$H_8Re_2P_4$[3,4] may be intercepted since it precipitates. We have shown directly that the Re(IV) polyhydride $H_8Re_2P_4$ undergoes facile thermal phosphine-induced reductive elimination of H_2 at 25 °C in benzene, and therefore propose that it, and not $H_6Re_2P_5$, is the first stable dimeric product of photolysis. The reduced polyhydride $H_6Re_2P_5$, whose coordination sphere is shown[10,11] in Figure 1b, is unusual in being a mixed oxidation state species. The metal-metal separation [2.589 (1) Å] is similar to that in $H_8Re_2P_4$ [2.538 (4) Å],[4] in spite of ^1H NMR evidence[12] which indicates $H_6Re_2P_5$ to have one terminal hydride on Re(1), and thus only three μ_2-H ligands.

H_5ReP_2 activates arene C-H bonds. Any of the above irradiations of H_5ReP_3, when carried out in C_6D_6, effects deuteration of the metal in both H_5ReP_3 and the dimeric products. In a competitive process, the aryl ring of the phosphine also undergoes deuteration by D_5ReP_3 during irradiation. This is evident if the photoassisted phosphine exchange experiment described above is performed in C_6D_6: the liberated phosphine appears (^{31}P NMR) as at least two lines of unequal intensity, due to a deuterium isotope effect on the ^{31}P chemical shift (8-Hz upfield at 40 MHz for the ring-deuterated species).[13] Remarkably, ^1H NMR shows that arylphosphine deuteration occurs only at the meta and para positions; no ortho deuteration is detected. This suggests that deuteration of coordinated phosphine is an intermolecular process, in which D_5ReP_2 acts on the aryl ring of D_5ReP_3 as it would on more conventionally substituted arenes.[14]

We are continuing to explore the reactivity of H_5ReP_2 and $H_6Re_2P_5$ as well as the synthetic generality of the concept of photocondensation of polyhydride monomers to polyhydride dimers.

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Supplementary Material Available: A table of atomic positional and thermal parameters (1 page) for $H_6Re_2(PMe_2Ph)_5$. Ordering information is given on any current masthead page.

(10) The two terminal hydride positions shown in Figure 1b were located in a difference Fourier map. We have suspended any search for the remaining four hydridic hydrogens pending a neutron diffraction study.

(11) Crystallographic data (−170 °C): a = 11.737 (3), b = 13.031 (4), c = 15.238 (5) Å; α = 73.39 (1), β = 90.76 (2), γ = 108.16 (1)°; V = 2114.8 Å^3; Z = 2 in space group $P\bar{1}$; $R(F)$ = 3.7%, $R_w(F)$ = 4.1% for 5020 observed [$F_o > 2.3\sigma(F_o)$] reflections using anisotropic thermal parameters for all nonhydrogen atoms; all hydrogens bound to carbon were refined isotropically.

(12) The 360-MHz ^1H NMR spectrum of $H_6Re_2(PMe_2Ph)_5$ in toluene-d_8 shows three hydride resonances at −90 °C: δ −6.30 (br s), −9.75 (t, J = 44.5 Hz), and −10.35 (quartet, J = 45.0 Hz) with intensities of 3:2:1 (integrated relative to the 30 methyl protons). At room temperature these collapse into a single broad resonance at −8.26 ppm.

(13) $P(2,6\text{-}D_2C_6H_3)_3$, kindly supplied by U. Klabunde and G. Parshall, experiences a ^{31}P deuterium isotope effect of 25 Hz (0.6 ppm).

(14) U. Klabunde has informed us of unpublished experiments in which he has observed exchange of D_2 with a variety of arenes catalyzed by $H_5Re(PMe_2Ph)_3$ at 108 °C. A detailed description of related thermal exchanges has been reported for other metal hydride catalysts.[15]

(15) Klabunde, U.; Parshall, G. W. *J. Am. Chem. Soc.* **1972**, *94*, 9081.

(16) Selected distances: Re(1)-P: 2.317 (2), 2.327 (2), and 2.345 (2) Å; Re(2)-P: 2.313 (2) and 2.298 (2) Å. Selected angles: P-Re(1)-P, 102.1-111.6°; P-Re(2)-P, 103.4°; P-Re(1)-Re(2), 104.5-117.5°; P-Re(2)-Re(1), 126.5 and 129.6°.

