1180^{-1} cm.). The tosylate ester of II is converted by short refluxing in dimethylformamide to an inner salt (m.p. 170–172°; *Anal.* Calcd. for $C_{38}H_{42}N_2O_{10}S \cdot H_2O$: C, 61.93; H, 5.98; N, 3.84. Found: C, 62.23; H, 6.28; N, 3.82, sharp tosyl ion absorption bands at 1010, 1034, 1029 and 1170^{-1} cm.) whose quaternary nature is indicated by the usual criteria.[9] Regardless of whether the tosyloxy group be placed at C-17 or at C-18 in the tosylate ester of II, the hydroxyl function at C-17 must be α-oriented for quaternization to occur by a concerted mechanism. If the tosyloxy group were at C-17, it would be displaced directly by N-4 and if at C-18, by participation of the trimethoxybenzoyloxy group at C-17.

Two pieces of evidence allow a choice of the position of the esterified hydroxyl of raunescine and isoraunescine to be made. However, this point cannot be regarded as established with the same certainty as the structure of the alkanol amine, methyl raunescate. II may be tosylated readily or trimethoxybenzoylated under conditions which will not esterify I. Isoraunescine (II) therefore probably possesses the free hydroxyl in the comparatively less hindered C-18 position. II in distinction to I shows no reserpine-like pharmacological activity. This also points to the presence of a C-18 hydroxyl in II. Unmasking of the C-18 hydroxyl in reserpine by methanolysis yields the inactive methyl reserpate.[10]

[9] P. A. Diassi, F. L. Weisenborn, C. M. Dylion and O. Wintersteiner, THIS JOURNAL, **77**, 2028 (1955).

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RECEIVED NOVEMBER 12, 1956

A FOUR MEMBERED PHOSPHORUS RING[1]

Sir:

The slightly volatile solid compound $(CF_3P)_4$, the first known example of a ring composed of four phosphorus atoms, has been made by three methods: the reaction of CF_3PI_2 with mercury at room temperature, the thermal decomposition of $P_2(CF_3)_4$ to form $(CF_3P)_4$ and $(CF_3)_3P$, and the thermal decomposition of $(CF_3)_2PH$ to form $(CF_3P)_4$ and HCF_3. The second method was fairly successful in a bomb tube at 300°, but since $(CF_3P)_4$ is somewhat unstable at that temperature, it was better to employ an apparatus permitting its removal by condensation from a zone at 350°. Only the latter procedure proved to be suitable for the pyrolysis of $(CF_3)_2PH$, which required 350° for appreciable reaction.

The constitution of $(CF_3P)_4$ was demonstrated by its reaction with iodine, quantitatively reverting to 4 CF_3PI_2. This in turn was converted to nearly $4HCF_3$ by alkaline hydrolysis. The direct alkaline hydrolysis of $(CF_3P)_4$ delivered only half of the CF_3 groups as HCF_3, while the others were partly broken down. Such behavior is consistent with the results of alkaline hydrolysis of $(CF_3)_2PH$ and $P_2(CF_3)_4$.[2] The vapor density of the new compound gave the molecular weight as 402; calcd., 400. The substance melted under its own pressure (51 mm.) at 65°, and the boiling point was estimated from the vapor tensions as 145°; Trouton constant, 22.7 cal./deg. mole. On storage in the vacuum system, the colorless solid varied its crystal form from square plates to long needles, frequently appearing as fairly regular or elongated hexagons (coffin shapes) or striated lozenges.

It is reasonable to suppose that the P_4 ring in $(CF_3P)_4$ is stabilized by extra bonding which involves the lone electron-pair on each P with the 3d orbitals of adjacent P atoms, much as the Cl_2 molecule is stabilized by 3p-3d pi bonding.[3] However, the exact manner of forming these extra bonds cannot be judged until the orientation of the CF_3 groups is known. Accordingly, the geometry of the $(CF_3P)_4$ molecule is being studied by physical methods. Studies of its chemical character also are in progress.

There are indications that higher $(CF_3P)_x$ polymers occurred as by-products, and these are being sought, as a part of a fuller study of the consequences of P-P bonding. The trimer is not expected for reasons of bond-strain, and the dimer would require 3p-3p pi bonding, which is not favored.[4,5] For this reason we suggest that the compound originally called "phosphobenzol," and formulated as $C_6H_5P{=}PC_6H_5$,[6] actually has a polymeric ring structure analogous to that of $(CF_3P)_4$.

[1] This research was supported by the United States Air Force under Contract AF 33(616)-2743, monitored by the Materials Laboratory, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio.

[2] F. W. Bennett, H. J. Emeléus and R. N. Haszeldine, *J. Chem. Soc.*, 3896 (1954).

[3] R. S. Mulliken, THIS JOURNAL, **77**, 885 (1955).

[4] K. S. Pitzer, *ibid.*, **70**, 2140 (1948).

[5] R. S. Mulliken, *ibid.*, **72**, 4493 (1950).

[6] H. Köhler and A. Michaelis, *Ber.*, **10**, 812 (1877).

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RECEIVED NOVEMBER 21, 1956

INVESTIGATIONS ON LIGNIN AND LIGNIFICATION. XVIII. INCORPORATION OF *p*-HYDROXYPHENYLPYRUVIC ACID INTO LIGNIN

Sir:

The detection of *p*-hydroxybenzaldehyde among the oxidation products of several native and enzymatically liberated lignins[1,2] necessitates a revision of some oft-quoted theories of the mechanism of lignin formation. After absorption of specifically C^{14}-labeled shikimic acid into a sugar cane plant, it was established that this compound was incorporated into the lignin.[3] Degradation of the lignin, *via* vanillin, revealed that the distribution of activity in the aromatic ring of vanillin was comparable to the distribution of activity in the ring of the incorporated shikimic acid. Hence, it was concluded that shikimic acid is an intermediate on the pathway to the aromatic rings of the lignin building stones.[3]

[1] F. F. Nord and G. De Stevens, *Die Naturwissenschaften*, **39**, 479 (1952).

