formation of tris(diphenylphosphino)-phosphine *(1a)* and -arsine *(1b)* or tris(diphenylarsino)-phosphine *(1c)* and -arsine *(1d)*, respectively:

$$[(CH_3)_3Sn]_3R + 3\,(C_6H_5)_2XCl \rightarrow \begin{matrix}(C_6H_5)_2X\\ \diagdown\\ R\\ \diagup\\ X(C_6H_5)_2\end{matrix}\;\; + 3\,(CH_3)_3SnCl$$

(1)

	X	R	M.p. (°C)	Yield (%)
(a)	P	P	118–120	85
(b)	P	As	120–123	59
(c)	As	P	169–172	60
(d)	As	As	143–147	51

After being stirred for 6 h the ethereal solutions were evaporated in a vacuum, and the products were precipitated by addition of pentane. Trimethyltin chloride can be isolated in quantitative yield from the filtrate. The compounds *(1a)–(1d)*, obtained in pure form after repeated reprecipitation from ether/pentane, are extremely sensitive to oxygen and decompose with yellow coloration immediately on access to air; after decomposition of *(1a)*, triphenylphosphine, tetraphenyldiphosphine, and yellow phenylphosphine $(C_6H_5P)_n$ were isolated.

Analogously, reaction of diphenylphosphorus chloride or diphenylarsenic chloride with phenyl bis(trimethylstannyl)-phosphine or phenylbis(trimethylstannyl)arsine[3] afforded syntheses of the new compounds bis(diphenylarsino)phenylphosphine *(2a)*, bis(diphenylphosphino)phenylarsine *(2b)*, and bis(diphenylarsino)phenylarsine *(2c)*; reaction of diphenylphosphorus chloride with diphenyl(trimethylstannyl)-arsine gave (diphenylphosphino)diphenylarsine *(3)*:

$$[(CH_3)_3Sn]_2RC_6H_5 + 2\,(C_6H_5)_2XCl \rightarrow \begin{matrix}(C_6H_5)_2X\\ \diagdown\\ R\\ \diagup\\ C_6H_5\end{matrix}\;\; + 2\,(CH_3)_3SnCl$$

(2)

	X	R	M.p. (°C)	Yield (%)
(a)	As	P	155–158	90
(b)	P	As	125–129	66
(c)	As	As	185–190	65

$$(CH_3)_3Sn{-}As(C_6H_5)_2 + (C_6H_5)_2PCl \rightarrow (C_6H_5)_2P{-}As(C_6H_5)_2 + (CH_3)_3SnCl$$

(3), m.p. 115–117 °C, yield 71 %

The properties of compounds *(2a)–(2c)* and *(3)* are the same as those of three-fold substituted phosphines and arsines, but the sensitivity to oxygen decreases in the order $RX_3 \rightarrow RX_2 \rightarrow RX$, also with increasing substitution of the central atom R by phenyl groups.

In the pure state all the compounds are colorless crystalline substances that are found to dissolve without decomposition in diethyl ether, cyclohexane, and aromatic hydrocarbons. Their structures were proved by complete elemental analyses, cryoscopic determinations of molecular weight, and IR spectra[4]. In the IR spectra are found, not only the vibration bands of the phenyl nuclei dependent on the P and As substituents, but also the bands required by the C_{3v} symmetry $\nu_{as}RX_3$ and ν_sRX_3 at 486 and 427 cm^{-1} *(1a)*, 357 and 280 cm^{-1} *(1b)*, 311 and 274 cm^{-1} *(1c)*, and 285 and 262 cm^{-1} *(1d)*, the bands required by the C_{2v} symmetry $\nu_{as}RX_2$ and ν_sRX_2 at 354 and 282 cm^{-1} *(2a)*, 311 and 293 cm^{-1} *(2b)*, and 293 and 262 cm^{-1} *(2c)*, as well as the bands required for the C_s symmetry ν P–As at 353 cm^{-1} *(3)*.

