be obtained from the amount of CH_3Br formed in the vessel during photolysis, combined with the known value of 0.1 for the rate constant ratio for methyl radical reaction with HBr and Br_2.[12] In photolyses lasting 1 min, about 20% of the TBr was decomposed, and the final ratio of CH_3Br to Br_2 was between 1 and 5 $\times$ 10^{-3}. The conversion of TBr to CH_3T by methyl radicals would be less by at least a factor of 10, and would therefore represent not more than 1–5 $\times$ 10^{-4} of the total TBr present and could not account for the $>10^{-2}$ actually converted to CH_3T.[13]

The relative yields of HT and CH_3T indicate that the abstraction reaction proceeds with a higher relative yield than the substitution reaction, when suitably averaged over the energy range from 3 ev down to thermal energies. This is not surprising, since the activation energy for the abstraction reaction is certainly lower than that of the substitution reaction. Since the total yields of hot reaction measured by Martin and Willard[3] are only 17% for 3-ev D atoms reacting with CH_4, as compared to the yields of approximately 50% for the sum of the abstraction and substitution products from recoil tritium reactions,[5–7] it is clear that a substantial fraction of the reactions of both substitution and abstraction occurs at energies above 3 ev. Crude estimates from the 3.5–4.0 ratio below 3 ev and 0.8 ratio for the entire range suggest that approximately 90% of the substitution reactions and 40% of the abstraction reactions occur at energies above 3 ev.[14] The estimates for ethane are similar.

(12) G. B. Kistiakowsky and E. R. Van Artsdalen, *J. Chem. Phys.,* **12**, 469 (1944).

(13) The measured CH_3Br yield probably arises chiefly or entirely from photolytic reactions of molecular bromine, and hence leads to a great overestimate of the extent of methyl radical reaction in the system; see T. A. Gover and J. E. Willard, *J. Am. Chem. Soc.*, **82**, 3816 (1960), for the reactions of I_2^* in similar systems.

(14) This estimate is based on the fragile assumption that the 17% hot yield with CH_4 below 3 ev will be the same for energetic D and T atoms. This assumption is almost certainly not quantitatively accurate but may not be too much in error. Measurement of the total hot yield in our system has not yet been performed, largely because of the uncertainties introduced through the use and handling of carrier-free TBr.

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The Preparation of Triphosphine.
An Intermediate in the Pyrolysis of Diphosphine

Sir:

It has been suggested[1] that hydrides of phosphorus containing three or more phosphorus atoms may exist. Presently, however, phosphine (PH_3) and diphosphine (P_2H_4) are the only stable hydrides well known.[1–3] In this communication we report the preparation and initial characterization of a phosphorus hydride containing three atoms of phosphorus.

Evidence for triphosphine was first uncovered during a mass spectrometric examination of the pyrolysis of diphosphine.[4] Briefly these experiments consisted of

(1) J. R. Van Wazer, "Phosphorus and Its Compounds," Vol. 1, Interscience Publishers, Inc., New York, N. Y., 1958, p 217.

(2) E. C. Evers and E. H. Street, Jr., *J. Am. Chem. Soc.*, **78**, 5726 (1956).

(3) The Raman spectrum of pyrolyzed diphosphine suggests the presence of higher hydrides of phosphorus; however, none were isolated and characterized: M. Baudler and L. Schmidt, *Naturwissenschaften,* **46**, 577 (1959).

pumping diphosphine through an electrically heated tubular flow reactor and examining the efflux of the reactor mass spectrometrically.[5] At pressures of *ca.* 0.1 torr and speeds of *ca.* 0.02 l./sec, the efflux of the reactor consisted of P_2H_4, P_2H_2, and PH_3 as shown by appearance potential measurements and by the change in the relative ionic abundances with reactor temperature.[4] At pressures of *ca.* 0.5 torr and speeds of *ca.* 10^{-4} l./sec, ions containing three phosphorus atoms and up to five hydrogen atoms were just detectable.[6] Further characterization with this apparatus was prevented by the inability to produce more than trace quantities of this substance.

