A New Class of Radical Cations: The Radical Cations of 1,4-Diphosphoniacyclohexa-2,5-diene Salts

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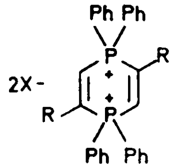
Summary Electrochemical reduction of a series of 1,4-diphosphoniacyclohexadiene salts has produced a new class of radical cations for which e.s.r. data are presented. The large phosphorus coupling constants and ring proton coupling constants strongly suggest that the odd electron is in a molecular orbital including all six ring atoms.

WE recently published preliminary results[1] on non-aqueous electrochemical studies of a series of 1,4-diphosphoniacyclohexa-2,5-diene salts.[2] Several of these salts showed reversible reduction characteristics on a polarographic time scale. We now report on our e.s.r. studies with these reduction products or radical cations. Many of these radical cations have lifetimes of the order of days at −40°.

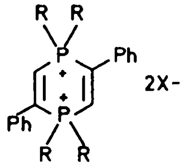
The observed hyperfine coupling constants for (I) and (II) are given in Table 1. The radical cations were generated *in situ* by controlled potential electrolysis, generally at −1·0 V, on a platinum wire cathode.†

Most of the spectra were characterized by a triplet of triplets. The phosphorus hyperfine coupling constants varied from 13·2—16·4G depending on substituents while the ring vinyl proton coupling constants were 2·80—4·8G.‡ Electron withdrawing or donating substituents on the phenyl groups in the 1,4 positions have little effect on spin densities. Inductive effects, however, are important.



(I)

a ; R = Me, X = Br^-
b ; R = Bu, X = Br^-
c ; R = Ph, X = Br^-



(II)

a ; R = Et, X = Cl^-
b ; R = p-OMe·C_6H_4, X = Br^-
c ; R = p-F·C_6H_4, X = Cl^-

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† The counter electrode was also a platinum wire with a plain silver wire as a reference electrode. The solvent was either dry DMF or acetonitrile with tetraethylammonium phosphate as electrolyte. The solutions were degassed in the electrolysis cell with dry nitrogen.

‡ The assignments are based on the magnitude of the two coupling constants and the assumption that the Q value for the vinyl protons is going to be reasonably close to 25G. If the larger coupling constant is assigned to the vinyl protons, a Q value of approximately 60G or larger would have to be invoked. Deuterium labelling is underway to make assignments unequivocal.

Replacement of the four phenyl with four ethyl groups produce a substantial lowering of the phosphorus coupling constant together with an increase of the vinyl proton coupling constant. Similar but opposite effects are observed when the phenyl groups in the 2,5-positions are replaced with alkyl groups.

The e.s.r. spectra of these compounds show that there is an unusually large temperature dependency of the phosphorus hyperfine coupling constants (hfcc) while at the same time the proton coupling constants remained constant within experimental error. Typical results for (Ib) are given in Table 2. The facts that the ions were generated electrochemically and that this effect was independent of the original counter ion rule out an ion-pairing explanation. The large change in phosphorus hfcc while the proton hfcc remained constant suggests there is no major change in spin densities throughout the temperature range. This suggests that the ions are undergoing some rapid conformational change with the equilibrium being temperature dependent. A likely explanation would be that the hybridization of the phosphorus atoms is changing with the change in conformation. It is known that large changes in phosphorus coupling constants can be observed with relatively small changes in hybridization of the phosphorus atom.[3] Considering the magnitude of the observed changes in this study, one would not have to postulate very large changes in geometry and hybridizations to account for this effect.

TABLE 1

Hyperfine splitting constants[a]

Compound	Line width[b]	g-Value[c]	a_H[d]	a_P[d]	a_{Me}[d]
(Ia)	1·00	2·0039	2·5	15·8	4·8
(Ib)	1·30	2·0043	2·8	16·0	—
(Ic)	2·00	2·0042	3·8	16·0	—
(IIa)	3·10	—	4·8	14·2	—
(IIb)	2·00	2·0043	3·8	16·4	—
(IIc)	1·95	2·0042	3·7	16·3	—

[a] In gauss, at −40°. [b] ±0·05 G. [c] ±0·0002 G. [d] ±0·1 G.

Crystallographic studies on the 1,1,4,4,2,5-hexaphenyl-1,4-diphosphoniacyclohexa-2,5-diene salt has shown that the molecule exists in a boat conformation.[4] On the other hand, the 1,1,4,4-tetraethyl-2,5-diphenyl-1,4-diphosphoniacyclohexa-2,5-diene salt was found to be planar.[5] Thus, it is not clear whether these radical ions are planar or not but it is likely that they are not very rigid. Therefore, rocking motion of the phosphorus atoms relative to the four ethylene carbon atoms seems likely.

TABLE 2.

Temperature effect on hyperfine coupling constants for (Ib)[2]

Temperature (°)	a_H	a_P[a]
−60	2·9	16·2
−20	2·8	15·7
0	2·8	15·5
+20	2·8	15·4

[a] ±0·1G; the large error is due to the large line width.

We thank the National Science Foundation and the National Institutes of Health for financial support.

(*Received*, 26*th June* 1972; *Com.* 1119.)

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