thylen-Gruppe); 3,18 (*s*, Hydroxyl-H); 1,74 (*s*, Feinstruktur, abzweigende Methyl-Gruppe) und 1,63 ppm (*d*, *J* = 7 Hz, endständige Methyl-Gruppe).

b) *3-Methyl-2-buten-1-ol* (Prenol; **7**). Ausgehend von **3** wurde ein analoger Versuch im 10 mmol-Maßstab unternommen. Gas-chromatographisch (2 *m*, 20% C-20-M, 8 Min. 100°, dann bis 200°; 2 *m*, 20% DEGS, 8 Min. 100°, dann bis 200°) erkannte man anhand authentischer Vergleichssubstanzen das Vorliegen von **7** (42%) und die Abwesenheit jeglicher Ausgangs- oder Nebenprodukte in Mengen > 3%.

c) (E)-*3-Methyl-2-penten-1,5-diol* (**8**). **3** (40 mmol) wurde wie im Abschnitt 2a beschrieben, mit *s*-Butyllithium (124 mmol) behandelt. Nach Wiederabkühlen auf – 78° versetzte man mit vorgekühltem Äthylenoxid (7,8 ml; 160 mmol). Mit eiskalter NaCl-Lösung (100 ml) hydrolysiert, wurden die Reaktionsprodukte durch 40stdg. Extraktion im *Kutscher/Steudel*-Perforator in Äther aufgenommen. Nach Trocknen und Abdampfen des Lösungsmittels fiel ein Rohdestillat an (3,4 g; Sdp. 98–105°/4 Torr). Anschliessend ging durch die Spaltrohrkolonne[4]) eine Fraktion über (1,5 g; 32%; Sdp. 102–105°/4 Torr), die weitgehend aus **8** bestand, das jedoch durch einige gas-chromatographisch (2 *m*, 20% C-20-M, 8 Min. 130°, dann bis 200°) sichtbare Begleitstoffe (Gesamtanteil ungefähr 7%) verunreinigt war. Es wurde deshalb säulenchromatographisch (1 m lange, innen 0,9 cm weite Glassäule; 7 atü Druck; Detektor: PYE/UNICAM LCM-1; Adsorbens: Merckogel SI 150; Laufmittel: Petroläther/Methanol 20:1) gesäubert.

$C_6H_{12}O_2$ (116,2) Ber. C 62,04 H 10,41% Gef. C 62,38 H 10,46%

MS.: *m/e* = 98 (24%, M^+—H_2O); 41 (100%). –IR.: 3360 (*s*, br., O—H); 1675 (*m*, C=C); 1040 (*s*, C—O); 1000 (*s*) und 875 cm^{-1} (*w*). – ^1H—NMR.: 5,43 (*t*, *J* = 6,5 Hz, 1 olefin. H); 4,60 (*s*, br., 2 Hydroxyl-H); 4,07 (*d*, *J* = 6,5 Hz, Methylen-Gruppe, sauerstoffbenachbart und allylständig); 3,67 (*t*, *J* = 6,5 Hz, andere sauerstoffbenachbarte Methylen-Gruppe); 2,22 (*t*, *J* = 6,5 Hz, andere allylständige Methylen-Gruppe) und 1,68 ppm (*s*, Methyl-Gruppe).

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278. Organic Phosphorus Compounds 67
The Exchange Cleavage of Dialkylaminomethylphosphines with Aryl and Diarylphosphines [1]

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(16. X. 74)

Summary. Interaction of dialkylaminomethyl-substituted tertiary phosphines with primary or secondary phosphines results often in the cleavage of a P—C bond and the formation of P—P bonds. Thus treatment of $Ph_2PCH_2NEt_2$ with Ph_2PH at 180° yields Ph_2P—PPh_2 and $HNEt_2$, and interaction of $PhP(CH_2NEt_2)_2$ and $PhPH_2$ at 150° results in the formation of $(PhP)_5$, $(PhP)_4CH_2$, $HNEt_2$ and CH_3NEt_2.

