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On the Redox Properties of Cyclotetraphosphanes. A Novel Dication Rearrangement

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Abstract: Electrochemical experiments on a selected variety of cyclotetraphosphanes were performed. In the first oxidation step a stable radical cation is formed. The ESR spectra of these radicals are recorded. Further oxidation yields for the amino-substituted cases dications that rapidly rearrange to diaminophosphenium cations and white phosphorus, as proven by bulk reaction of the cyclotetraphosphanes with $AlCl_3$ in CH_2Cl_2. The rapid rearrangements of the dications even occur under the condition of low-temperature cyclic voltammetry at −100 °C. Quantum-chemical calculations indicate a facile 1.2-shift at the four-membered-ring moiety with formation of carbene-like structures. Finally, fragmentation of the ring moiety (after dication formation) causes the formation of phosphenium cations and an intermediary P_2 unit. The latter dimerizes.

While dications of sulfur, selenium, and tellurium rings form stable, isolable entities,[1] corresponding dications of the cyclophosphanes are not known. Here we report on the electrochemical formation of the mono- and dication of the cyclotetraphosphanes, **1** (R = N(*i*-Pr)$_2$, N(SiMe$_3$)$_2$, *t*-Bu). The dications are isoelectronic with the stable S_4^{2+}, **2**,[1b] Se_4^{2+},[1c] and Te_4^{2+} [1d] systems.

It will be shown that the monocation of **1** is a stable radical at room temperature while the dication is easily formed in case of R = NR$_2$. It undergoes rapid 1,2-shift with subsequent decomposition into the diaminophosphenium cation,[2] **3**, and P_2. The latter dimerizes to white phosphorus. An insight into the mechanism of this new dication rearrangement process will be provided by quantum chemical calculations.

Results and Discussion

(a) Electrochemical Oxidation of Cyclotetraphosphanes. The electron rich character of **1** is already revealed by their photoelectron spectra. For **1** (R = N(*i*-Pr)$_2$) the first two ionization bands appear at 6.4 and 7.3 eV,[3] i.e., at relatively low energies. Compared to in **1**, R = N(SiMe$_3$)$_2$ and *t*-Bu ionization is less facile, i.e., at 7.5 eV.[3b]

The redox behavior of **1** in solution is established by a cyclic voltammogram, here shown for R = N(*i*-Pr)$_2$ (Figure 1).

Accordingly, the electrochemical oxidation occurs in two steps: (1) The first oxidation step is reversible. The peak potentials $E_{p,1}$ are not dependent on the sweep rate v (Figure 1b). The peak separation $E_{p,1a} - E_{p,1c}$ is 60 mV, $i_p v^{-1/2}$ is constant, and the current ratio $i_{p,a}/i_{p,c}$ is unity. All these criteria[4] indicate a reversible one-electron transfer reaction with the Nernst potenial $E_1° = 0.45$ V. The formed stable radical cation is intensely violet colored. (2) In the second oxidation step (Figure 1a) the radical cation is further oxidized to the dication. Low-temperature cyclic voltammetry shows that the oxidation remains irreversible even at a temperature of −100 °C. Accordingly a rapid reaction of the dication must follow the oxidation of $\mathbf{1a}^{\bullet +}$ to the dication. In order to reveal the nature of this reaction, the oxidation of **1a** was alternatively performed with $AlCl_3$ in CH_2Cl_2.[5] Reaction of both components[6] at −78 °C yields a stable solution of the radical cation. On warming it rearranges to the diaminophosphenium cation **3** (R = N(*i*-Pr)$_2$) and white phosphorus. The products were identified by ^{31}P NMR. Independent synthesis of **3** (R = N(*i*-Pr)$_2$) from bis(diisopropylamino)chlorophosphane and $AlCl_3$[7] confirmed the analysis of the products. Further evidence for the formation of the diaminophosphenium cation **3** (R = N(*i*-Pr)$_2$) from the cyclotetraphosphane system is obtained by the mass spectrum of the latter. The peak at mass 231, which is one of the most intense ones, corresponds to the mass of the cation **3** (R = N(*i*-Pr)$_2$).

