Two-electron Reduction of 1,1,4,4-Tetraphenylbutadiene by Sodium or Potassium to But-2-ene-1,4-diyl Salts of Different Stucture†

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The reduction of 1,1,4,4-tetraphenylbutadiene in ether solution at sodium or potassium metal mirrors proceeds *via* C=C double bond shifts and yields either a monomeric contact ion triple unit {tetraphenylbutadiene^{2-}-[Na$^+$(dimethoxyethane)$_2$]$_2$}$_1$, or a polymeric contact ion aggregate, [tetraphenylbutadiene^{2-}-(K$^+$ diethyl ether)$_2$]$_\infty$.

The interest in multiple reductions of unsaturated hydrocarbon molecules R is shifting more and more from the structural changes in the polyanions R^{n-} generated[1-4] to the dependence of the crystallizing contact ion agregates {R^{n-}[Me$^+$(Solv)$_x$]$_n$}$_z$ on the size of the counter cation Me$^+$ and its x-fold solvation. For example, reactions of 1,1-diphenylethylene in diethyl ether solution with lithium or sodium yield novel butane-1,4-diyl salts,[1] which are produced *via* CC bond formation and, therefore, are intermediates of a 1,1,4,4-tetraphenylbutane synthesis. Despite the comparability of reaction conditions, however, their structures are different (Scheme 1) for lithium and sodium.

We have now investigated the reductions with sodium and potassium of 1,1,4,4-tetraphenylbutadiene, which contains two fewer hydrogen atoms and the structure of which (Fig. 1, A) shows two C=C bonds each 136 pm long as well as a rather short central C–C bond of 144 pm length.[5] The products, with dimethoxyethane as solvent for the sodium reaction and diethyl ether for potassium, again exhibit two different types of crystal structure (Fig. 1, B, C).‡§

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† For Part 9 of the Series Structures of Charge-perturbed or Sterically Overcrowded Molecules, see ref. 1.

‡ *Disodium salt. Preparation*: A sodium metal mirror was generated by vacuum distillation of Na (150 mg, 6.5 mmol) into a carefully dried Schlenk trap. Under argon, absolute 1,2-dimethoxyethane (DME) (10 ml) and 1,1,4,4-tetraphenylbuta-1,3-diene (300 mg, 0.8 mmol) were added. After 3 days all the sodium had vanished and from the resulting violet-blue solution, after addition of a layer of a n-hexane nearly black air- and moisture-sensitive crystals grew.

Crystal data: [(C$_6$H$_5$)$_2$C–CH=CH–C(C$_6$H$_5$)$_2$]$^{2-}$·2Na$^+$·4 DME, a = 999.8(6), b = 1043.5(9), c = 1143.1(9) pm, α = 79.80(3), β = 71.37(2), γ = 67.50(3)°, V = 1041.9 × 10^6 pm^3, T = 90 K, Z = 1, D$_c$ = 1.22 g cm^{-3}, μ(Mo-Kα) = 0.9 cm^{-1}, triclinic, space group P1, Siemens AED II four-circle diffractometer, 4581 measured reflexions within 3 < 2θ < 53°, of which 3184 are independent with I > 2.0σ(I), structure solution by direct methods (SHELXTL-PLUS), N$_R$ = 3184, N$_P$ = 369, R = 0.033, R$_W$ = 0.033, w = 1/σ^2(F) + 0.00015F^2. C, O, Na atoms anisotropically, H atoms isotropically refined. The molecule is located about a crystallographic inversion centre.

§ *Dipotassium salt. Preparation*: Analogous to the preparation of the disodium salt, a sodium–potassium alloy from K (250 mg, 6.3 mmol) and Na (83 mg, 3.6 mmol) was treated with 1,1,4,4-tetraphenylbutadiene (300 mg) in diethyl ether (15 ml). After 1 h the solution turned violet and after 48 h under intense shaking black, air- and moisture-sensitive cyrstals had grown.

