Tetrahedron Letters,Vol.26,No.10,pp 1265-1268,1985 0040-4039/85 $3.00 + .00
Printed in Great Britain

ELECTRO-OXIDATION OF PHENYLINDENES.

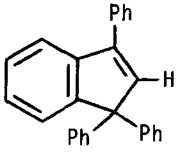
REACTION DEPENDENCE ON THE ELECTROLYTE ANION IN NON-NUCLEOPHILIC SOLVENTS

John J. McCullough* and Shahin Yeroushalmi
Chemistry Department, McMaster University
Hamilton, Ontario, Canada L8S 4M1

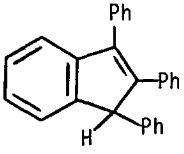
Summary: Cyclic voltammetry studies have shown that in the electro-oxidation of phenylindenes, the reaction pathway can be markedly dependent on the salt used as electrolyte, particularly when the substrate (indene) contains a relatively acidic hydrogen.

Reactions of radical cations, formed from neutral molecules by photochemical[1] or electrochemical[2] electron transfer, or by reaction with ground state oxidizing agents[1a,3], are being widely studied by a variety of methods. The unimolecular reactions of radical cations, such as the 2+2 retroaddition of cage compounds, usually involve strained systems, and have received particular attention.[1b-f]

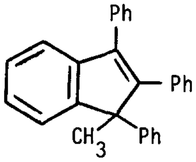
The rearrangement of 1,1,3-triphenylindene (1) on anodic oxidation in SO_2-methanol[2d] giving 1-methoxy-1,2,3-triphenylindene interested us as a means of studying radical cations produced in various ways. In the course of studying this reaction, we have investigated the anodic oxidation of 1,2,3-triphenylindene[4] (2) and 1-methyl-1,2,3-triphenylindene[4] (3), in CH_2Cl_2 and CH_2ClCH_2Cl, using different electrolyte salts.[5] By using cyclic voltammetry (CV), we have found that the lifetimes and reaction pathways of the radical cations of (2) and (3) depend on the electrolyte anion. This effect is particularly marked in the case of (2).



(1)



(2)



(3)

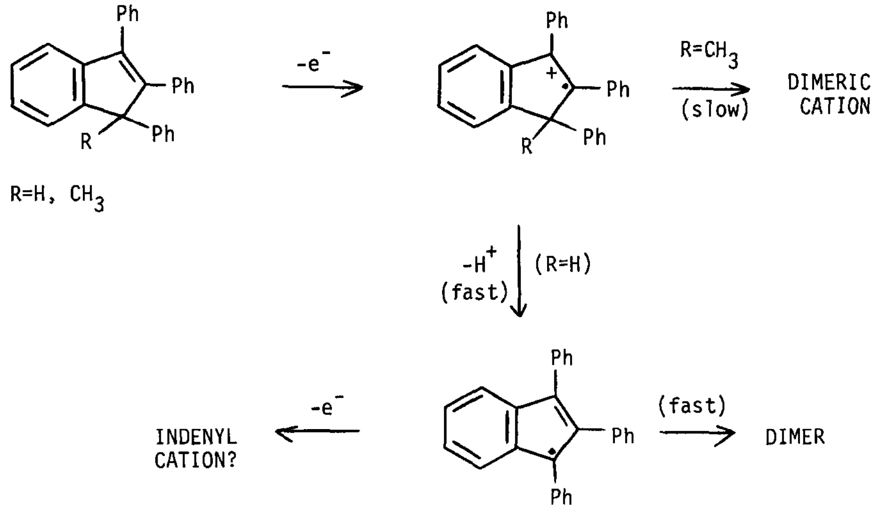
Cyclic voltammetric scans[6] of 1,2,3-triphenylindene (2) and the methyl derivative (3) under various conditions, are shown in the Figure. On scanning to positive potential[7], an oxidative wave is observed in the range E_{pa} = + 1.50 – + 1.70 V, in each case. However, a corresponding reductive wave (E_{pc} = + 1.30 – + 1.40 V) is only observed if (i) the acidic proton of (2) is replaced by a methyl group (scans B,D) or (ii) the electrolyte anion is PF_6^- (scan E). We have not observed the radical cation of (2) in the presence of perchlorate, triflate or nitrate, at scan rates up to 500 mV/sec. We propose that the first step in reaction of the radical cation of (2) in these solvents is proton loss to the electrolyte anion, and this is rapid, even with the weakly basic perchlorate or triflate anions. Thus, the difference in basicity between hexafluorophosphate and perchlorate is sufficient to affect the reaction pathway.