Scheme I

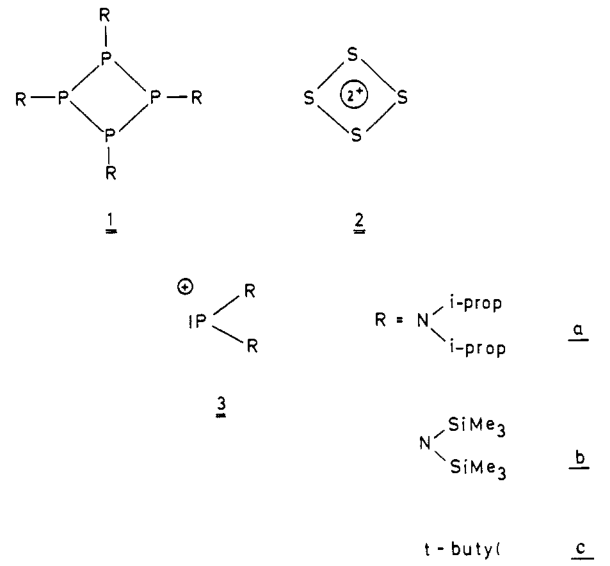

Table I. Electrochemical Oxidation of Cyclotetraphosphanes

compd	$E_1°$[V][a]	$E_{p,1a} - E_{p,1c}$ [mV]	$E_{p,2a}$ [V][a]	IP [eV]
1a	0.45	60	1.08	6.4[b]
1b	0.76	80	1.20	7.5[c]
1c	1.33	75	1.65[d]	7.4[e]

[a] Versus SCE. [b] H. Bock, personal communication. [c] P. Rademacher, personal communication. [d] Broad peak. [e] Reference 3a.

The anodic and cathodic peak potential values of all cyclotetraphosphanes are listed in Table I, together with the first

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† Deceased 1983.

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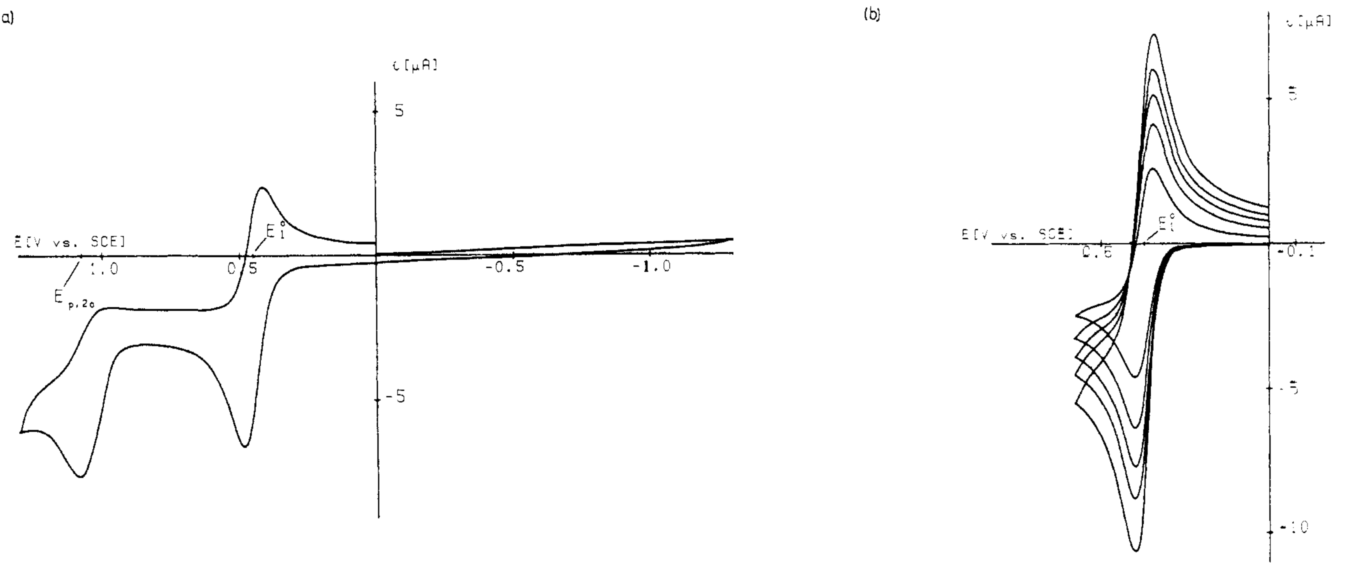