Crystal data structure: [(C$_6$H$_5$)$_2$C–CH=CH–C(C$_6$H$_5$)$_2$]$^{2-}$2K$^+$·2 Et$_2$O, a = 797.5(6), b = 964.8(6), c = 1106.6(8) pm, α = 87.68(5), β = 82.91(6), γ = 74.85(6)°, V = 815.6 × 10^6 pm^3, T = 200 K, Z = 1, D$_c$ = 1.19 g cm^{-3}, μ(Mo-Kα) = 2.91 cm^{-1}, triclinic, space group P1, Siemens AED II four-circle diffractometer, 3105 measured reflexions within 3° < 2θ < 50°, of which are 1984 independent with I > 1.5σ(I), structure solution by direct methods (SHELXS-86, SHELXL 76), N$_R$ = 1984, N$_P$ = 266, R = 0.048, R$_W$ = 0.037, w = 1.3380/σ^2(F) + 0.000172F^2. C, O, K atoms anisotropically, H atoms isotropically refined. The molecule is located about a crystallographic inversion centre.

For this and the disodium salt, atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

Reaction of 1,1,4,4-tetraphenylbutadiene with sodium yields dark-blue to black rhomboids of a monomeric contact ion triple unit,‡ in which two bis-dimethyoxyethane-solvated Na$^{δ+}$ (DME)$_2$ counter cations are η^3-coordinated to both
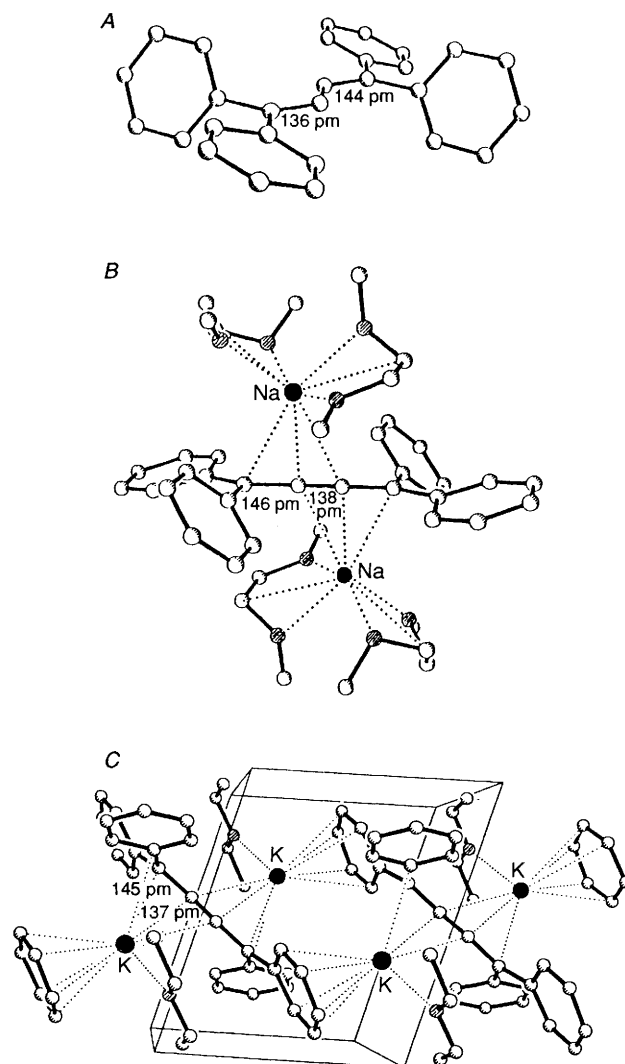