Controlled potential electrolysis of (2) or (3) (+ 1.65 V) in 1,2-dichloroethane with $TBClO_4$ as electrolyte afforded mixtures of dimers[8] in ∿ 70% yield. These are probably biaryl derivatives[9], but further work remains to be done on their structures.

Finally, the partially reversible waves at E_{pc} = + 0.20 V, E_{pa} = + 0.35 V, observed in most of the scans, deserve comment. These waves are particularly intense when the substrate has the hydrogen substituent (2), or when perchlorate or triflate salts are used, and are also observed on cyclic voltammetry of the electrolyzed[10] solution. This indicates that long-lived species are being observed and we suggest the latter are delocalized carbonium ions, for the following reasons.

The electrolyzed[10] solution of (2) is red, $\lambda_{max}^{CH_2ClCH_2Cl}$ = 450 nm; the red colour fades on addition of methanol, and the CV waves at + 0.2 — + 0.4 V shift to negative potential. For comparison, a solution containing 1,2,3-triphenylindenyl cation was prepared from 1-bromo-1,2,3-triphenylindene and silver perchlorate. This solution also was red λ_{max}^{PhH} = 435 nm, but on CV[10] showed irreversible reduction waves at -0.05 and -0.30 V. Thus, the species could be the indenyl cation (formed from (2) by loss of $2e^-$ and H^+) but may be a cation dimer, perhaps an intermediate in the dimerization. Interestingly, the mass spectrum of the mixture of products formed on electrolysis of (2) followed by quenching with methanol, showed a molecular ion of m/e = 717, corresponding to $(triphenylindenyl)_2$ + methoxyl. The proposed mechanism is summarized in the Scheme.