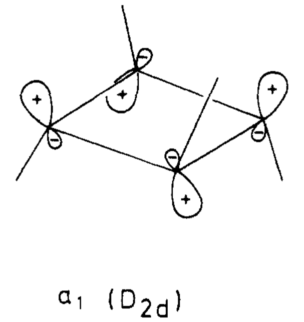
Figure 1. Cyclic voltammogram (a) of **1** (R = N(i-Pr)$_2$ in CH_2Cl_2/0.1 M Bu_4NBF_4 at a Pt electrode; $c = 1.15 \times 10^{-3}$ mol/L, v = 100 mV/s. (b) The first reversible oxidation at different scan rates: 50, 100, 150, 200, 300 mV/s.

ionization potentials. Accordingly, **1b** shows an analogous electrochemical behavior, but the potentials needed for the oxidation to the cation and the dication are higher. Most difficult to oxidize is **1c** (see Table I). The data indicate that the amino groups (in **1a** and **1b**) are considerably effective in stabilization of a positive charge in the cations and dications.

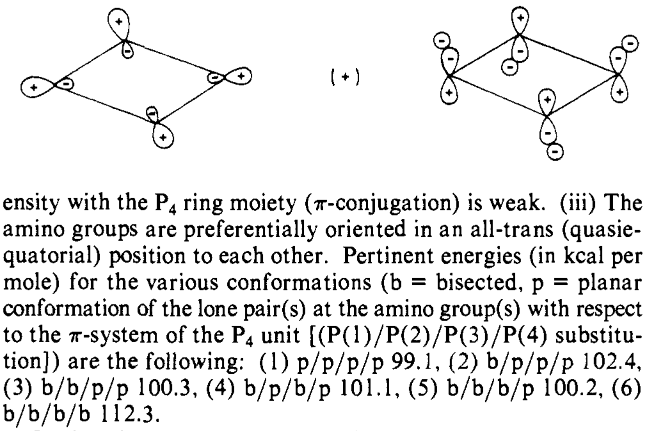
All attempts to prepare the cation **3** (R = N(i-Pr)$_2$) via electrolysis (in CH_2Cl_2 with 0.1 M NBu_4BF_4, NBu_4ClO_4, or NBu_4PF_6 as supporting electrolyte) failed so far. The formed product is not stable toward the supporting electrolyte. Indicative of this conclusion is the reaction of $PR_2^+AlCl_4^-$ (R = N(i-Pr)$_2$),[7] which was independently synthesized, in CH_2Cl_2 with NBu_4BF_4, NBu_4ClO_4, or NBu_4PF_6. The halogen derivatives such as PR_2Cl and $PRCl_2$ (R = N(i-Pr)$_2$) were observed. We were not successful in preparing the cation **3** with other counterions as BF_4^- or PF_6^- via reaction of the corresponding silver salts with PR_2Cl (R = N(i-Pr)$_2$). On this basis it also was not possible to record an unequivocal, reproducible cyclic voltammogram of **3** (R = N(i-Pr)$_2$). In the bulk electrolysis of **1** in CH_2Cl_2/0.1 M NBu_4Cl at +0.55 V only one product was observed, which was identified as ClRP–PRCl (R = N(i-Pr)$_2$).

ESR spectra of $\mathbf{1a}^{\bullet+}$ and $\mathbf{1b}^{\bullet+}$ were obtained by oxidation of the corresponding cyclophosphanes with $AlCl_3/CH_2Cl_2$ in the cavity of the ESR spectrometer. They are recorded in Figure 2A,B. For $\mathbf{1a}^{\bullet+}$ 13 lines were observed, g = 2.00957. The intensity ratio of the two outermost lines is 1:4. The spectrum did not change in the temperature range from −57 to +10 °C. The interpretation of its hyperfine structure was based on the results of energy optimized MNDO calculations on the radical cation of tetraaminocyclotetraphosphane. Accordingly, (i) the phosphorus atoms are strongly pyramidalized and (ii) electronic coupling of the amino groups with respect to conjugation propensity with the P_4 ring moiety (π-conjugation) is weak. (iii) The amino groups are preferentially oriented in an all-trans (quasiequatorial) position to each other. Pertinent energies (in kcal per mole) for the various conformations (b = bisected, p = planar conformation of the lone pair(s) at the amino group(s) with respect to the π-system of the P_4 unit [(P(1)/P(2)/P(3)/P(4) substitution]) are the following: (1) p/p/p/p 99.1, (2) b/p/p/p 102.4, (3) b/b/p/p 100.3, (4) b/p/b/p 101.1, (5) b/b/b/p 100.2, (6) b/b/b/b 112.3.

