aminooctane and 2-aminodecane (6–12% net retention at 0.76 *M*) represent the latter case, which is probably an extreme for this type of system.

The traditional mechanistic concepts of nitrous acid deamination[2-4] are thus incomplete. The reaction stereochemistry is concentration dependent for a given amine and chain length dependent for homologous amines at certain given concentrations. We suggest that alkylammonium ion micelles are responsible for these effects. We are exploring these and related phenomena.

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Phosphonitrilic Radical Anions

Sir:

We wish to report the preparation of the first cyclophosphazene (phosphonitrilic) radical anions, together with their electron spin resonance spectra. The information derived from a study of these species is applicable to the controversial question of bonding in phosphorus–nitrogen systems.[1-11]

Radical anions of organic aromatic species are well known, and those of inorganic heterocyclic compounds such as borazines have also been reported.[12] Unsuccessful previous attempts have been made to prepare cyclophosphazene radical anions by treatment of $[NP(C_6H_5)_2]_3$ with an alkali metal,[13] but decomposition products, such as biphenyl, were the only reaction products detected. We have prepared the radical anions of a number of phosphazenes by electrolytic techniques with the use of dimethylformamide solvent and *t*-butylammonium halides or perchlorate as the supporting electrolyte. The formation of one-electron reduced species was followed by polarography, coulometry, and cyclic voltammetry. Reductions were also performed within the cavity of an esr spectrometer at potentials near the $E_{1/2}$ values.

Certain phosphazenes could not be reduced at potentials more positive than −3 V (relative to a saturated calomel electrode). These included $[NP(OC_6H_5)_2]_3$, $[NP(OC_6H_5)_2]_n$, $[NP(NHC_6H_5)_2]_3$, $[NP(OCH_2CF_3)_2]_3$, $[NP(OCH_2CF_3)_2]_4$, $[NP(OCH_2CF_3)_2]_n$, $[NP(OCH_3)_2]_3$, and $[NP(O_2C_6H_4\text{-}o)]_3$ (where $n \approx 15{,}000$). No esr spectra were detected during attempted reduction of these species. The halophosphazenes $(NPF_2)_3$, $(NPCl_2)_3$, $(NPCl_2)_4$, and $(NPBr_2)_3$ showed spurious polarographic behavior, part of which was attributed to ligand ionization at low negative potentials.

However, the following compounds[14] showed well-defined one-electron polarographic reduction peaks: hexaphenylcyclotriphosphazene, $[NP(C_6H_5)_2]_3$, I; octaphenylcyclotetraphosphazene, $[NP(C_6H_5)_2]_4$, II; hexa(*p*-nitrophenoxy)cyclotriphosphazene, $[NP(OC_6H_4NO_2)_2]_3$, III; tris(2,3-dioxynaphthyl)cyclotriphosphazene, $[NP(2,3\text{-}O_2C_{10}H_6)]_3$, IV; tris(1,8-dioxynaphthyl)cyclotriphosphazene, $[NP(1,8\text{-}O_2C_{10}H_6)]_3$, V; tris(2,2′-dioxybiphenyl)cyclotriphosphazene, $[NP(2,2'\text{-}O_2C_{12}H_8)]_3$, VI; and tris-1,3,5-triphenyltris-1,3,5-trifluoroethoxycyclotriphosphazene, $[NP(C_6H_5)(OCH_2CF_3)]_3$, VII. $E_{1/2}$ values (relative to sce) are as follows: I, −2.65; II, −2.67; III, −1.24; IV, −1.83 dec; V, −2.15; VI, −2.33; VII (*trans*), −2.45 V. Cyclic voltammetric experiments indicated that the radicals derived from I, II, and VII had a shorter lifetime (<1 sec) than those from III and IV (>10 sec). However, polarographic and prolonged, low-frequency cyclic voltammetric experiments suggested that, with the exception of IV, irreversible decomposition of the radical is not the primary deactivation process.

The esr spectra of the radical anions from the two phenylphosphazenes I and II consisted of an unresolvable singlet at $g = 2$ with a 20–30-G band width. A series of careful experiments designed to vary the solvent, temperature, concentration, and polarographic technique failed to produce hyperfine splitting in this spectrum. On the other hand, hyperfine splitting was readily observed in the spectra derived from III (13–15 lines), IV (5 lines), and V (15–20 lines). It is considered unlikely that these spectra result solely from secondary decomposition products. Thus, termination of reduction during esr experiments was followed by a simple decay of each spectrum with no secondary spectra being evident. Also, in the case of the phenyl derivatives I and II, the esr spectrum of biphenyl (the most likely decomposition product) was not seen, although it was readily visible when small amounts of biphenyl were added. No esr signals have yet been detected from the radical anions of VI and VII, presumably because of their short lifetime.

These observations can be interpreted as follows. Reduction of a phosphazene to the radical anion apparently does not occur unless the side group itself is independently reducible in the same potential range or unless an aryl group is bonded directly to phosphorus. For example, *p*-nitroanisole or substituted naphthalenes

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and biphenyls can be reduced in the 0 to −3 V range, but trifluoroethoxy, phenoxy, *o*-dioxyphenyl, and methoxy units cannot. Benzene cannot be reduced in the 0 to −3 V range but, when a phenyl group is bonded directly to phosphorus in I or II, the reduction potential is lowered until it is comparable to that of free naphthalene. This result is consistent with observations reported by Santhanam and Bard for triphenylphosphine and triphenylphosphine oxide reductions.[15] Thus, it appears that the reducibility of the phenylcyclophosphazenes I and II results from delocalization effects involving the phenyl groups and the skeleton.