[2] G. De Stevens and F. F. Nord, *Proc. Natl. Acad. Sci.*, *U. S.*, **39**, 80 (1953).

[3] G. Eberhardt and W. J. Schubert, THIS JOURNAL, **78**, 2835 (1956).

During the course of related investigations on the biogenesis of methyl *p*-methoxycinnamate by the mold *Lentinus lepideus*,[4] there were detected in the culture medium shikimic acid and five keto-acids, including *p*-hydroxyphenylpyruvic acid. The structural relationship of this acid to the suggested building stones of lignin, namely, coumaryl alcohol, coniferyl alcohol and sinapyl alcohol, prompted an investigation of the possible role of this acid in the mechanism of lignification.

p-Hydroxyphenylpyruvic acid-$C^{14}OOH$ was prepared by an azlactone synthesis[5] employing *p*-hydroxybenzaldehyde and tagged acetyl glycine, which in turn was prepared by acetylation of glycine-1-C^{14} (obtained from Tracerlab, Inc., Boston, Mass.). The resulting azlactone of 4-acetoxy-α-acetamidocinnamic acid was hydrolyzed to 4-acetoxy-α-acetamido cinnamic acid, and this in turn was hydrolyzed by the standard method[5] to *p*-hydroxyphenylpyruvic acid, m.p. 218–220°.

Anal. Calcd.; C, 60.00; H, 4.44. Found: C, 59.44; H, 4.53.

76 mg. of the tagged acid was diluted with 54 mg. of "cold" compound, and the mixture was dissolved in water. An equimolar amount of KH_2PO_4 was added, and the whole was brought to 50 ml. The solution was divided into six aliquots of 8.33 ml. each, which were placed in individual test tubes.

The six uppermost leaves of a mature sugar cane plant (*Saccharum officinarum*) were cut about six inches from their tips, and the cut ends of the leaves were rolled lengthwise and immersed into the solutions of the tagged acid. Cotton plugs were inserted in the tubes and, after the acid solutions had been completely absorbed, they were replaced with equal volumes of distilled water.

Fifteen days after absorbing the tagged acid solutions, the plant was cut down, and the leaves were removed. The resulting stalk was cut, air-dried, milled to 60-mesh, and re-dried. Lignin was isolated from the powder by a standard method.[6] The lignin was then subjected to a Van Slyke–Folch oxidation,[7] and the resulting barium carbonate was collected and counted.

TABLE I

COMPARISON OF ACTIVITIES OF *p*-HYDROXYPHENYLPYRUVIC ACID AND BARIUM CARBONATE

	Activity	
	C.p.m./Mg. C	Total c.p.m.
p-Hydroxyphenylpyruvic acid	9123	750,230
$BaCO_3$	246	533,662

In Table I are recorded the activity measurements of the incorporated *p*-hydroxyphenylpyruvic acid, and of the barium carbonate obtained on combustion of the lignin together with the calculated total activities of each. From these data, it appears that most of the activity of the introduced *p*-hydroxyphenylpyruvic acid was indeed incorporated into the lignin. Hence, these results provide strong evidence that *p*-hydroxyphenylpyruvic acid is an intermediate on the pathway between shikimic acid, derived from carbohydrates, and the lignin building stones, in the biogenesis of lignin itself.

Thus, the process of lignification may now be formulated as follows: carbohydrates are enzymatically transformed *via* shikimic acid to a *p*-hydroxyphenylpropane unit. Such a primary building stone then can undergo methoxylation to give a guaiacyl unit. In softwoods, the two aromatic building stones may form lignin by repeated condensations. Obviously, in hardwood lignins a syringyl type building stone is also required.

Acknowledgments—The authors wish to express their gratitude to Dr. Wm. J. Robbins of the New York Botanical Gardens for his courtesy in arranging for the cultivation of the sugar cane plants. This study was supported by grants of the National Science Foundation, the U. S. Public Health Service and the U. S. Atomic Energy Commission.

COMMUNICATION NO. 318 FROM THE
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RECEIVED NOVEMBER 1, 1956

AN ENHANCEMENT OF CATALYTIC ACTIVITY BY GAMMA RADIATION[1]

Sir:

The possibility of altering catalytic activity by high-energy radiation has long been considered.[2] Results have been reported for gamma rays[3] and for fast neutrons[4]; in both cases the effect was small. Evidence is presented herewith for the production by gamma rays of a marked increase in catalytic activity of aluminum oxide.

Previous observations upon zinc oxide[3] showed a definite, deleterious effect of gamma rays upon the catalytic activity for ethylene hydrogenation, but the rate of decline under radiation was much lower than the rate of production of those phenomena (color centers, etc.) usually explained by electron trapping. The present work employed the H_2–D_2 exchange to permit activity measurement at −78°, where the effects of displaced electrons would be more likely to persist. Among several catalysts tried, gamma-alumina demonstrated the effect most clearly.

The alumina catalyst was prepared from Fischer Adsorption Alumina (originally inactive) by moistening with water and evacuating at 400° for several hours. Its identity as gamma alumina was established by X-ray diffraction. The analysis for HD was by mass spectrometer. Irradiation was done *in vacuo* between activity measurements using a Co^{60} source. It is estimated that the samples absorbed about 2×10^{17} e.v./g., min.

Catalysts prepared at 400° showed an approximate seven-fold increase in catalytic activity when irradiated at −78° for as little as thirty minutes.

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(1) This document is based on work performed for the U. S. Atomic Energy Commission at the Oak Ridge National Laboratory.

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