However, it was felt that a triphospine might be stable enough to be prepared in macroquantities. Consequently a hot–cold reactor was constructed.[7] The inner tube was maintained at a temperature of 65–70° while the outside tube was immersed in a cold bath at $-63°$, a temperature at which diphosphine has a vapor pressure of 2 mm^2. In a typical preparation diphosphine, which was prepared in a mercury-free system by the hydrolysis of calcium phosphide[2] and which was purified by trap-to-trap distillation, was held in the annular space between the two tubes (*i.e.*, pyrolyzed) for 1 hr under the above conditions. Roughly half the diphosphine decomposed into phosphine and a white solid (at $-63°$). Phosphine and diphosphine were distilled away; the hot bath was removed and the white solid sublimed out at $-23°$. On warming, this product decomposed before or during melting into a yellow solid while giving off phosphine in the process.[8] Fortunately the white solid had sufficient vapor pressure and stability at $-23°$ for the mass spectrum to be obtained.[9] A partial mass spectrum at 70 ev of the vapor over the purified product at $-23°$ is given in Table I.[10]

The neutral progenitor of the $P_3H_x^+$ ions contains three phosphorus atoms as no ions with leak-dependent intensities were observed above mass 98.[11] Also samples known to contain P_2H_4 were examined and the ratio of the intensities of $P_3H_x^+$ and $P_2H_x^+$ varied accordingly. Further, the $P_3H_x^+$ ions are assigned to the P_3H_5 molecule for the following reasons. First the ion of highest mass corresponds to $P_3H_5^+$, and as PH_3, P_2H_4, P_2H_2, and P_2H_3 produce parent ions of substantial intensity[4,12] one might expect the same behavior for a triphosphine. Second, the appearance potential of

(4) T. P. Fehlner, *J. Am. Chem. Soc.*, **88**, 1819 (1966).

(5) The technique used incorporated a collision-free sampling system capable of strong discrimination against products of decomposition in the source and other background effects; see, for example, S. N. Foner and R. L. Hudson, *J. Chem. Phys.*, **21**, 1374 (1953).

(6) Approximately 0.1% of the $P_2H_4^+$ intensity.

(7) M. J. Klein, B. C. Harrison, and I. J. Solomon, *J. Am. Chem. Soc.*, **80**, 4149 (1958).

(8) Shown mass spectrometrically.

(9) A Bendix Model 12-107 time-of-flight mass spectrometer with conventional sampling was used to obtain the following data. Because of the characteristics of this compound the advantage of rapid acquisition of data outweighed the advantages of collision-free sampling.

(10) Ion masses were obtained by counting background peaks from a known ion peak. The ion intensities contained in Table I were dependent on the leak setting and were a linear function of the pressure. With the exception of small amounts of P_4^+ and P_3^+, no ions whose intensity was dependent on the leak setting were observed at masses greater than m/e 66 when pure P_2H_4 is introduced into the spectrometer. Consequently, the ions contained in Table I are not due to pyrolysis of diphosphine in the source.

(11) See also ref 10.

(12) The mass spectrum of diphosphine is given in Y. Wada and R. W. Kiser, *Inorg. Chem.*, **3**, 174 (1964).

Table I. Relative Abundances of the $P_3H_x^+$ and $P_2H_x^+$ Ions from P_3H_5

Ion mass	Rel abundance at 70 ev
98	100
97	3
96	4
95	7
94	11
93	54
66	72[a]
65	29[a]
64	61[a]
63	67[a]
62	88[a]

[a] Contribution due to P_2H_4 unknown.

$P_3H_5^+$ was found to be 0.3 ± 0.2 ev less than the appearance potential of $P_2H_4^+$ from diphosphine ($I(P_3H_5)$ = 9.1 ev, $I(P_2H_4)$ = 9.4 ev).[13] One would expect the ionization potential of P_3H_5 to be slightly less than that of P_2H_4, whereas if $P_3H_5^+$ were a fragment ion a higher appearance potential might well be expected. Finally, the intensity of $P_2H_3^+$ is substantial even if one assigns $P_2H_4^+$ completely to P_2H_4.[12] If the triphosphine is P_3H_5, the simple loss of a PH_2 group from $P_3H_5^+$ would yield $P_2H_3^+$. Thus the intensity of $P_2H_3^+$ is also consistent with this interpretation.

On the basis of these experiments it is concluded that triphosphine, P_3H_5, is formed during the pyrolysis of diphosphine. Not only does the formation of this compound point out an additional step in the net pyrolytic reaction to produce PH_3 and the polymer P_2H,[2] but it also should provide a means to obtain further insight into the chemistry of the hydrides of phosphorus.