Scheme II



Scheme III



On the other hand, molecular models suggest considerable steric hindrance for the actual cases R = N(i-Pr)$_2$ and even larger for R = N($SiMe_3$)$_2$. Hence most likely is for $\mathbf{1a}^{\bullet+}$ a geometry in which two 1,3-positioned amino groups are in conjugation (p) with the π-system of the ring while the other two are forced into a bisected (b) orientation. On this basis the hyperfine structure in the ESR spectrum of $\mathbf{1a}^{\bullet+}$ can be explained by assuming four equivalent phosphorus nuclei which couple (coupling constant a_P = 5 G) and two equivalent nitrogen nuclei (a_N = 10 G). The coupling of the other two nuclei was not resolved. A simulation of the spectrum (not recorded here) with the given parameters agrees with the experimental spectrum.

The ESR spectrum of $\mathbf{1b}^{\bullet+}$ shows only one broad line (Figure 2B) (g = 2.00728). Its underlying hyperfine structure is not resolvable. Again the spectrum did not change from −57 to +38 °C. The bis(trimethylsilyl)amino groups are more bulky than

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(3) (a) The measurement of the photoelectron spectrum was performed by Prof. H. Bock. For the PE spectra of other cyclophosphanes see also: Cowley, A. H.; Dewar, M. J. S.; Lattmann, M.; Mills, J. L.; McKee, M. *J. Am. Chem. Soc.* **1978**, *100*, 3349. Gleiter, R.; Böhm, M. C.; Baudler, M. *Chem. Ber.* **1981**, *114*, 1004. (b) Gleiter, R.; Schäfer, W.; Baudler, M. *J. Am. Chem. Soc.* **1985**, *107*, 8043.

(4) Bard, A.; Faulkner, L. R. *Electrochemical* Methods; Wiley: New York, 1980.

(5) $AlCl_3$ in CH_2Cl_2 can function as an oxidizing reagent. Bock, H.; Kaim, W. *Acc. Chem. Res.* **1982**, *15*, 9 and cited literature.

(6) 200 mg of **1** (R = N(i-Pr)$_2$) in a 1:1 mixture with fresh sublimated $AlCl_3$ was put in a NMR tube. 1,5 mL of dry CH_2Cl_2 was added and cooled at −78 °C. The solution becomes violet and the radical cation is formed. Warming up above −78 °C causes disappearance of the violet color, and the diaminophosphenium cation is formed.

(7) Cowley, A. H.; Cushner, M. C.; Lattmann, M.; McKee, M. L.; Szobota, J. S.; Wilburn, J. C. *Pure Appl. Chem.* **1980**, *52*, 789.