Fig. 1 Single crystal structures of (A) 1,1,4,4-tetraphenylbutadiene, and (B) its disodium and (C) its dipotassium salts. Important distances and angles. (A) Hydrocarbon[5] (distances ± 1 pm; angles ± 0.5°): C$_4$ chain (C=C 135.9, C–C 144.4, pm; ∠CCC 125.3°), diphenylmethyl groups [C–C$_{Ph}$ 149 pm; ∠C$_{Ph}$CC$_{Ph}$ 117.8, ω(CC–C$_6$H$_5$) 18 and 70°] phenyl rings (CC 135.2–139.0 pm; CCC$_{ipso}$ 117.8°). (B) Disodium salt (distances ± 0.3 pm; angles ± 0.2°): C$_4$ chain (C–C 145.7, C=C 137.7 pm; ∠CCC 129.0°), diphenylmethyl groups [C–C$_{Ph}$ 144.4 and 148.0 pm; ∠C$_{Ph}$CC$_{Ph}$ 120.6° ω(CC–C$_6$H$_5$) 23.4 and 51.2°], phenyl rings (CC 138.5–143.5 pm; ∠CCC$_{ipso}$ 114.0 and 115.8°), contact distances (Na···O 232.0–243.4, Na···C$_{chain}$ 264.9–274.8, Na···phenyl >350 pm). (C) Dipotassium salt (distances ± 0.6 pm; angles ± 0.4°): C$_4$ chain (C–C 144.6, C=C 136.8 pm; ∠CCC 130.9), diphenylmethyl groups [C–C$_{Ph}$ 143.4 and 146.4 pm; ∠C$_{Ph}$CC$_{Ph}$ 120.7°, ω(CC–C$_6$H$_5$) 20.1 and 35.5°], phenyl rings (CC 137.5–143.0 pm; ∠CCC$_{ipso}$ 113.8 and 115.6°), contact distances (K···O 271.8, K···C$_{chain}$ 298.4–303.7, K···phenyl intramolecular 312.2, intermolecular 302.4–307.5 pm).
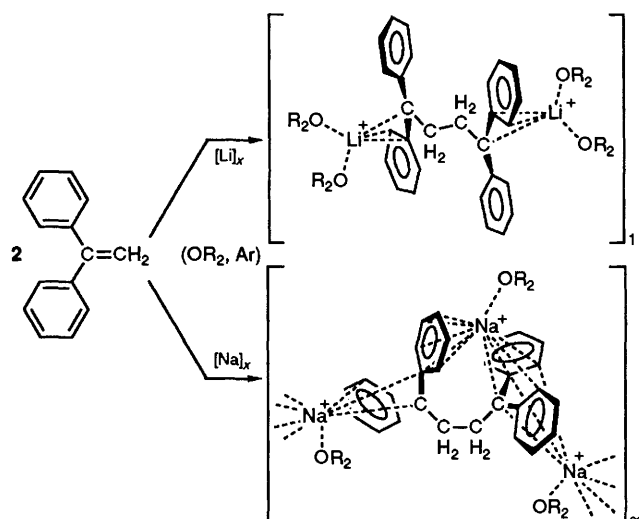
Scheme 1 Reaction of 1,1-diphenylethylene with lithium and sodium in diethyl ether under argon to give contact ion aggregates of the tetraphenylbutane-1,4-diyl dianion exhibiting different structures[1]

sides of the central $-C-HC=CH-C^-$ chain (Fig. 1, B). The formation of 1- and 4-carbanion centres leads to a central C=C bond and two terminal C–C bonds; the hydrocarbon skeleton initially contained two terminal bonds 136 pm long and one central bond 144 pm long, whereas the product has two terminal 146 pm bonds and a central bond 138 pm long. A but-2-ene-1,4-diyl dianion is also formed on reduction with potassium in diethyl ether, with comparable bond lengths (2 of 145 pm; 1 of 137 pm) (Fig. 1, C).§ The black rhomboids with a metallic lustre obtained in the potassium reduction show a different structure from that obtained with sodium, a polymeric chain being energetically favoured with a diagonal arrangement of tetraphenylbutadiene dianions doubly bridged by mono-Et_2O-solvated $K^{\delta+}(OR_2)$ counter cations each η^4-coordinated to the phenylbutene chain and η^3-coordinated to an opposite phenyl ring. Additional comparison should be made with the dilithium salt of 1,4-diphenyl-cis-but-2-ene containing $Li^{\delta+}$(tetramethylethanediamine) counter cations but also showing a C_4 chain with alternating CC bonds of 150, 142 and 150 pm length.[2,6]

