$$\text{PAT} \longrightarrow \text{Ph}\cdot \qquad (1)$$

$$\text{Ph}\cdot + \text{PBN} \longrightarrow \text{Ph-SA} \qquad (2)$$

$$\text{Ph}\cdot + CH_3OH \longrightarrow \cdot CH_2OH \qquad (4)$$

$$\cdot CH_2OH + \text{PBN} \longrightarrow \text{HM-SA} \qquad (5)$$

then

$$\frac{d[\text{Ph-SA}]/dt}{d[\text{HM-SA}]/dt} = \frac{k_2[\text{PBN}]}{k_4[CH_3OH]}$$

From computer simulation matching of partially overlapped spectra, the relative concentrations of the two spin adducts could be obtained. This analysis gave $k_2/k_4 = 86$. Using the value of $1.4 \times 10^5\ M^{-1}\ \sec^{-1}$ for k_4 reported by Packer[6] for the *p*-methylphenyl radical, $k_2 = 1.2 \times 10^7\ M^{-1}\ \sec^{-1}$ for the rate constant of phenyl radical trapping by PBN in methanol at 25°. The rate constants for spin trapping other radicals with other traps[3] fall in the range 1×10^6 to $5 \times 10^8\ M^{-1}\ \sec^{-1}$ at room temperature.

The phenylation of benzene in benzene gave $k_3/k_2 = 0.0065$ as stated above. If the value $k_2 = 1.2 \times 10^7\ M^{-1}\ \sec^{-1}$ determined in methanol is used for benzene, $k_3 = 7.8 \times 10^4\ M^{-1}\ \sec^{-1}$. A recent study is in agreement with this estimate.[8] The ratio of the rate constants for phenylation of benzene and for the reaction of phenyl radicals with iodine in methylcyclohexane was found to be[8] $k_3/k_{I_2} = 5.0 \times 10^{-5}$. These authors assumed that the rate of reaction of phenyl radicals with I_2 is diffusion controlled. Thus as an upper limit $k_{I_2} \sim 10^{10}\ M^{-1}\ \sec^{-1}$ and $k_3 \sim 5 \times 10^5\ M^{-1}\ \sec^{-1}$, only a factor of 6 larger than our value in benzene. For the phenylation of chlorobenzene in methylcyclohexane $k_3{}^{\text{PhCl}}/k_{I_2} = 7.7 \times 10^{-5}$ was obtained[8] and thus $k_3{}^{\text{PhCl}} \sim 8 \times 10^5\ M^{-1}\ \sec^{-1}$. From trapping phenyl radicals in chlorobenzene, we[9] obtain $k_3{}^{\text{PhCl}} = 1.8 \times 10^5\ M^{-1}\ \sec^{-1}$. The relatively good agreement obtained from these different sources lends support to the conclusion that the absolute rate constant for phenylation of benzene is $\sim 10^5\ M^{-1}\ \sec^{-1}$.[11]

In an extensive analysis of the rate constants involved in the phenylation of benzene using benzoyl peroxide as a source of phenyl radicals DeTar[14] used $k_3 = 2 \times 10^3\ M^{-1}\ \sec^{-1}$ at 87° for his calculations. Although this value now appears to be too low, the ratio of the rate constants of decarboxylation of benzoyloxy radicals and phenylation of benzene reported by DeTar ($1 \times 10^4/2 \times 10^3 = 5$) may still be correct because this ratio was based on yields of products isolated for the experiments considered. Using the present estimate for phenylation of benzene ($\sim 10^5\ M^{-1}\ \sec^{-1}$), one obtains $\sim 5 \times 10^5\ M^{-1}\ \sec^{-1}$ for the rate constant of decarboxylation of benzoyloxy radicals. Assuming an energy of activation of 13.6 kcal/mol for this reaction,[15] decarboxylation rate constants of 5×10^7 to $1 \times 10^8\ \sec^{-1}$ are calculated at 100 and 130° in benzene. These numbers are of interest because they overlap with CIDNP estimates of the lifetime of benzoyloxy radicals produced by the thermal decomposition of propionyl benzoyl peroxide in *o*-dichlorobenzene at 100°[16] and 130°.[17]

