

tion with iodine and following injection of phthalic anhydride yielded essentially the same rate of loss of the absorbing species. Measurements at 302 $m\mu$ yielded excellent linear semilogarithmic plots against time with a half-life of 69 sec in both instances. This is in good agreement with the hydrolytic rate of phthalic anhydride previously observed in this laboratory.⁴

Although both spontaneous⁵ and catalyzed formation⁶ of acid anhydrides in aqueous solution have been demonstrated, the equilibrium concentrations of these unstable species are usually quite low. In the present instance the deficit in free energy has been provided through coupled oxidation of a sulfur-containing compound.

Since it has already been shown that the anhydride character of cyclic dicarboxylic anhydrides can be rapidly and readily interconverted to other forms of high-energy species including acylimidazole⁷ and acyl phosphate in aqueous solution,⁴ it is evident that mechanisms of this type can play a significant role in biochemical energy transfer.

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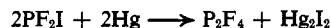
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Diphosphorus Tetrafluoride and Diphosphorus Oxytetrafluoride¹

Sir:

Although diphosphorus tetrachloride and diphosphorus tetraiodide have been prepared, the corresponding fluoride is unknown. A report concerning its possible existence has appeared,² but little evidence was given. We have now obtained diphosphorus tetrafluoride, P_2F_4 , in yields up to 85% by the reaction of phosphorus(III) iododifluoride³ with mercury at ambient temperature.



Purification of the product was accomplished by fractionation through -95 , -135 , and -196° cold traps. The product was retained in the trap set at -135° .

Characterization of P_2F_4 was accomplished by elementary analysis (*Anal.* Calcd for P_2F_4 : P, 44.9; F, 55.1. Found: P, 44.1; F, 53.8), vapor density molecular weight [138.7 g/mole (calcd for P_2F_4 , 138.0)], melting point ($-86.5 \pm 0.5^\circ$), boiling point ($-6.2 \pm 0.4^\circ$), Trouton constant (22.11 eu), and heat of vaporization (5.90 kcal/mole). The vapor pressure data follow the equation $\log p = (-1290/T) + 7.716$. In addition the mass cracking pattern is also consistent with its formulation as P_2F_4 and contained the following major peaks given as mass number (species) and relative abundance: 31 (P^+), 7.7; 50 (PF^+), 15.9; 69 (PF_2^+), 100.0; 119 ($P_2F_3^+$), 6.9; and 138 ($P_2F_4^+$), 27.0. The peak due to the parent molecule ion is considerably stronger in

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the pattern of P_2F_4 than it is in that of N_2F_4 . In fact, under the experimental conditions used, the spectrum of N_2F_4 has no parent peak. This has been attributed to the facile dissociation of N_2F_4 into NF_2 radicals.⁴ The contrasting behavior of P_2F_4 is perhaps indicative of its greater P-P bond strength than the N-N bond energy found in N_2F_4 . The infrared spectrum of P_2F_4 contains absorptions at 842 (s), 830 (vs) and 820 (s) (P-F str), 408 (vw), and 356 cm^{-1} (w). The ^{19}F nmr spectrum taken at room temperature in CCl_3F solvent is complex and symmetric and is centered at ϕ 115.2. The spectrum is currently being analyzed as an $A_2A_2'XX'$ system.

A side product formed in small yield in the preparation of P_2F_4 has tentatively been identified as diphosphorus oxytetrafluoride, PF_2OPF_2 , by its vapor density molecular weight [153.0 (calcd for P_2F_4O , 154.0)], infrared spectrum [bands at 1081 (w), 971 (vs) (P-O-P asym str), 850 (vs, broad) (P-F str), 678 (m) (P-O-P sym str), 518 (m), 459 (w), and 353 cm^{-1} (w)], and mass spectrum [major absorptions at 31 (P^+), 2.7; 47 (PO^+), 28.3; 50 (PF^+), 13.1; 66 (POF^+), 2.8; 69 (PF_2^+), 100.0; 85 (POF_2^+), 2.6; 88 (PF_3^+), 2.9; 135 (PF_2OPF^+), 1.1; 154 ($PF_2OPF_2^+$), 16.7]. The same compound can be also prepared directly in a 67% yield by reaction between P_2F_4 and oxygen.

Acknowledgment. This work was carried out under Army Ordnance Contract No. DA-01-021 AMC-11536 (Z).

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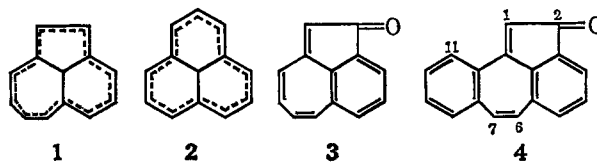
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2H-Dibenz[*c,d,h*]azulen-2-one

Sir:

Preparative pathways have been recently opened¹ to benz[*c,d*]azulenyl (1), a theoretically interesting² non-alternant analog of the phenalenyl system 2. Yet unknown is 2H-benz[*c,d*]azulen-2-one (3), analogous to phenalene, the unusually basic and polarized ketone with a key role in phenalene chemistry.³



Now we find 2H-dibenz[*c,d,h*]azulen-2-one (4) to be accessible by facile Friedel-Crafts cyclization. 5 (mp 103°), prepared from 5H-dibenzo[*a,d*]cyclohepten-5-one by the Reformatsky sequence, is added at -10° to 2 moles of $AlCl_3$ in CS_2 and the violet complex decomposed (0° , 2 *N* HCl, light excluded) to yield, almost

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