with an isomeric ion which reacts much more rapidly with hydroxide ion than I itself.

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(10) Alfred P. Sloan Research Fellow.

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Acylation through a Sulfonium Ion Intermediate. Coupled Conversion of a Carboxylic Acid to an Acid Anhydride during Oxidation of a Thioether to a Sulfoxide[1]

Sir:

Earlier studies in our laboratory had suggested that oxidation of thioethers in the presence of aqueous phosphate buffer may be mediated by formation of an energetic phosphate bond.[2] The catalytic role has also been observed for a series of carboxylate species especially among those capable of forming a ring structure.[3] We wish to present direct evidence which strongly suggests that the energy derived from oxidation of alkyl sulfides to sulfoxide can drive such dicarboxylic acids to their more energetic anhydride form.

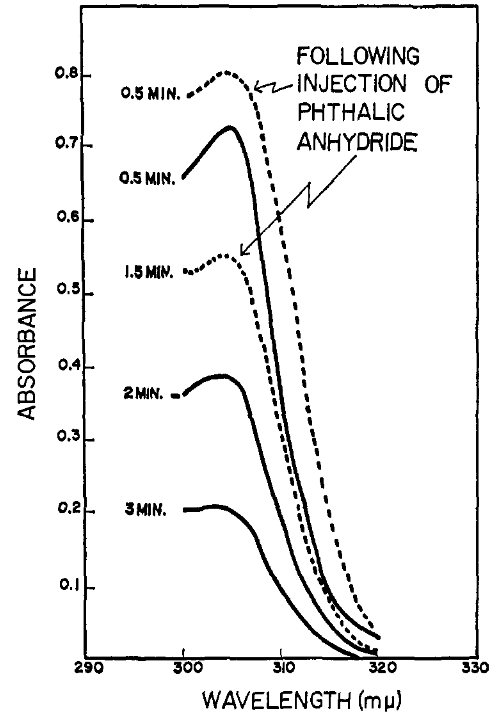
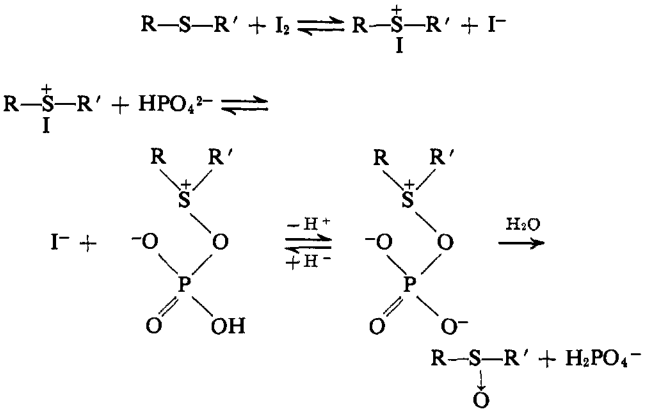
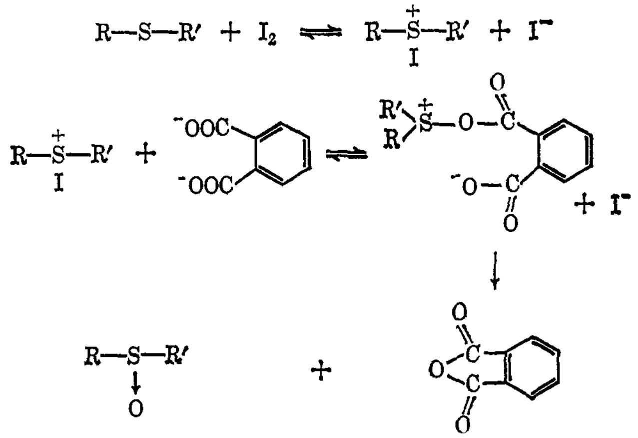


Figure 1. Comparison of spectra shown as solid lines obtained following injection of iodine into an aqueous solution of tetramethylene sulfide in phthalate buffer with spectra shown as dotted lines obtained by direct injection of a stoichiometrically equivalent amount of phthalic anhydride in dioxane into a comparable system. The change in spectra with time is assumed to be due to the hydrolysis of phthalic anhydride. In both instances the phthalate buffer concentration was 0.06 *M* at pH 5.1. Approximately 7 x 10^{-4} *M* iodine and phthalic anhydride were injected in the respective cases.