Scheme



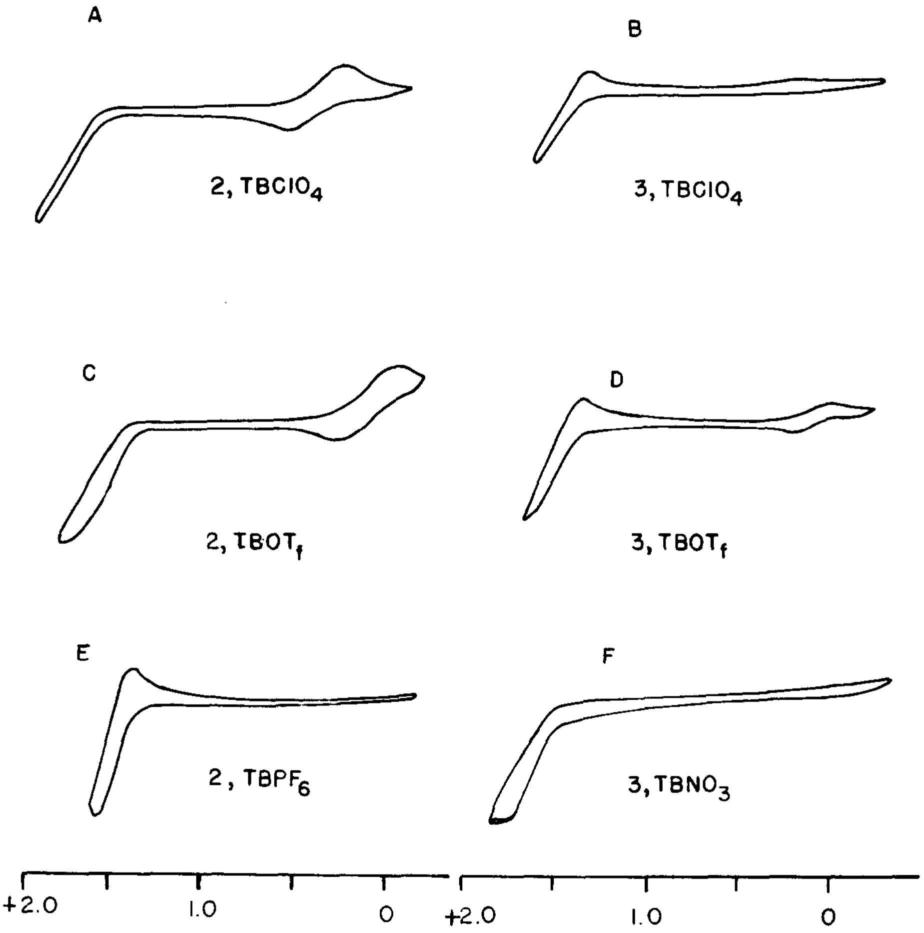


Figure. Cyclic voltammetric scans of 1,2,3-triphenylindene (2) and 1-methyl-1,2,3-triphenylindene (3), in 1,2-dichloroethane using different electrolyte salts. Voltage is shown on the horizontal axis, current on vertical axis, and oxidative waves are shown as negative peaks. Vertical bar represents 50 μA. Scan rates were 500 mV/sec.

In conclusion, we find that the anodic oxidation of phenylindenes is a complex process. Long-lived cations are formed, and the reaction pathway depends on the electrolyte anion, in the absence of other bases.

Acknowledgements One of the authors (J.J.McC) acknowledges support from the Chemistry Department, University of North Carolina, Chapel Hill, during a sabbatical leave in 1982-83, and helpful discussions with Dr. D.G. Whitten and his group. The work was also supported by the Natural Sciences and Engineering Research Council of Canada.

1. (a) A. Ledwith, *Accts. Chem. Res.*, 5, 133 (1972); (b) B.S. Solomon, C. Steel, and A. Weller, *Chem. Commun.*, 927 (1969); (c) K. Okada, K. Hisamitsu, T. Miyashi, and T. Mukai, *ibid.*, 974 (1982); (d) H.D. Roth and M.L. Manion Schilling, *J. Am. Chem. Soc.*, 103, 7410 (1981); (e) G. Jones, W.G. Becker, and S.-H. Chiang, *ibid.*, 105, 1269 (1983); (f) G. Jones and W.G. Becker, *ibid.*, 105, 1276 (1983).

2. (a) J.S. Swenton, *Accts. Chem. Res.*, 16, 74 (1983); (b) V.D. Parker, *ibid.*, 17, 243 (1984); (c) L.L. Miller, *Pure Appl. Chem.*, 51, 2125 (1979); (d) L.L. Miller and E.A. Mayeda, *J. Am. Chem. Soc.*, 92, 5818 (1970); (e) M.A. Fox and R. Akaba, *ibid.*, 105, 3460 (1983).

3. (a) N.J. Peacock and G.B. Schuster, *J. Am. Chem. Soc.*, 105, 3632 (1983); (b) R.W. Hoffmann and W. Barth, *J. Chem. Soc., Chem. Commun.*, 345 (1983).

4. (2), m.p. 130-132°, Lit., 134-136° (L.L. Miller and R.F. Boyer, *J. Am. Chem. Soc.*, 93, 650 (1971); (3), m.p. 97-99°, Lit., 96-98 (C.F. Koelsch and R.V. White, *J. Org. Chem.*, 6, 602 (1941)).

5. Salts used were tetrabutylammonium (TB) perchlorate, trifluoromethanesulfonate (triflate), hexafluorophosphate, and nitrate. These were obtained commercially or prepared by literature methods.

6. For cyclic voltammetry, a two-compartment cell was used. Solvents were carefully purified, distilled from CaH_2, and stored under nitrogen in a dry box. Samples were deoxygenated by bubbling with argon. The working electrode was platinum, and the reference was a standard calomel electrode. Electrolytes were approximately 0.1 M. Sweep rates were in the range 100-500 mV/sec.

7. At more positive potentials, the second oxidation waves of (2) and (3) are observed, but this work is only concerned with the first oxidation waves.

8. There are three dimers formed, only partially resolved on HPLC. These showed molecular ions at m/e = 686 (dimer from (2)) and at 714 (dimer from (3)).

9. L. Eberson, K. Nyberg, and H. Sternerup, *Acta. Chem. Scand.*, 27, 1679 (1973).

10. Solvent and electrolyte were 1,2-dichloroethane and $TBClO_4$, respectively.

(Received in USA 4 December 1984)