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(13) The method used is given in S. N. Foner and R. L. Hudson, *J. Chem. Phys.*, **25**, 602 (1956).

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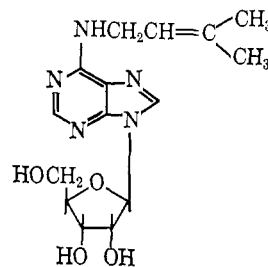*Received April 4, 1966*

Isolation of N^6-(γ,γ-Dimethylallyl)adenosine from Soluble Ribonucleic Acid[1]

Sir:

We wish to report the isolation of a nucleoside from yeast soluble ribonucleic acid (s-RNA) which has been

identified as 6-N-(3-methyl-2-butenylamino)-9-β-D-ribofuranosylpurine (I). Soluble RNA was extracted from Bakers' yeast according to the method of Holley.[2]

I

The s-RNA was hydrolyzed enzymically to its constituent nucleosides and this mixture was resolved by means of partition chromatography on columns.[3] The separated nucleoside was crystallized from acetonitrile–ethanol, 3:1; mp 139°. The crystalline product was homogeneous when chromatographed in solvent systems A–E listed in ref 3. Fifteen milligrams was obtained from 60 g of s-RNA; $[\alpha]^{25}_{546}$ −100° (c 0.07, ethanol). *Anal.* Calcd for $C_{15}H_{21}N_5O_4$ (mol wt 335.4): C, 53.72; H, 6.31; N, 20.89. Found: C, 53.68; H, 6.25; N, 20.36. The ultraviolet absorption spectra [$\lambda^{pH\ 1}_{max}$ 265 mμ (ϵ 20,300), $\lambda^{pH\ 7-12}_{max}$ 269 mμ (ϵ 19,900)] are indicative of an N^6-(alkyl-substituted) adenosine. The nmr spectrum obtained in deuterated acetone–deuterium oxide solution exhibited the basic pattern associated with adenosine and in addition showed the following peaks: a split peak at δ 1.75 integrating for six protons (two vinyl methyl groups), a multiplet centered at δ 5.4 integrating for one proton (vinyl proton), and a multiplet centered at δ 4.2 integrating for three protons which presumably is due to the methylene group attached to N^6 and the C_4 proton of ribose. The mass spectrum of this compound showed a parent peak at m/e 335 and significant peaks at m/e 292 and at 203 (free base). There are also prominent peaks at m/e 188, 160, 148, 136, and 135 (adenine), and this general fragmentation pattern is identical with that reported for 6-N-(4-hydroxy-3-methyl-2-butenylamino)purine.[4] All of these data are consistent with the assignment of structure I to the isolated natural product.

In order to provide direct confirmation of this structure assignment, we synthesized compound I. β,β-Dimethylacrylonitrile[5] was reduced with lithium aluminum hydride to afford γ,γ-dimethylallylamine, bp 110° (reported 110.5°).[6] The amine was condensed with 6-chloro-9-β-D-ribofuranosylpurine[7] in refluxing ethanol to yield (96%) a product which after three crystallizations from acetonitrile–ethanol (3:1) gave white needles, mp 145–147°; $[\alpha]^{25}_{546}$ −97° (c 0.07, ethanol). *Anal.* Found: C, 53.50; H, 6.36; N, 21.01. Ultraviolet spectra showed $\lambda^{pH\ 1}_{max}$ 265 mμ

(2) R. W. Holley, *Biochem. Biophys. Res. Commun.*, **10**, 186 (1963).
(3) The hydrolysis and isolation method has been described previously: R. H. Hall, *Biochemistry*, **4**, 661 (1965). Compound I was found in the fraction corresponding to peak 1, Figure 1, of this reference.
(4) D. S. Letham, J. S. Shannon, and I. R. McDonald, *Proc. Chem. Soc.*, 230 (1964).
(5) K & K Laboratories, Inc.
(6) D. Semenow, C.-H. Shih, and W. G. Young, *J. Am. Chem. Soc.*, **80**, 5472 (1958).
(7) This sample was generously supplied by the Cancer Chemotherapy Service Center of the National Cancer Institute, U. S. Public Health Service.