On the Mechanism of T4 RNA Ligase[1]

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The bacteriophage T4 RNA ligase catalyzes the formation of a 5′-3′-phosphodiester linkage, thereby joining two oligoribonucleotides with the concomitant conversion of ATP to AMP and inorganic pyrophosphate (PP_i).[2] A plausible minimum reaction sequence constructed from the observation of an adenylated enzyme (AMP-ligase)[3] and under certain experimental conditions an adenylated pyrophosphoryl intermediate (App(Np)$_n$)[4] is given in Scheme I, where p(Np)$_n$ represents an oligoribonucleotide where $n \geq 1$ (the 5′-phosphoryl donor) and (Np)$_m$N represents an oligoribonucleotide where $m \geq 2$ (the 3′-hydroxyl acceptor). We have sought the answers to two questions: (1) Is there, possibly for reasons of symmetry, an undetected reaction intermediate involving a covalent bond between the ligase and the donor in the last step of the above sequence? (2) Is there a preferred chirality at phosphorus maintained in the activation and transfer of the 5′-phosphoryl moiety in steps 2 and 3?

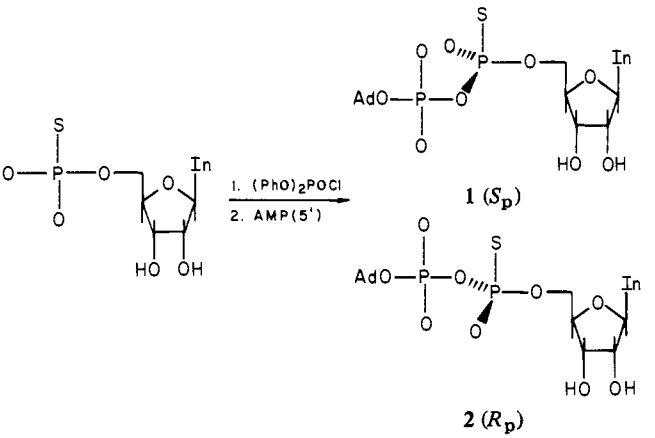
Scheme I

$$\text{ATP} + \text{ligase} \rightleftharpoons \text{AMP-ligase} + PP_i \quad (1)$$

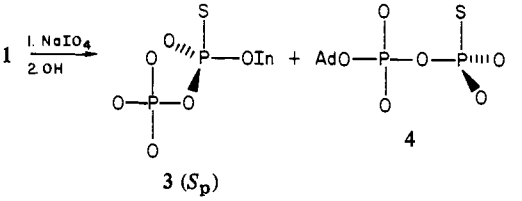
$$\text{AMP-ligase} + p(Np)_n \rightleftharpoons App(Np)_n + \text{ligase} \quad (2)$$

$$App(Np)_n + (Np)_mN \overset{\text{ligase}}{\rightleftharpoons} (Np)_mNp(Np)_n \quad (3)$$

Scheme II



Scheme III



The stereochemical course of step 3 with respect to phosphorus was investigated by using **1** and **2**, which were synthesized as outlined in Scheme II. Activation of inosine 5′-phosphorothioate[5] by diphenyl phosphorochloridate[6] was followed by coupling to adenosine monophosphate to yield **1** and **2** in 44% total yield. These were separated by column chromatography on DEAE-

(1) Supported by Grant No. GM 13306 from the National Institutes of Health.

(2) (a) R. Silber, V. G. Malathi, and J. Hurwitz, *Proc. Natl. Acad. Sci. U.S.A.*, **69**, 3009-3013 (1972); (b) G. K. Kaufmann and N. R. Kallenbach, *Nature (London)*, **254**, 452-454 (1975); (c) G. C. Walker, O. C. Uhlenbeck, E. Bedows, and R. I. Gumport, *Proc. Natl. Acad. Sci. U.S.A.*, **72**, 122-126 (1975).

(3) J. W. Cranston, R. Silber, V. G. Malathi, and J. Hurwitz, *J. Biol. Chem.*, **249**, 7447-7456 (1974).

(4) (a) E. Ohtsuka, S. Nishikawa, M. Sugiura, and M. Ikehara, *Nucleic Acids Res.*, **3**, 1613-1623 (1976). (b) J. J. Sninsky, J. A. Last and P. T. Gilham, *ibid.*, **33**, 3157-3166 (1976).

(5) W. A. Murray and M. R. Atkinson, *Biochemistry*, **7**, 4023-4029 (1968). The desired nucleotide was prepared from adenosine 5′-phosphorothioate by employing adenylic acid deaminase.