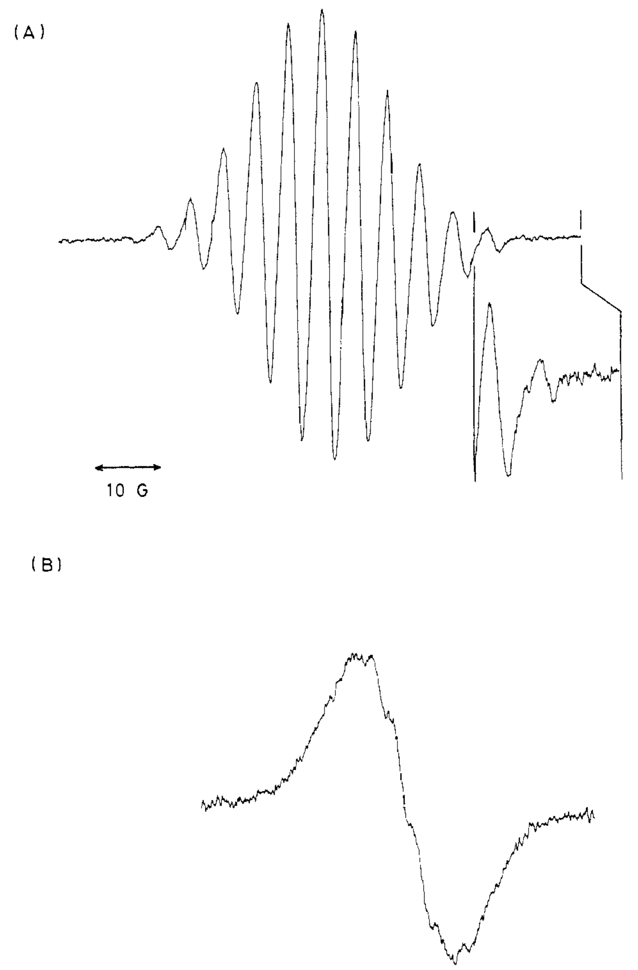

Figure 2. ESR spectra of the tetraaminocyclotetraphosphane cation radicals (A) $\mathbf{1a}^{\bullet+}$ and (B) $\mathbf{1b}^{\bullet+}$, generated by oxidation with aluminum trichloride in methylene chloride.

the diisopropylamino group, and π-conjugation becomes less facile in **1b** compared with **1a**. Consequently **1b** is more difficult to oxidize than **1a**, and in accordance with the electrochemical data (Table I).

(b) Quantum Chemical Investigations on the Dication. So far the oxidation experiments indicate that only the radical cations (first oxidation step) are stable species, while the dications $\mathbf{1a}^{2+}$ and $\mathbf{1b}^{2+}$ undergo fast reaction to the phosphenium cations **3**. We will now rationalize these findings with MO considerations. Consider first the parent (uncharged) cyclotetraphosphane, **1** (R = H), within D_{2d} symmetry.[8] The HOMO refers to a π-type orbital (Hückel array).[9,10] In more detail this orbital is constituted by superposition of two Hückel-type orbitals.[10] The removal of two electrons, i.e., the formation of the dication, has two consequences. (1) It reduces the vicinal antibonding interaction between the lone pairs. (2) Simultaneously the σ-bonds of the ring moiety are weakened, because they mix considerably into the HOMO.

Next we will discuss the various isomers of the dication, summarized as follows. They differ in a consecutive shift[12] of the substituent(s) (R = H) around the ring moiety. The stability of these structures depends on two factors: (1) The first factor is the ability of the structure to delocalize positive charge over the ring system. Recent ab initio calculations[11] on the diphosphine radical cation indicate a strong tendency for pyramidalization at phosphorus. On this basis the delocalization of positive charge is offset, i.e., it is diminished. (2) In structures **4b** and **4c** one phosphorus atom bears a nonbonding orbital. This is of advantage to the stability of these species. Similar considerations hold for the species **4d** and **4e**. Hence the energy balance between the various isomers is determined by these opposing factors. Structure **4e** can be viewed as two phosphenium cations interacting with a P_2 unit. According to an orbital correlation diagram (not recorded here) the fragmentation of **4e** in P_2 and two phosphenium cations is forbidden. The species **4d** is a biradical, the pendant to the bicyclic structure **4e**.

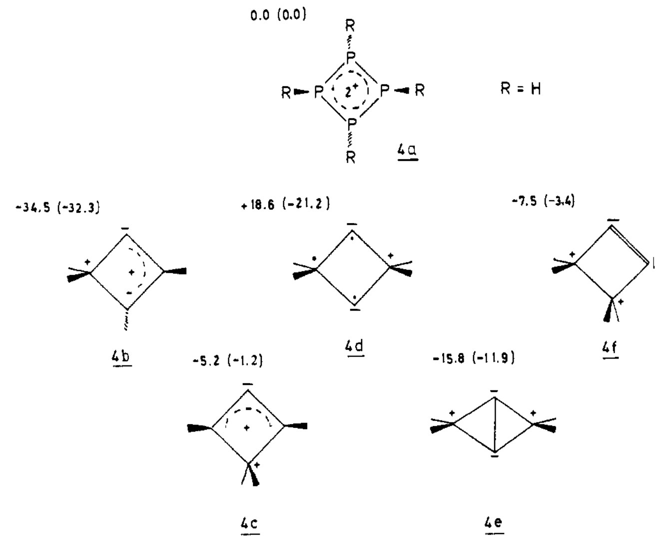

Figure 3. Family of 1,2-shifted isomers of **4** (R = H). Energies (in kcal per mol) are obtained from energy optimized MNDO calculations at a SCF level. In parentheses are the corresponding values for optimization at a SCF plus 2 × 2 CI level between HOMO and LUMO.