The insertion of two electrons perturbs the molecular skeleton of 1,1,4,4-tetraphenylbutadiene (Fig. 1, A) extensively. In addition to the shift of the C=C bonds within the central C_4 chain there also occurs a straightening of the chain ($\angle$ CCC 4 and 6°), a twisting of its CC_2 forks ($\Delta\omega$C=C–CC_2 10 and 11°), a shortening of the C–C_{Ph} distances (149 to 143 pm), a change in the phenyl twisting from 19 and 71° (Fig. 1, A) to 14 an 51° (Fig. 1, B) or to 28 and 47° (Fig. 1, C), and a contraction of the phenyl ipso angles from 118 to 116 and 114°, respectively. All these changes can be traced predominantly to the generation of the carbanionic centres at the ends of the C_4 chain and to a lesser extent to the contacts between the counter cation and the carbon centres.

The influences due to the different size of the counter cations and their differing solvation are reflected in results of MNDO calculations¶ for the stuctures determined. For the

sodium ion triple unit, the enthalpies of formation calculated for the structures with either no or fourfold DME solvation differ considerably, $\Delta\Delta H_f^{MNDO} = 1850$ kJ mol^{-1}, whereas for the weaker solvation of the $K^{\delta+}$ centres by each single diethyl ether only $\Delta\Delta H_f^{MNDO} = 350$ kJ mol^{-1} is predicted. Furthermore, for each of the $Na^{\delta+}$ centres in the disodium salt a partial charge of only +0.28 results, and +0.47 should be transferred into the two solvating dimethoxyethane ligands. In contrast and despite the rather even distribution of the negative charge over the hydrocarbon skeleton, the positive partial charges at the $K^{\delta+}$ centres are predicted to increase to +0.63 at each centre, while the partial changes at the ether oxygens drop to +0.14.

Summarizing, the structural changes in both tetraphenylbutane-1,4-diyl and tetraphenylbut-2-ene-1,4-diyl-salts (Scheme 1 and Fig. 1, B and C) both reflect the same effect: the smaller and more strongly soviated counter cation forms a monomeric contact ion triple unit in each case, whereas the larger and weaker solvated cation prefers a polymeric chain of contact ion aggregates, in which its coordination number is increased by additional contacts to the phenyl rings. Further structure determinations‖ are needed to substantiate whether and to what extent this structural concept can be generalized, and whether it can contribute to the solution of the presently intensively reinvestigated question: 'What compound crystallizes; how and why?'[7]

References

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¶ MNDO calculations were based on the crystallographic data without further geometry optimization. The Na parameters are reported in ref. 4; the optimized K parameters used are: $U_{ss} = -4.0934$ eV; $U_{pp} = 2.0075$; $\zeta_s = 0.7653$ a.u.; $\zeta_p = 0.9568$ a.u.; $\beta_s = -0.9405$ eV; $\beta_p = -0.9320$ eV; $\alpha = 1.2737$ Å^{-1}; $g_{ss} = 7.1030$ a.u.; $g_{sp} = 4.9411$ a.u.; $g_{pp} = 5.8638$ a.u.; $g_{pp}' = 3.9468$ a.u.; $h_{sp} = 0.4557$ a.u. (Z. Havlas, S. Nick and H. Bock, J. Int. Quantum Chem., in the press).

‖ Consistently, the reduction of perylene (R) with sodium or potassium yields the monomeric $[R^{2-}(Na^+DME_2)_2]_1$ and the polymeric $[R^{2-}(K^+DME)_2]_\infty$ dianion salts (H. Bock and C. Näther, Angew. Chem., in the press).