(6) A. M. Michaelson, *Biochim. Biophys. Acta*, **91**, 1-13 (1964).

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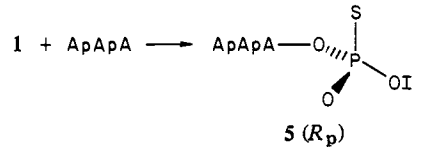
Scheme IV



5 (R_p)

cellulose[7] in >95% isomeric purity.[8]

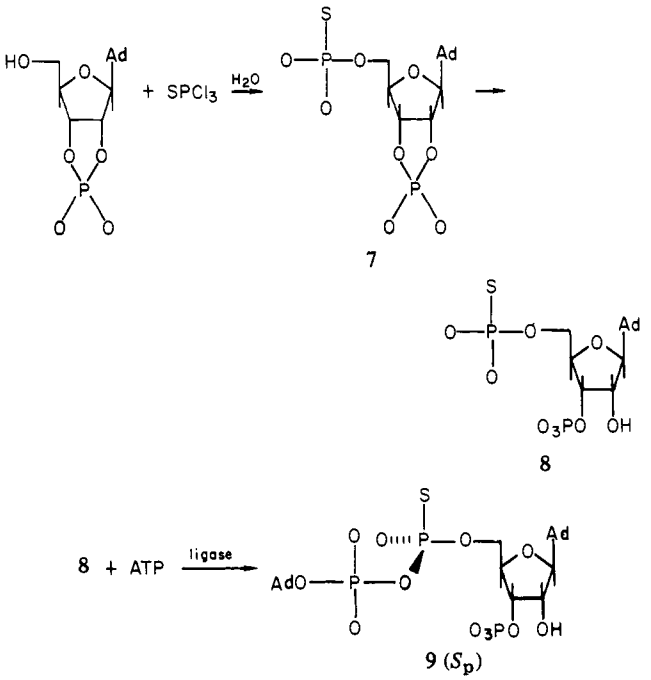
Determination of the absolute stereochemistry at the thiophosphoryl center in **1** and **2** was achieved via the sequence illustrated for **1** in Scheme III. Compounds **3** (IDPαS) and **4** (ADPβS) were cleanly separated by column chromatography on DEAE-Sephadex A-25.[9] The IDPαS derived from **1** was reactive in a pyruvate kinase–lactate dehydrogenase couple whereas the IDPαS derived from **2** was unreactive. Since this enzyme couple is specific for an α-thiophosphoryl of S_p configuration,[10] **1** and **2** have absolute configurations as written. The design of **1** and **2** was predicated by earlier experiments that demonstrated dinucleotide pyrophosphates would substitute for App(Np)$_n$ in step 3 of Scheme I and that AMP is strongly favored as the leaving group.[11]

Incubation of either **1** or **2** in the presence of ApApA and ligase at pH 8.3[11] revealed that **1** but not **2** yielded the oligoribonucleotide product, ApApAp(S)I (**5**). The product was isolated on DEAE-Sephadex A-25[12] and identified by UV spectroscopy [λ_{max} 255 nm, λ_{max} (predicted) 254.9 nm], position of elution, and digestion by spleen diesterase which gave 3′-AMP and Ap(S)I.[13] The absolute stereochemistry of the thiophosphoryl linkage was established by its cleavage in the presence of venom phosphodiesterase at a rate comparable to that for Ap(S)A (R_p).[14] Under identical conditions the Ap(S)A (S_p) dinucleotide was not degraded. Since the stereochemistry of **5** is R_p at the Ap(S)I linkage, step 3 of the ligase reaction proceeds with inversion of configuration and is consistent with a direct displacement process (Scheme IV).

The stereochemical course of step 2 was traced by employing p(S)Ap (**8**)—step 2 requires a 3′-phosphate when n = 1[15]—synthesized from cyclic 2′,3′-AMP and thiophosphoryl chloride[16] followed by acid hydrolysis (0.1 M HCl) to give a mixture of 2′ and 3′ isomers.[17] Incubation of the mixture (2′ isomer is noninhibitory) in the presence of ligase and ATP, pH 7.2,[18] proceeds to form App(S)Ap (**9**) as shown in Scheme V.

The structure of **9** was inferred by alkaline phosphatase catalyzed hydrolysis to App(S)A, which was isolated by DEAE-Sephadex A-25 column chromatography.[19] The absolute stereochemistry of App(S)A was obtained by comparison to authentic samples obtained via Scheme II except with adenosine substituted for inosine and shown to have the S_p configuration.[20] Thus the

Scheme V



absolute configuration at the reacting phosphoryl center is the same in both steps.