For a quantitative substantiation of these considerations we performed ab initio and MNDO calculations. The results at both computational levels agree. Therefore we will report only the energy optimized MNDO calculations. Relative energies (in kcal per mol) of the various isomers, at times in reference to **4a**, are included in Figure 3. In parentheses are the corresponding values obtained from energy optimized SCF plus CI (double excitation from HOMO to LUMO) calculations. Accordingly the inclusion of CI in the wave function is only important for the proper bonding description of the biradical structure **4e**. For all the other species the relative energy balances are already well represented at the SCF level. Lowest in energy is the 1,2-shifted isomer **4b**. All species are lower in energy than the precursor dication **4a**. The fragmentation of **4a** into P_2 and $2PH_2^+$ is slightly endothermic, at a SCF level by 20.5 kcal per mol.

Next we will consider the isomers for the case **4** (R = NH_2). Again energy optimized MNDO calculations at a (a) SCF level and (b) SCF plus 2 × 2 CI level (between HOMO and LUMO) were carried out. All the possible structural isomers were taken into consideration. Now the fragmentation of **4a** (R = NH_2) into P_2 and two diaminophosphenium cations, $^+P(NH_2)_2$, is exothermic. At a SCF level a reaction energy of −46.8 kcal per mol results. All the isomers, **4b** to **4f**, become unstable toward splitting off one (two) phosphenium cation(s). In other words the driving force for the formation of the thermodynamically most stable structures, i.e., the phosphenium cations, is large enough to break the PP–ring bonds.

In our description of the electronic hypersurface we have not discussed so far the pathways interconnecting the various isomers. Due to the fact that in the case of **4** (R = NH_2) all isomers separate from a phosphenium unit, a further refinement of the electronic hypersurface does not seem to be worthwhile. It must be emphasized that our quantum chemical treatment of the electronic hypersurface for **4** must be considered as semiquan-

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[8] The cyclotetraphosphanes adopt a slightly puckered conformation: Palenik, G. J.; Donohue, J. *Acta Crystallogr.* **1962**, *15*, 564. Bart, J. C. J. *Acta Crystallogr., Sect. B* **1969**, *25*, 762. Sanz, F.; Daly, J. J. *J. Chem. Soc. A* **1971**, 1083.

[9] The valence orbitals of cyclobutane are lucidly discussed in the following: Hoffmann, R.; Davidson, R. B. *J. Am. Chem. Soc.* **1971**, *93*, 5699.

[10] Schoeller, W. W.; Dabisch, T. *J. Chem. Soc., Dalton Trans.* **1983**, 2411.

[11] Feller, D.; Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1985**, *107*, 2596. Clark, T. *J. Am. Chem. Soc.* **1985**, *107*, 2597.

[12] For a review on 1,2-hydrogen shifts see: Schaefer, HF., III. *Acc. Chem. Res.* **1979**, *12*, 288.

titative, since we do not account for possible solvation effects on the stability of the various species; steric effects as well, exerted from the bulky amino groups, are in our analysis not taken into consideration.

Experimental Section

Materials. Tetrakis(diisopropylamino)cyclotetraphosphane[13] was synthesized according to the procedure of Schäfer.[13b] (Diisopropylamino)dichlorophosphane [$(Me_2CH)_2NPCl_2$] was stirred with 20% excess of dry magnesium chips in dried tetrahydrofuran (THF). After refluxing 1 day the yield is quantitative. The product is only soluble in hot THF. Hence, after decantation from $Mg/MgCl_2$, the product **1** (R = $N(i\text{-}Pr)_2$) is obtained in yields up to 70% and is already spectroscopically pure. Similarly **1b** was obtained while **1c** was synthesized according to the procedure of Issleib et al.[13c]

In the electrochemical measurements methylene chloride and butyronitrile were used as solvents. CH_2Cl_2 (Merck p.a. quality) was distilled from CaH_2 and passed through a column packed with Al_2O_3 (Woelm, Super 1, neutral). Butyronitrile (Merck for synthesis) was purified and dried according to Van Duyne and Reilley.[14] The supporting electrolytes NBu_4BF_4, NBu_4ClO_4, and NBu_4PF_6 were recrystallized from ethanol/water and dried under vacuum at 80 °C over P_2O_5 for at least 24 h. NBu_4Cl was used without further purification and dried as the other electrolytes.

