

## Electrochemical Reduction of 1,4-Diphosphoniacyclohexa-2,5-diene Salts without Accompanying Cleavage

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**Summary** Controlled potential electrochemical reduction of 1,4-diphosphoniacyclohexa-2,5-diene salts in aqueous ethanol provides good yields of 1,1,4,4-tetrasubstituted-1,4-diphosphoniacyclohexane dichlorides or dibromides without reductive cleavage of the ring or any external carbon-phosphorus bonds, including those of substituted benzyl groups.

THERE are a number of reports of electrolytic carbon-phosphorus bond cleavage, including phenyl,<sup>1</sup> simple alkyl,<sup>2</sup> and benzyl<sup>3-5</sup> groups. In the cathodic cleavage of an optically active phosphonium salt (Me, Ph, allyl, and benzyl groups), cleavage of the benzyl group only occurred, and the allylic double bond was not reduced under conditions sufficient for cleavage of the benzyl group.<sup>3</sup> In a

more extensive study,<sup>4</sup> cleavage of the benzyl group, usually in good yield, occurred whenever this group was present. Electrolytic reduction of a functional group within a benzyl substituted phosphonium salt without benzyl group cleavage has apparently not been reported. Chemical reduction also leads to cleavage; LiAlH<sub>4</sub><sup>6,7</sup> and Na-NH<sub>3</sub> have been reported to remove benzyl groups, in stepwise fashion, from phosphonium salts. Brophy and Gallagher reported that ethylene was formed from reduction of diphosphonium salts with an unsaturated bridge (P-C=C-P) by NaH.<sup>8</sup>

In the present study, compounds of type (II) were prepared from the precursor dienes (I) or monoene (III). No evidence of reductive cleavage of any of the carbon-phosphorus bonds was observed.

TABLE  
Cathodic reduction of diphosphonium salts<sup>a</sup>

Reactant <sup>b</sup>		Cathodic potential <sup>c</sup>	Initial current/ma	Solvent <sup>d</sup> (%MeOH)	Supporting electrolyte <sup>e</sup>	Time/h	Product	Yield (%)
Cation	Anion							
(Ia)	2Br <sup>-</sup>	-0.53	160	85	LiCl	1.5	(IIa)	80
(Ia)	2Br <sup>-</sup>	-0.51	130	80	LiBr	6.5	(IIa)	90
(Ib)	2Cl <sup>-</sup>	-0.64	160	80	LiCl	1.0	(IIb)	55
(III)	2Br <sup>-</sup>	-0.64	70	80	LiBr	2.5	(IIb)	64
(Ic)	2Cl <sup>-</sup>	-0.9	130	80	LiCl	3.0	(IIc)	98

<sup>a</sup> Under conditions of controlled potential, Hg-pool cathode, 25 °C. See also J. H. Stocker and R. M. Jenevein (*J. Org. Chem.*, 1968, **33**, 294) for details of the instrumentation and cell. <sup>b</sup> 0.4–2.5 g of salt used normally. <sup>c</sup> vs. Ag–AgCl electrode. <sup>d</sup> 60 ml, ca. 1.5M in AcOH. <sup>e</sup> 1M in all cases.

Experimental details are summarized in the Table. The compounds were synthesized as described elsewhere.<sup>9</sup> Rough tabulation of the coulombs used did not lead to

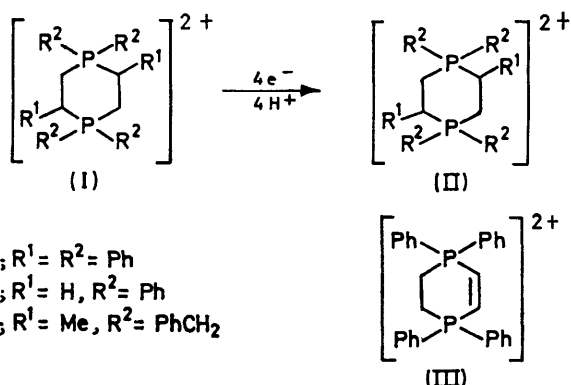
made to maximize the latter. Structure assignments of the products were based on microanalysis (as dipicrates), n.m.r. spectra, and, for (IIa) and (IIb), independent syntheses.<sup>9,10</sup>

If the reduction of the two carbon–carbon bonds proceeds stepwise, the difference in their reduction potentials must be so small as to be unobservable. No monoene products were isolated; monoene (III) was reduced at the same cathodic potential (–1.64 V) as the correspondingly substituted diene (Ib). The present study apparently involves lower voltages (chosen on the basis of preliminary polarographic studies), controlled potential techniques, and more protic media than in previous studies. Control of these parameters ensured that the reductions were carried out at minimum potentials and should suggest guidelines for other studies in which cleavage, notably of benzyl groups, is to be avoided.

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satisfactory *e/m* ratios; since the emphasis of the present study was on yields rather than efficiencies, no attempt was



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