Received: December 1, 1967. Revised: December 15, 1967 [Z 693 IE]
German version: Angew. Chem. *80*, 240 (1968)

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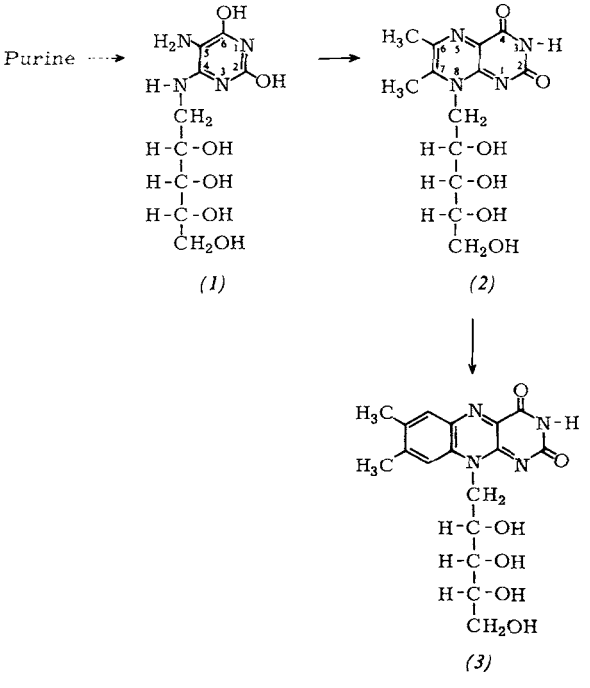
Accumulation of 2,5-Diamino-6-hydroxy-4-ribityl-aminopyrimidine in a Riboflavin-deficient Mutant of *Saccharomyces cerevisiae*

By *A. Bacher* and *F. Lingens*[*]

The biosynthesis of riboflavin *(3)* leads from a purine compound[1] by way of several intermediates to 5-amino-2,6-dihydroxy-4-ribitylaminopyrimidine *(1)*[2] and then to 6,7-dimethyl-8-rityllumazine *(2)*[3]. 4,5-diaminopyrimidine compounds were expected to be precursors of *(1)*.



(1) *(2)* *(3)*

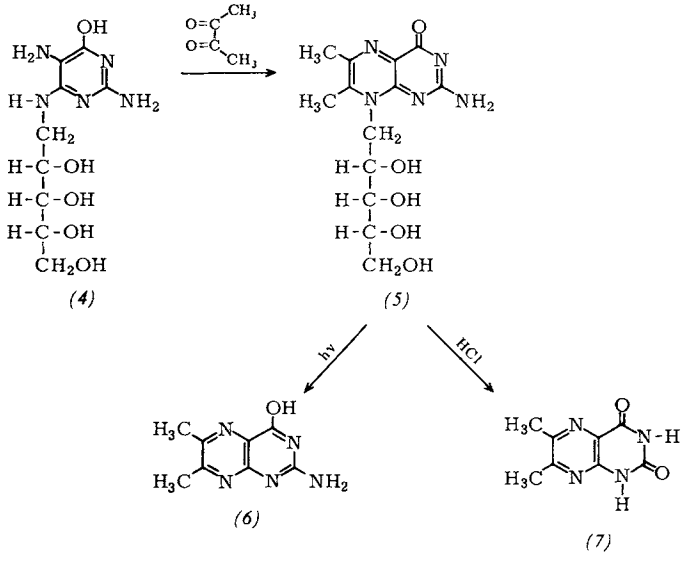
We have shown that a riboflavin-deficient mutant of *Saccharomyces cerevisiae*, HK 859[4], forms an intensely blue-green fluorescing compound on incubation in minimal medium supplemented with biacetyl. This product, which is not formed in absence of biacetyl, was isolated as follows: The yeast was grown in minimal medium[4] supplemented with yeast extract, peptone, and riboflavin, centrifuged off, and incubated with fresh minimal medium containing 0.8 ml biacetyl per liter. The cell-free medium was placed on a column of Magnesiumsilikat "Woelm". The column was washed with deionized water and eluted with acetone/4 N ammonia (2:1). The eluate was evaporated to dryness in a vacuum and placed on a column of Dowex 50Wx 8 (NH_4^+ form). The column was washed with deionized water and

eluted with 0.1 N phosphate buffer (pH = 7). The green-fluorescing fractions were combined and once more adsorbed on Magnesiumsilikat "Woelm" (elution as described above). Further purification was by chromatography on a column of CM-Sephadex C-25 (Na^+ form, elution with distilled water). The green-fluorescing fractions were combined and lyophilized. All operations were conducted in dim light in a darkroom.