Electrochemical Procedures. The measurements were performed on a Princeton Applied Research (PAR) Model 173 potentiostat equipped with a PAR Model 179 digital coulometer and the PAR 175 universal programmer. The PAR 179 digital coulometer provided a positive feedback compensation for ohmic drop between the working and the reference electrode. The results were recorded directly on an X/Y recorder.

For cyclic voltammetry a cell with a three-electrode configuration similar to that of Van Duyne and Reilley[14] was used. The cell for low-temperature cyclic voltammetry resembled Van Duyne and Reilley's variable-temperature electrochemical cryostat.[14] The jacketed cell was cooled with cold nitrogen, and temperature control was obtained by controlling the flow rate of N_2. In both cells the working electrode was a Pt disk electrode and the reference electrode a saturated calomel electrode (SCE). The distance between the working electrode and the tip of the Haber–Luggin capillary probe was about 1 mm to minimize the iR drop. If necessary, positive feedback compensation was applied. A platinum wire served as the counter electrode. All values of the reported electrode potentials refer to the SCE.

Before each measurement the Pt disk was polished with 0.5 μm of Al_2O_3, and the solution was purged with dried argon in order to remove oxygen. The peak potentials were always reproducible to within ±50 mV. Low-temperature cyclic voltammetry was performed in butyronitrile/0.1 M NBu_4BF_4.

Potential controlled bulk electrolysis experiments were performed with a two-compartment cell of cylindrical symmetry, the anodic and cathodic half cell connected by a fine frit. A Pt gauze cylinder was used as the working electrode, a Pt coil was used as the counter electrode, and the reference electrode was the SCE.

Theoretical Procedure. The quantum chemical calculations were carried out on model geometries utilizing the ab initio STO-3G basis et.[15a] Alternatively MNDO[15b] calculations were performed on the various isomers of the dication of **1** (R = H, NH_2). Within the latter method geometry optimization was performed with the Davidon–Fletcher–Powell algorithm[16] within the method of finite differences[17] for the evaluation of the gradients. The calculations for the radical cations $\mathbf{1a}^{\bullet+}$ and $\mathbf{1b}^{\bullet+}$ were performed with the half-electron model.[15c]

Conclusions

The summary of our study is as follows: The oxidation experiments at some model cyclotetraphosphanes reveal stable radical cations. In case of tetraamino substitution at the ring moiety the oxidation processes are extremely facilitated and corresponding dications are formed. They rearrange rapidly. As a final product diaminophosphenium cations are obtained. The mechanism for the reaction is as follows: (1) In the first step the removal of one electron in **1** leads to a stable radical cation. Its formation is reversible to the electrochemical time scale and proven by various independent electrochemical criteria. Quantum chemical investigations reveal for the radical cations strong pyramidalization at the phosphorus atoms and only weak electronic coupling of the amino groups. On this basis the most likely conformation of the $\mathbf{1a}^{\bullet+}$ and $\mathbf{1b}^{\bullet+}$ is determined by minimization of the steric hindrance of the bulky amino groups. Our results may be compared with the important findings on hydrazine radical cations.[18] (2) Further oxidation to the dication is irreversible. Even at temperatures at −100 °C the electrochemical experiments indicate fast rearrangement toward diaminophosphenium cations and white phosphorus. The course of the reaction can be rationalized by MO considerations. Accordingly the pyramidalization force at phosphorus is rather large[19] and the four-membered ring will not flatten toward D_{4h} symmetry, as in the case of the planar S_4^{2+} system.[1b] Hence, depletion of electron density (caused by the removal of electrons) weakens the bonds of the ring moiety *and* the bonds of the substituents attached to the phosphorus atoms. (3) 1,2-Shifts of the substituents, in analogy to the very facile Wagner–Meerwein rearrangement,[12] bring thermodynamically more stable structures to the fore. They owe their stability to the presence of a nonbonding lone-pair orbital at phosphorus. (4) Finally, these structures are unstable toward splitting off very stable diaminophosphenium cations.

Acknowledgment. This work was supported by the Fonds der Chemischen Industrie and the Deutschen Forschugsgemeinschaft. We thank Dr. H.-G. Korth and Prof. R. Sustmann (university of Essen) for the measurements of the ESR spectra. We also thank a referee for very valuable comments.

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