Combining data previously obtained on trapping benzoyloxy radicals[2] with the rate constants reported here on the addition of phenyl radicals to PBN and benzene, an absolute rate constant of trapping benzoyloxy radicals by PBN in benzene at room temperature of $4 \times 10^7\ M^{-1}\ \sec^{-1}$ is estimated.[18]

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(18) The intercept of the plot of d[BzO-SA]/d[Ph-SA] *vs.* PBN equals $k_\text{B}k_3[\text{PhH}]/k_\text{D}k_2 = 5.3$ where k_D and k_B are the rate constants for the decarboxylation and trapping of benzoyloxy radicals, respectively. If the above values for k_2, k_3, and k_D are used $k_\text{B} = 4 \times 10^7\ M^{-1}\ \sec^{-1}$.

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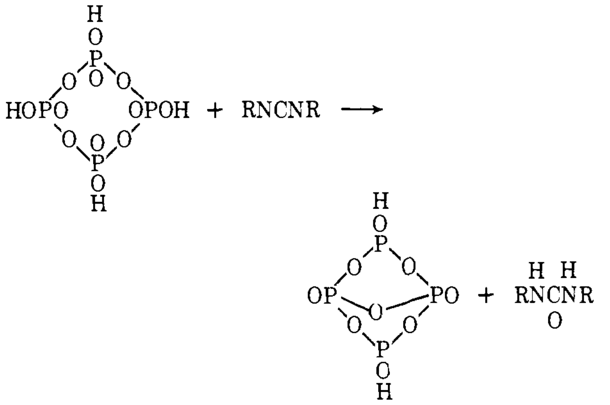
Synthesis of an Organic Adduct of the P_4O_{10} Cage Structure

Sir:

In spite of considerable effort being devoted to the problem for more than a century, no one prior to this time has been able to adduce any reasonably acceptable evidence for the production of the P_4O_{10} birdcage structure in solution nor has there been any evidence to show that phosphorus pentoxide could be dissolved in any solvent without rupture of the P-O-P bridges. In previous studies, we have shown[1,2] that simple orthophosphoric acid as well as the various chain polphosphoric acids, the ring metaphosphoric acids, and/or mixtures of any of these can be condensed to 1,5-μ-oxo-tetrametaphosphoric acid, $H_2P_4O_{11}$, which is the product that would be formed by scission of a single P-O-P bridge in the P_4O_{10} molecule through interaction with a single molecule of water. When a carbodiimide condensing agent is employed at the usual concentration range (around 0.8 M of RNCNR per 0.2 M of phosphate phosphorus), it is found that the reaction stops (and indeed seems to come to equilibrium) at an overall H_2O/P_2O_5 mole ratio of 0.5, with the $H_2P_4O_{11}$ molecule accounting for essentially all of the phosphorus. Not surprisingly, the cleanest condensation reaction to make 1,5-μ-oxo-tetrametaphosphoric acid involves tetrametaphosphoric acid as the phosphatic reagent.

In thinking about this reaction, we reasoned that by a simple application of the law of mass action, it ought to be possible to push the reaction to an even higher degree of



(1)

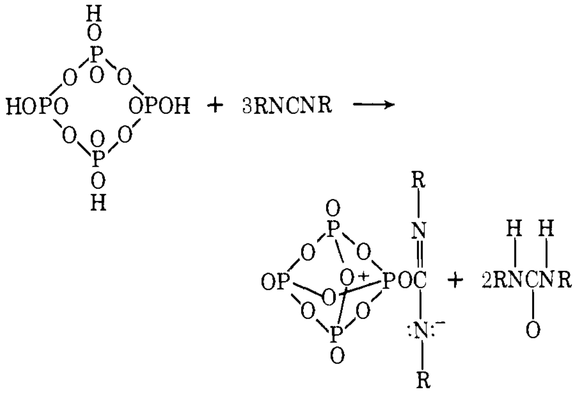
condensation so that the P_4O_{10} molecule would be a product. Thus, in the solution, the carbodiimide concentration should be increased while that of its urea hydrolysis product should be decreased concomitantly. Fortunately, dicyclohexylcarbodiimide ($R = C_6H_{11}$ in eq 1), which exhibits a melting point near room temperature, is a poor solvent for its urea while being a good solvent for small ultraphosphate molecules.

