Generation of the 1,4-Diphenylcyclohexane-1,4-diyl Radical Cation by $\mathrm{Ce^{IV}}$-catalysed Denitrogenation of the Azoalkane 1,4-Diphenyl-2,3-diazabicyclo[2.2.2]oct-2-ene and its Reluctance to undergo Cope Rearrangement

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It is experimentally confirmed that the radical cation of 1,4-diphenylcyclohexane-1,4-diyl does not isomerize thermally to the radical cation of 2,5-diphenylhexa-1,5-diene, but is instead quantitatively dehydrogenated to *p*-terphenyl.

Recent theoretical interpretation of the reactivity of organic radical cations has allowed rationalization of previous experimental findings.[1] At the same time predictions have been made about the chemical behaviour of these reactive species, whose validity remains to be tested experimentally. Thus, MINDO/3 calculations show that thermal C(3)–C(4) bond cleavage in the cyclohexane-1,4-diyl radical cation is endothermic by 34 kcal $\mathrm{mol^{-1}}$ (1 cal = 4.184 J), making ring opening *via* a Cope-type process to give the radical cation of hexa-1,5-diene unlikely. In sharp contrast, the analogous 1,4-diradical, which can be generated by photochemical and thermal denitrogenation of the azo precursor, produces the open-chain 1,5-diene quantitatively.[2]

This led us to study the cerium(IV) ammonium nitrate-mediated oxidation[3] of 1,4-diphenyl-2,3-diazabicyclo[2.2.2]-oct-2-ene (**1**),[2] which was expected to afford the radical cation (**4**) *via* initial single electron transfer (SET) leading to the azoalkane radical cation and subsequent denitrogenation (Scheme 1).[4] The reaction was carried out in refluxing chloroform, using tetra-n-butylammonium hydrogen sulphate as the phase transfer catalyst.[5] Under these conditions, the loss of nitrogen was complete within 4 h. In the chromatographic work-up, *p*-terphenyl (**7**) was isolated in 46% yield, but undefined higher-molecular-weight products were also observed. This result can be rationalized by successive deprotonation–oxidation steps, as shown in Scheme 1. In fact, by monitoring the reaction with t.l.c., the intermediate 1,4-diphenylcyclohexa-1,3-diene (**6**)[6] could be detected in the complex sequence leading from the azo compound (**1**) to *p*-terphenyl. Furthermore, an independent oxidation of the diene (**6**) with cerium(IV) resulted in *p*-terphenyl quantitatively. Interestingly, the photocatalytic oxidation of 1-phenylcyclohexa-1,3-diene with $\mathrm{TiO_2}$ afforded the biphenyl in 65% yield *via* aromatization of the intermediate diene cation radical.[7]

In view of the reluctance of the diphenyl-substituted cyclohexane-1,4-diyl radical cation (**4**) to undergo ring opening, the cerium(IV) oxidation of 2,5-diphenylhexa-1,5-diene (**3**)[8] was carried out, to investigate whether its open-chain radical cation (**5**) undergoes cyclization to its cyclic valence isomer, the radical cation (**4**). When the reaction was carried out at 35 °C, besides large amounts of undefined higher-weight material, the isomeric dienes (**8**) (*ca.* 16% yield)† and (**9**) (*ca.* 14% yield)[8b] were isolated, but no *p*-terphenyl could be detected by ^{1}H n.m.r. spectroscopy. Thus, 1,3-sigmatropic shifts dominate over ring closure.[1d] However, when the temperature was raised to *ca.* 70 °C, an appreciable amount (*ca.* 15%) of *p*-terphenyl was isolated, with the diene (**8**) (*ca.* 5%). Unfortunately, polymerization was more prominent at higher temperatures.

In summary, the theoretically predicted[1c] reluctance of the cyclohexane-1,4-diyl radical cation to undergo retrocyclization was experimentally verified for the 1,4-diphenyl-substi-

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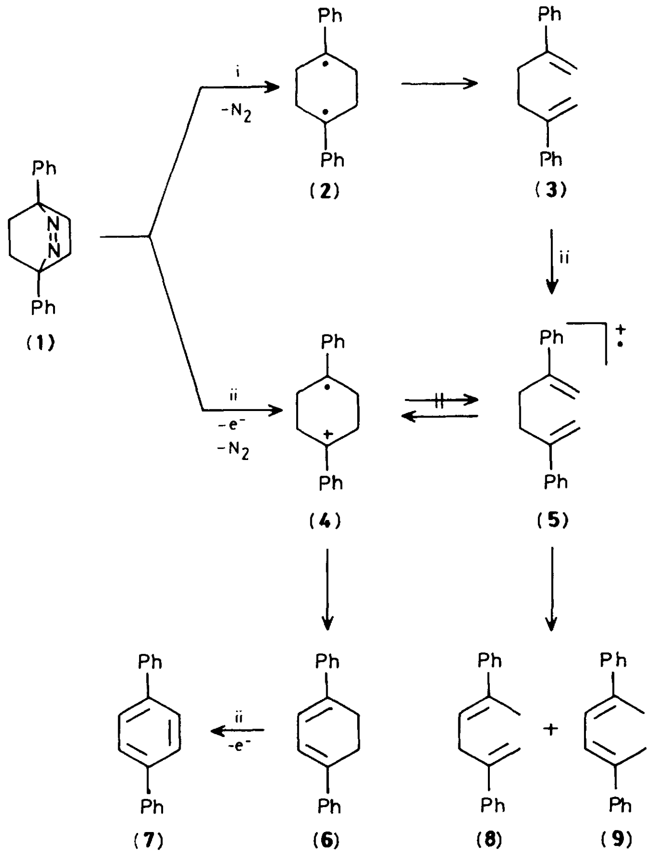
† *Spectral data* for (**8**): ^{1}H n.m.r. (200 MHz, $\mathrm{CDCl_3}$) δ 7.54—7.20 (m, 10H, ArH), 5.88 (tq, J_1 7.1, J_2 1.4 Hz, 1H, $\mathrm{CH_2}$–C*H*=), 5.39 and 5.14 (m, 2H, $=\mathrm{CH_2}$), 3.39 (dt, J_1 7.1, J_2 0.8 Hz, 2H, $\mathrm{CH_2}$), 2.09 (br. s, 3H, $\mathrm{CH_3}$).



Scheme 1. *Reagents:* i, *hν* or heat; ii, $Ce(NH_4)_2(NO_3)_6$, $Bu^n{}_4 NHSO_4$, $CHCl_3$.

tuted derivative (**4**). However, while at lower temperatures (*ca.* 35 °C) the open-chain radical cation (**5**) preferentially undergoes 1,3-sigmatropic shifts, at elevated temperatures (*ca.* 70 °C) appreciable cyclization to *p*-terphenyl, presumably *via* radical cation (**4**), is observed.

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