The ligation in step 3 is identical in terms of its inversion stereochemical course with other displacements at phosphoric diesters[21] with the exception of the retention stereochemistry noted for venom[14,22] and intestinal phosphodiesterases.[23] Moreover the S_p absolute configuration at the thiophosphoryl center is generally preferred in reactions that maintain a diester linkage after the displacement. These results suggest the possibility of common active-site and mechanistic features linking polymerization, ligation, and transfer reactions. The ability to introduce a thiophosphoryl center into RNA also should furnish us with a sensitive probe of RNA structure.

Acknowledgment. We thank Professor O. Uhlenbeck for his advice and generous gift of T4 RNA ligase.

(7) Separated by a linear gradient (0.1–0.5 M) of $(NH_4)HCO_3$. For resolution of the isomers a second column employing a similar gradient was required.

(8) **1** (S_p): δ(PS) 44.0, δ(PO) −11.2 downfield from H_3PO_4. **2** (R_p): δ(PS) 44.2, δ(PO) −11.2 downfield from H_3PO_4. J_{PS-PO} = 28.5 ± 1 Hz for both compounds. λ_{max} 252 nm (ϵ 21 300) for **1** and **2**.

(9) Separated by a linear gradient (0.1–0.85 M) of $[(C_2H_5)_3NH]HCO_3$. Peak assignments were based on λ_{max} 248 nm for **3** and λ_{max} 258 nm for **4**. Compound **3** gave a single spot on TLC (poly(ethylenimine)–cellulose) eluted with 0.75 M KH_2PO_4, pH 3.5.

(10) F. Eckstein and R. S. Goody, *Biochemistry*, **15**, 1685–1691 (1976). We are presuming the substitution of inosine for adenosine does not alter the enzyme couple's specificity.

(11) T. E. England, R. I. Gumport, and O. C. Uhlenbeck, *Proc. Natl. Acad. Sci. U.S.A.*, **74**, 4839–4842 (1977).

(12) A linear gradient (0.1–0.9 M) of $[(C_2H_5)_3NH]HCO_3$ was employed.

(13) These products were chromatographed by TLC (poly(ethylenimine)–cellulose) eluted with 0.75 M KH_2PO_4, pH 3.5, and compared to standards.

(14) F. R. Bryant and S. J. Benkovic, *Biochemistry*, **18**, 2825–2828 (1979).

(15) (a) Y. Kikuchi, F. Hishinuma, and K. Sakaguchi, *Proc Natl. Acad. Sci. U.S.A*, **75**, 1270–1273 (1978). (b) T. E. England and O. C. Uhlenbeck, *Biochemistry*, **17**, 2069–2076 (1978).

(16) **7**: δ(PS) 43.2; δ(PO) 19.2 downfield from H_3PO_4.

(17) Alternatively, digestion of **7** with RNase T_2 yields only the 3′ isomer.

(18) O. Uhlenbeck, personal communication.

(19) A linear gradient (0.1–0.7 M) of $(NH_4)HCO_3$ was used.

(20) S_p, δ(PS) 43.3, δ(PO) −11.9 downfield from H_3PO_4 for **1** where inosine is replaced by adenosine. R_p, δ(PS) 43.6, δ(PO) −11.9 downfield from H_3PO_4 for **2** where inosine is replaced by adenosine. J_{PS-PO} = 27.7 ± 2 Hz for both compounds. The diastereomers were identified by comparing these parameters with the parameters previously reported by Richards, J. P., et al. [*J. Am. Chem. Soc.*, **100**, 7756–7757 (1978)] and with those reported for the S_p and R_p diastereomers of **1** and **2** in ref 8.

(21) J. R. Knowles, *Annu. Rev. Biochem.*, **49**, 877–919 (1980).

(22) P. M. J. Burgers, F. Eckstein, and D. H. Hunneman, *J. Biol. Chem.* **254**, 7476–7478 (1979).

(23) F. R. Bryant, J. F. Marlier, and S. J. Benkovic, "Phosphorus Chemistry Directed Towards Biology", W. J. Stec, Ed., Pergamon Press, Oxford, 1980, pp 129–131.

Mechanistic Photochemistry of Acylsilanes. 1. Reaction with Alcohols

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In recent years the exploratory photochemistry of acylsilanes (α-silyl ketones) has generated considerable interest.[1-3] Brook

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