Although other procedures have proven suitable, we have obtained good results in carrying the condensation beyond the 1,5-μ-oxo-tetrametaphosphoric acid stage by using the following sequences of steps. To a solution of 0.4 m*M* tetrakistetra-*n*-butylammonium tetrametaphosphate in 5 ml of tetramethylurea, 3.04 m*M* of the hydrochloride of dicyclohexylurea is added to give a clear homogenous solution exhibiting only a single peak in its ^{31}P nmr pattern, the peak corresponding to the tetrametaphosphate anion. An equal volume of molten dicyclohexylcarbodiimide is then added and the resulting precipitated urea is removed by decantation after centrifugation (*Note:* All operations must be carried out with careful avoidance of contamination by moisture.[2]) The resulting solution shows only ^{31}P nmr resonances attributable to the 1,5-μ-oxo-tetrametaphosphate anion.[1,2] Additional molten carbodiimide is added in several steps, removing the precipitated urea after each addition. After each step a diminution is seen in the area of the second-order double–triplet nmr pattern of the 1,5-μ-oxo-tetrametaphosphate anion appearing approximately 35 ppm upfield of the resonance position of 85% H_3PO_4, while concomitantly a new set of resonances lying approximately 60 ppm above that of 85% H_3PO_4 is seen to appear and grow in area. Finally, when approximately 90 weight per cent of the clear homogenous solution consists of dicyclohexylcarbodiimide, the sole ^{31}P resonances consist of the new pattern appearing near +60 ppm.

This new pattern consists of a pair of barely resolvable multiplets composed of a doublet having a relative area of 3.0 at +59.5 ppm and a quartet having a relative area of 1.0 at +64.2 ppm, with a single coupling constant of 18.0 Hz applying to both multiplets. This classic pseudo-first-order pattern has been well simulated by a calculation corresponding to an a_3x system. Heteronuclear decoupling experiments show that there is no coupling between phosphorus and hydrogen atoms in this molecule; and signal-averaged homonuclear ^{31}P–^{31}P INDOR experiments demonstrate that the two multiplets are in fact coupled. By completely dissolving the urea precipitates removed during the preparation of this entity and obtaining time-averaged ^{31}P nmr patterns of the resulting solutions, it was shown that the amount of phosphorus lost during these precipitation steps was slight, being due to the usual occlusion of the solution by the precipitate.

Dilution of the system with dry, but not scrupulously dry, tetramethylurea causes the area of the ^{31}P nmr pattern at +60 ppm to decrease while that of the pattern at +40 ppm increases. Likewise similar behavior is found upon dilution with the urea dissolved in scrupulously dry (CaH_2) tetramethylurea. Controlled hydrolysis[2] of the solution exhibiting the ^{31}P nmr pattern at +60 ppm leads to the quantitative production of the tetrametaphosphate starting material.

The reasonable interpretation of these results is that the entity exhibiting the nmr pattern at +60 ppm consists of a P_4O_{10} birdcage molecule which is solvated at only one of its apices with a carbodiimide molecule. Since there is no coupling between phosphorus and hydrogen, the point of coordination to the carbodiimide must be at the electropositive carbon atom, as indicated in the product of eq 2 in which the formal charges are indicated for one resonance form.



(2)

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Synthesis of Dihydroxycyclopropenone (Deltic Acid)

Sir:

The cyclic oxycarbon anions, $C_nO_n^{m-}$, have been recognized as a series of aromatic compounds,[1] and the unknown deltate dianion (n = 3, m = 2) has been predicted to have an exceptionally high delocalization energy per π-electron.[2]