The yellow compound thus obtained decomposed in aqueous solution in sunlight with separation of colorless crystals, which were identified as 2-amino-4-hydroxy-6,7-dimethylpteridine *(6)* by comparative thin-layer chromatography with six different solvents. Hydrolysis of the accumulated substance in 6 N HCl at 115 °C (24 h) yielded 6,7-dimethyllumazine *(7)*, which was identified in the same way. The UV spectrum of the accumulated substance closely resembled that of 2-amino-4,8-dihydro-6,7,8-trimethyl-4-oxopteridine. Measurement of the optical rotatory dispersion and the mass spectrum revealed close similarity to 6,7-dimethyl-8-ribityllumazine *(2)*. We thus assign to the accumulated compound the structure 2-amino-4,8-dihydro-6,7-dimethyl-4-oxo-8-ribitylpteridine *(5)*. Compound *(5)* was synthesized[5] and proved identical with the accumulated compound in UV and IR spectra and in R_F values in four different solvents.

These results lead us to the conclusion that the mutant investigated originally accumulates 2,5-diamino-6-hydroxy-4-ribitylaminopyrimidine *(4)*.

We assume that *(4)* or a phosphoric ester of *(4)* is an intermediate in riboflavin biosynthesis and is converted by enzymatic deamination into the 5-amino-2,6-dihydroxy-4-ribitylaminopyrimidine *(1)* previously detected[2]. We further assume that riboflavin is formed from a guanine compound rather than from a xanthine compound as supposed hitherto[6].



(4) *(5)* *(6)* *(7)*

Received: December 5, 1967 [Z 694 IE]
German version: Angew. Chem. *80*, 237 (1968)

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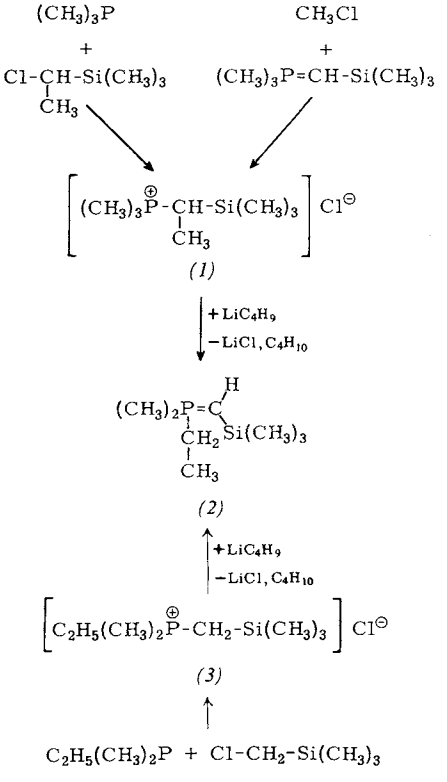
Silyl Shift in Phosphorus Ylides

By *H. Schmidbaur* and *W. Tronich* [*]

The ylide function in trialkylalkylidenephosphoranes is stabilized by silyl residues and destabilized by alkyl residues[1]. While examining the combined effects of silyl and alkyl ligands on an ylide C atom in alkylidenephosphoranes, we discovered a new type of 1,3-silyl shift.

1-(Trimethylsilyl)ethyltrimethylphosphonium chloride *(1)* can be obtained from trimethylphosphine and 1-chloroethyltrimethylsilane under mild conditions (8 days, < 50 °C). The same product is obtainable in quantitative yield from trimethyl(trimethylsilylmethylene)phosphorane[1] and methyl chloride (1 day, −30 °C). Volatile impurities are removed in a vacuum to leave colorless crystals of *(1)*, decomp. 180–185 °C.

Deprotonation of this phosphonium salt *(1)* with *n*-butyllithium at 20 °C in suspension in diethyl ether/*n*-hexane, followed by filtration to remove the precipitated LiCl and distillation under vacuum, surprisingly leads to ethyldimethyl(trimethylsilylmethylene)phosphorane *(2)*, b.p. 83–84 °C/14 torr, m.p. −32 to −30 °C, 65% yield. The structure of *(2)* is established by the ^1H-NMR spectrum[1] and by independent synthesis from ethyldimethylphosphine and chloromethyltrimethylsilane. The structures of *(1)* and *(3)* were also verified by NMR spectroscopy.



(1) *(2)* *(3)*

The formation of *(2)* from *(1)* on deprotonation with n-C_4H_9Li is interpreted as a silyl transfer from an ethyl group attached to phosphorus onto one of the methyl groups at the phosphorus, and corresponds to an exchange of a proton and a trimethylsilyl cation. Experiments with homologous compounds have shown that the silyl shift is a general phenomenon.

Received: January 2, 1968 [Z 701 IE]
German version: Angew. Chem. *80*, 239 (1968)

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