Generation of the 1,4-Diphenylcyclohexane-1,4-diyl Radical Cation by 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

Waldemar Adam,*[a] Sven Grabowski,[a] Miguel A. Miranda,[b] and Martin Rübenacker[a]

[a] *Institute of Organic Chemistry, University of Würzburg, Am Hubland, D-8700 Würzburg, West Germany*
[b] *Department of Organic Chemistry, Faculty of Pharmacy, University of Valencia, E-46010 Valencia, Spain*

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 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]

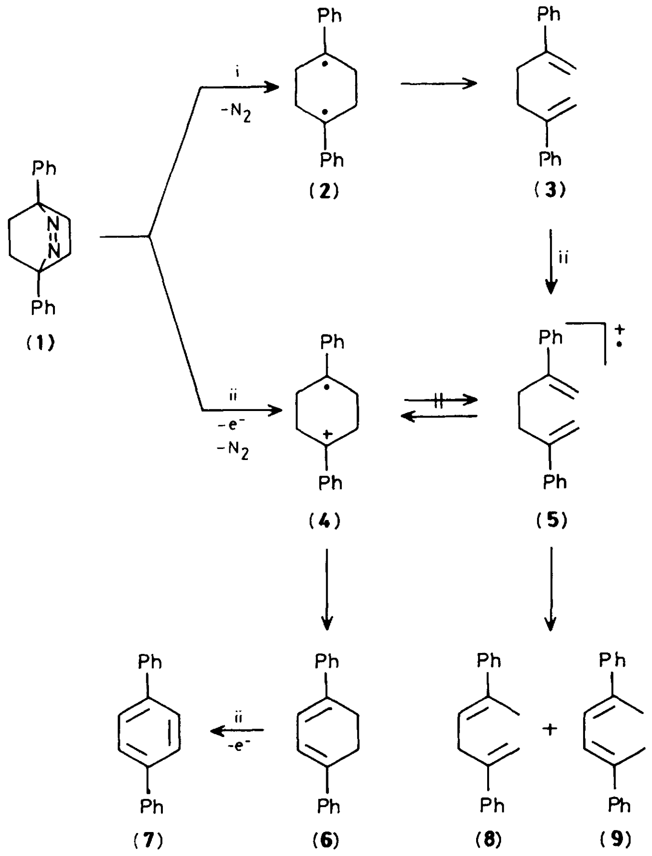
This led us to study the cerium(IV) ammonium nitrate-mediated oxidation[3] of 1,4-diphenyl-2,3-diazabicyclo[2.2.2]-oct-2-ene (**1**),[2] which was expected to afford the radical cation (**4**) *via* initial single electron transfer (SET) leading to the azoalkane radical cation and subsequent denitrogenation (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 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-

---

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



Scheme 1. *Reagents:* i, *h*ν or heat; ii, $Ce(NH_4)_2(NO_3)_6$, $Bu^n{}_4NHSO_4$, $CHCl_3$.

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.

Financial support by the Deutsche Forschungsgemeinschaft, the A.v. Humboldt Foundation, and the Fonds der Chemischen Industrie is gratefully acknowledged. S. G. is a Kekulé Doctoral Fellow (1985—1987), M. A. M., an A. v. Humboldt Postdoctorial Fellow (1986—1987) on leave of absence from the University of Valencia, and M. R., an Undergraduate Research Participant (Spring, 1987).

Received, 10th August 1987; Com. 1172

References

1 (a) E. Haselbach, T. Bally, and Z. Lanyiova, *Helv. Chim. Acta*, 1979, **62**, 577; (b) E. Haselbach, T. Bally, Z. Lanyiova, and P. Baertschi, *ibid.*, 583; (c) N. L. Bauld, D. J. Bellville, R. Pabon, R. Chelsky, and G. Green, *J. Am. Chem. Soc.*, 1983, **105**, 2378; (d) I. R. Dunkin and L. Andrews, *Tetrahedron*, 1985, **41**, 145.

2 P. S. Engel, C. J. Nalepa, D. W. Horsey, D. E. Keys, and R. T. Grow, *J. Am. Chem. Soc.*, 1983, **105**, 7102; P. S. Engel, D. W. Horsey, D. E. Keys, C. J. Nalepa, and L. R. Soltero, *ibid.*, 7108.

3 For related electron-transfer oxidation of azo compounds using Ce^{IV}, see: J. Martelli and R. Grée, *J. Chem. Soc., Chem. Commun.*, 1980, 355; W. Adam, A. Casado, and M. A. Miranda, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 797.

4 For related denitrogenations of radical cations derived from zero compounds, see: D. H. Bae, P. S. Engel, A. K. M. Mansurul Hoque, D. E. Keys, W. K. Lee, R. W. Shaw, and H. J. Shine, *J. Am. Chem. Soc.*, 1985, **107**, 2561; P. S. Engel, D. E. Keys, and A. Kitamura, *ibid.*, 4964; A. K. M. Mansurul Hoque, A. C. Kovelesky, W. K. Lee, and H. J. Shine, *Tetrahedron Lett.*, 1985, 5655; H. J. Shine, D. H. Bae, A. K. M. Mansurul Hoque, A. Kojstura, W. K. Lee, and R. W. Shaw, *Phosphorus Sulfur*, 1985, **23**, 111; W. Adam and M. Dörr, *J. Am. Chem. Soc.*, 1987, **109**, 1570; S. C. Blackstock and J. K. Kochi, *ibid.*, 2484.

5 E. V. Dehmlov and J. K. Makrandi, *J. Chem. Res.* (*S*), 1986, 32.

6 P. Courtot and O. Le Goff-Hays, *Bull. Soc. Chim. Fr.*, 1968, 3401.

7 M. A. Fox, D. D. Sackett, and J. N. Younathan, *Tetrahedron*, 1987, **43**, 1643.

8 (a) C. S. Marvel and E. J. Gall, *J. Org. Chem.*, 1960, **25**, 1784; (b) R. Engels, H. J. Schäfer, and E. Steckhan, *Liebigs Ann. Chem.*, 1977, 204.