This interpretation is confirmed by the esr data. The spectra derived from III, IV, and V can be rationalized in terms of hyperfine splittings within each discrete side group unit only. For example, the spectra are similar to those of *p*-nitroanisole, or the appropriate disubstituted naphthalenes. Presumably the oxygen atoms effectively insulate the reduced organic aromatic component from the phosphazene ring. This is further confirmed by the nonreducibility of $[NP(OC_6H_5)_2]_3$ and $[NP(OC_6H_5)_2]_n$ below −3 V.

However, the esr singlet obtained from I and II must indicate delocalization of the unpaired electron either within a C_6H_5–P–C_6H_5 unit or into the phosphazene skeleton as a whole. Interaction within a C_6H_5–P–C_6H_5 segment could give rise to as many as 150 lines (648 lines if the phenyl groups are nonequivalent), and this is probably beyond the resolution limit for this system. Delocalization involving the whole skeleton[2-4] is also possible, but the failure of the skeleton to reduce when aliphatic substituents are present, coupled with the almost identical results obtained from $[NP(C_6H_5)_2]_3$ and $[NP(C_6H_5)_2]_4$, and the inability of long-chain species such as $[NP(OC_6H_5)_2]_n$ and $[NP(OCH_2CF_3)_2]_n$ to stabilize an unpaired electron, force us to the view that extensive skeletal delocalization does not occur under these conditions. It appears more likely that in phenylphosphazenes an unpaired electron can be delocalized within a C_6H_5–P–C_6H_5 unit or, at the most, into a very short adjacent skeletal segment.[1,8]

A more detailed discussion of these results and of additional work now in progress will be given in a subsequent publication.

Acknowledgment. We are indebted to Dr. M. D. Morris for his suggestions concerning the polarographic technique.

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Steric Effects in *ortho*-Substituted Triarylmethanes

Sir:

Triarylmethane derivatives in which all *ortho* positions have bulky substituents reflect[1-3] in their chemical and physical properties the effects of the large nonbonded interactions between *ortho* substituents. Compound **1** (Figure 1), mp 156–157°, was prepared from dimesitylcarbinol and 1,3,5-trimethoxybenzene by treatment with sulfuric acid in acetic acid. It shows unprecedentedly large interactions of this sort (a) in nmr evidence for hindered rotation, (b) in $J_{^{13}C-H}$ for the methane proton, and (c) in a structure determined by X-ray crystallography.

Below −30° compound **1** shows three peaks (with areas 3:6:3, separated by about 12 Hz at 60 MHz) for four nonequivalent *o*-methyls and two peaks (of area 3 and separated by 20 Hz) for two *o*-methoxyls. The methyl peaks coalesce to a single peak near −20°, but the methoxyl peaks require a much higher temperature, near 145°. Line-shape analyses[4] over the temperature range 118–176° for the nmr signals for the *o*-methoxyl groups show $\Delta H^* = 17.7 \pm 0.4$ kcal/mol and $\Delta S^* = -9.8 \pm 1.0$ eu for the process interconverting *exo*- and *endo*-methoxyl groups. These data suggest the importance in solution of a distorted propeller conformation similar to that established by X-ray analysis for crystalline **1**. The higher energy barrier for the position exchange of methoxyl groups than for methyl groups in **1** is in accord with the order of size ($CH_3 > OCH_3$) established from rate data for biphenyl racemization[5] and from consideration of the relative van der Waals radii of oxygen and methyl groups[6] if the detailed mechanism for rotation about the C_α–aryl bond is considered. Individual steps in this rotation must involve a reversal of the pitch of the propeller, with simultaneous 90° rotations of each ring about the C_α–aryl bond.

The pictured process moves *exo*-methyl group Z_1 (in **1a**) to an *endo* position (in **1b**) and moves Z_2 *endo* to *exo*. No *exo–endo* interconversion of methoxyl groups is effected by this process. It involves a "gear-meshing" correlation of the rotations of rings A and C and of rings B and C.[7] The "gear-clashing" correlation of rotation of rings A and B which is necessary in this mechanism provides the largest steric interaction in the transition state, that between *endo* substituents X_2 (OCH_3) and Y_2 (CH_3).

The related processes which would interconvert *exo*- and *endo*-methoxyls in **1a** would involve rings B and C in a "gear-clashing" counterrotation with a resulting large nonbonded transition-state interaction between juxtaposed *endo*-methyls (*e.g.*, Y_2 and Z_2) in the transition state. This interaction would be expected to be less favorable than the methyl–methoxyl interaction in the pictured process (**1a** → **1b**) which exchanges methyls.

As expected, the rotation of the methoxylated rings in **2**, which involves only the much smaller methoxyl–methoxyl interactions, is much faster, $\Delta H^* = 8 \pm 1$ kcal/mol and $\Delta S^* = -10 \pm 5$ eu (over the range −69 to −81°)[8] as established by the line-shape analysis of the

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