$$R{-}S{-}R' + I_2 \rightleftharpoons R{-}\underset{I}{\overset{+}{S}}{-}R' + I^-$$

Thioethers in the absence of catalytic species react exceedingly slowly with iodine. On addition of certain nucleophiles the reaction proceeds very rapidly, apparently involving intermediate formation of acylsulfonium species. Thus in the case where phthalate ion acts as the nucleophile we presume that it is driven to its anhydride through the following sequence.



$$R{-}S{-}R' + I_2 \rightleftharpoons R{-}\underset{I}{\overset{+}{S}}{-}R' + I^-$$

The evidence for formation of the anhydride is based on observation of appearance of a peak at 304 mμ characteristic of phthalic anhydride when tetramethylene sulfide was oxidized with iodine in the presence of 0.06 *M* phthalate buffer (pH 5.1). Although free iodine in the system may be expected to interfere with spectral measurements, the halogen reacts extremely rapidly under these conditions, being essentially all consumed in less than a second. In Figure 1 is shown the spectrum of the solution in the range 300–320 mμ 30 sec after disappearance of added iodine (7 × 10^{-4} *M*), after approximately 2 min, and after 3 min. In the same figure, spectra of only the phthalate buffer containing added sulfide are shown following injection of approximately stoichiometric equivalence of phthalic anhydride (in 40 μl of dioxane) at two time intervals. The general spectral agreement strongly supports the presumed formation of the anhydride.

The identity of the reactive species formed in phthalate buffer during the oxidation of the sulfide to sulfoxide is further supported by the observed hydrolytic rate of the absorbing substance. Spectrophotometric kinetic measurements on these systems following oxida-

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[1] This work was supported in part by grants from the National Institutes of Health (GM-05830 and AM-03437).

[2] T. Higuchi and K.-H. Gensch, unpublished work.

[3] T. Higuchi and K.-H. Gensch, in preparation.

tion with iodine and following injection of phthalic anhydride yielded essentially the same rate of loss of the absorbing species. Measurements at 302 mμ 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 spontaneous[5] and catalyzed formation[6] 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 acylimidazole[7] 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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(5) T. Higuchi, T. Miki, A. C. Shah, and A. Herd, *J. Am. Chem. Soc.*, **85**, 3655, 1963.

(6) T. Higuchi, A. C. Shah, J. McRae, and H. Uno, *ibid.*, in press.

(7) A. Shah, Ph.D. Dissertation, University of Wisconsin, 1965.

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Diphosphorus Tetrafluoride and Diphosphorus Oxytetrafluoride[1]

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) iododifluoride[3] with mercury at ambient temperature.

$$2PF_2I + 2Hg \longrightarrow P_2F_4 + Hg_2I_2$$

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 ($-86.5 \pm 0.5°$), boiling point ($-6.2 \pm 0.4°$), 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 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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(2) D. S. Payne, *Quart. Rev.* (London), **15**, 189 (1961).

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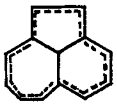
2H-Dibenz[*c*,*d*,*h*]azulen-2-one

Sir:

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



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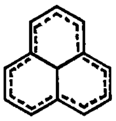

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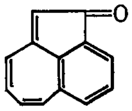

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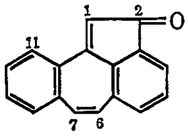

4

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

(1) (a) V. Boekelheide and C. D. Smith, 146th National Meeting of American Chemical Society, Chicago, Ill., Sept 1964, Abstracts of Papers, p 34C; *J. Am. Chem. Soc.*, in press. We thank V. Boekelheide for a manuscript. (b) K. Hafner and H. Schaum, *Angew. Chem. Intern. Ed. Engl.*, **2**, 95 (1963); **3**, 165 (1964).

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(3) D. H. Reid, *Quart. Rev.* (London), **19**, 274 (1965).