Previously we reported [2] on the reaction of primary and secondary phosphines with dialkylaminomethyl-substituted tertiary phosphines. Combustion analysis of the reaction products indicated that the reaction had proceeded according to the equation:

$$>P-CH_2-N< + H-P< \rightarrow >P-CH_2-P< + H-N<$$

Thus it was reported that treatment of diphenylphosphine with N,N-diethylaminomethyl-diphenylphosphine gave diethylamine and bis(diphenylphosphino) methane as the sole products [2]:

$$(C_6H_5)_2P-CH_2-N(C_2H_5)_2 + H-P(C_6H_5)_2 \rightarrow (C_6H_5)_2P-CH_2-P(C_6H_5)_2 + H-N(C_2H_5)_2$$

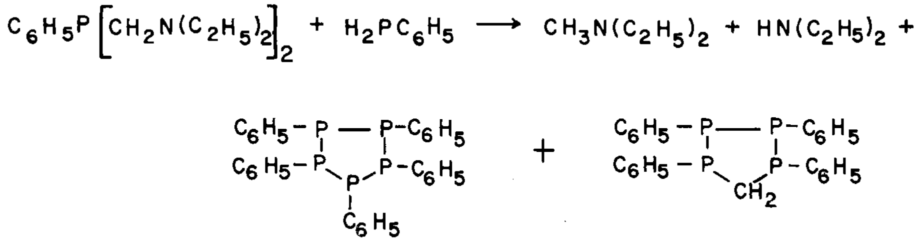
This work is in error. We now observe that the products actually obtained are tetraphenyldiphosphine and diethylmethylamine, which result from phosphorus-carbon bond cleavage instead of nitrogen-carbon bond cleavage:

$$(C_6H_5)_2P-CH_2-N(C_2H_5)_2 + H-P(C_6H_5)_2 \rightarrow (C_6H_5)_2P-P(C_6H_5)_2 + CH_3-N(C_2H_5)_2$$

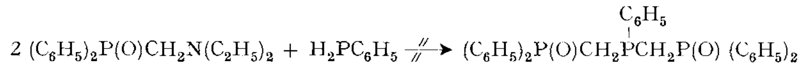
The products isolated after heating bis(diethylaminomethyl) phenylphosphine with phenylphosphine were previously reported to be diethylamine and a phenylphosphinemethylene tetramer, 1,3,5,7-tetraphenyl-1,3,5,7-tetraphosphocane [2].

$$C_6H_5P[CH_2N(C_2H_5)_2]_2 + H_2PC_6H_5 \rightarrow [C_6H_5PCH_2]_4 + HN(C_2H_5)_2$$

We now observe that the products of the reaction are pentaphenylcyclopentaphosphine [3], 1,2,3,4-Tetraphenyl-cyclo-5-carba-1,2,3,4-tetraphosphine [4], diethylamine and diethylmethylamine.



Comparison experiments with diethylaminomethyldiphenylphosphine oxide and phenylphosphine showed that no reaction occurred.



$$2\,(C_6H_5)_2P(O)CH_2N(C_2H_5)_2 + H_2PC_6H_5 \not\rightarrow (C_6H_5)_2P(O)CH_2\overset{C_6H_5}{\overset{|}{P}}CH_2P(O)\,(C_6H_5)_2$$

The precise mechanism for these cleavage reactions demands further investigation, although it is not unreasonable to suggest a nucleophilic attack on P^{III} by P^{III} [5] with concurrent cleavage of the phosphorus-carbon bond instead of the nitrogen-carbon bond. The occurrence of both phosphorus-carbon and nitrogen-carbon bond cleavage in the reaction of phenylphosphine with bis(diethylaminomethyl)phenylphosphine can be explained by the added stability achieved with five-membered ring formation.

