129.4 (2x), 128.5 (2x), 128.3 (2x), 127.4 (2x), 126.9, 126.5, 126.2, 126.1, 124.4 (2x), 54.0, 51.4, 40.8, 40.5. **7**: ^{1}H-NMR (200 MHz, CDCl$_3$, rt): δ = 7.65-7.10 (m, 15H, arom. + olef.), 7.01 (d, J = 16 Hz, part of an AB-type spin system, 1H, olef.), 3.07+2.94 (AA'BB'- spin system, 4H); ^{13}C-NMR (50 MHz, CDCl$_3$, rt): δ = 142.3, 140.1, 138.3, 136.7, 131.0, 130.2, 129.3 (2x), 129.0 (4x), 128.3, 128.2 (2x), 127.1 (2x), 126.8, 126.6, 126.4, 38.1, 36.1; mass (EI, 70eV): m/z = 284 (M^{+}, 39%), 193 (M - benzyl, 100%), 178 ($C_{14}H_{10}$, 30%), 115 (C_9H_9, 75%), 91 (benzyl, 28%). **8**: ^{1}H-NMR (200 MHz, CDCl$_3$, rt): δ = 7.40-7.15 (m, 14H, arom.), 2.94 (bs, 8H); ^{13}C-NMR (50 MHz, CDCl$_3$, rt): δ = 141.9, 139.5, 129.3, 128.4 (4x), 126.3, 126.0, 37.3, 34.8.

[9] Under aprotic conditions the formation of the head-to-head cycloadduct 2,3-diphenyl-1,4-dihydronaphthalene (1-3%) and the corresponding head-to-tail cycloadduct 1-benzyl-2-phenyl-3H-indene (3-6%) is observed; ESR-spectroscopic results indicate that these rearrangement reactions proceed via the radical monoanion of **2**.

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