Experimental Part

1. *The interaction of phenylphosphine with bis(diethylaminomethyl)phenylphosphine.* The phenylphosphine 5.30 g (0.0189 mol) was mixed neat under nitrogen with 2.08 g (0.0189 mol) of bis(diethylaminomethyl)phenylphosphine and the mixture heated for 5 h at 140–150°. The receiver was cooled in an ice bath. After no further amine was collected in the receiver, the mixture was allowed to cool, whereupon it solidified to a pale yellow-white solid. The amount of amine collected was 2.40 g (87%). The pale white solid was mixed with 100 ml of degassed ethanol and heated to reflux under nitrogen for 15 min. A portion of the original solid remained; this was separated from the soluble fraction. The alcohol insoluble portion weighed 1.60 g and the ethanol soluble portion weighed 3.00 g. These combined weights account for 99% of the cyclic phosphines expected on the basis of mass balance. A total of 7.38 g of reactants gave a total of 6.00 g of isolated products (no gas was evolved during the reaction). The mass balance is 80%. Apparently some of the amine remains in the reaction mixture and is removed by washing the crude mixture of polyphosphines with pentane.

Analysis of the insoluble portion showed it to be $[C_6H_5P]_5$, m.p. 150–152°, (lit. m.p. 148–152°, [3]); *m/e* $(C_6H_5P)_5^+$ (15 eV and 70 eV) 540.

$C_{30}H_{25}P_5$ (540.4) Calc. C 66.68 H 4.66 P 28.66% Found C 67.37 H 4.69 P 27.46%

The soluble portion was allowed to crystallize from ethanol in the form of needles, m.p. 141–143°, (lit. m.p. 134–138° [4]). Analysis showed this material to be 1,2,3,4-tetraphenyl-cyclo-5-carba-1,2,3,4-tetraphosphine, $(C_6H_5P)_4CH_2$, *m/e* $(C_6H_5P)_4CH_2^+$, (15 eV and 70 eV) 446.

$C_{25}H_{22}P_4$ (446.3) Calc. C 67.27 H 4.97 P 27.76% Found C 67.66 H 4.81 P 27.25%

There was no direct evidence in the mass spectrometer for the original postulated tetramer $(C_6H_5PCH_2)_4$, *m/e* 488, although a peak at *m/e* 480 does suggest that loss of 8 H atoms from the tetramer could give the peak at *m/e* 480. In any case the presence of the tetramer in the reaction mixture is so small that it does not represent a convenient synthetic route to this compound.

2. *The interaction of diphenylphosphine with diethylaminomethyldiphenylphosphine.* The diphenylphosphine 1.92 g (0.0103 mol) and diethylaminomethyldiphenylphosphine 2.80 g (0.0103 mol) were mixed under nitrogen and heated to 180° for 30 h. The amine was collected in an ice cooled receiver. The amount of amine collected was 0.6 g (82%). The crude solid after washing with cold pentane weighed 3.50 g (94%). The crude solid was recrystallized from ethanol under nitrogen, m.p. 116–135°. A ^{31}P–NMR. spectrum in chloroform showed a single peak for tetraphenyldiphosphine at $\delta\,^{31}P$ + 15 ppm (lit. $\delta\,^{31}P = +15.2$ ppm [2], from H_3PO_4 external standard). A mass spectrum of the product showed the presence of $(C_6H_5)_4P_2$, *m/e* 370 and $(C_6H_5)_4P_2O$, *m/e* 386, but no peak for the bis(diphenylphosphino)methane. The mass spectrum of bis(diphenylphosphino)methane has been studied by *Colton & Porter.*

The parent ion can be observed at 70 eV and the fragmentation pattern of the known bis(diphenylphosphino)methane does not correspond with the spectrum taken of the crude reaction mixture. Our product was analyzed as the monoxide.

$C_{24}H_{20}P_2O$ (346.36) Calc. C 74.60 H 5.21 P 16.03% Found C 74.55 H 5.34 P 16.17%

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