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ORIENTATION OF PIPERIDINE ADDITION TO VINYL COMPOUNDS OF TRIVALENT PHOSPHORUS*

M.I. Kabachnik, E.N. Tsvetkov and Chang Chung Yu

Institute of Organo-element Compounds of the U.S.S.R. Academy of Sciences, Moscow

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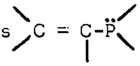
THE effect of atomic trivalent phosphorus on physical and chemical properties of the molecules it involves has been little investigated. In particular, no study has been made of the conjugation of the lone pair of electrons of the phosphorus atom with π-electrons of the double carbon-carbon bond in systems  and its action on the orientation in addition reactions. By analogy with vinyl compounds of other elements that also have lone pairs of electrons (e.g. nitrogen or oxygen) one could have supposed to observe α-orientation on nucleophilic reagent addition to vinyl compounds of trivalent phosphorus.

We have investigated the orientation of piperidine addition to dibutyl vinylphosphonite (I)[1] and vinyldi-butyl-phosphine (II)[2] and found that, contrary to the analogy above, the vinyl compounds of trivalent phosphorus under study add the piperidine nucleus in β-position. Dibutyl vinylphosphonite (I) reacts with piperidine on prolonged heating, in nitrogen at 140-150°. After 46.5 hours heating dibutyl β-piperidinoethylphosphonite (III) is isolated in 31% yield, (b.p. 188-118.5° 1 mm, n_D^{20} 1.4710, d_4^{20} 0.9399,

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* Translated by A.L. Pumpiansky, Moscow.

[1] M.I. Kabachnik, E.N. Tsvetkov and Chang Chung Yu, Dokl. Akad. Nauk SSSR **131**, 1334 (1960).

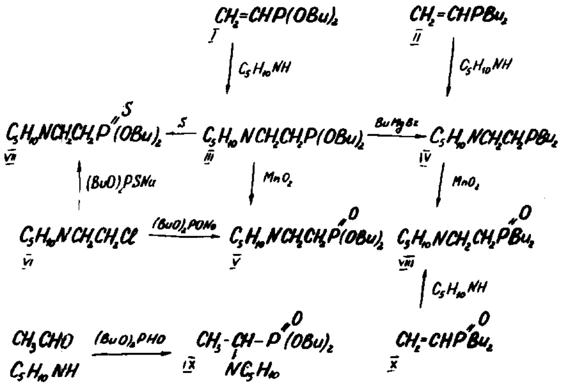
[2] M.I. Kabachnik, Chang Chung Yu and E.N. Tsvetkov, Dokl. Akad. Nauk SSSR **135**, 603 (1960).

MR_D 86.06. Calc. MR_D 85.34. Found: C, 61.9, 62.0; H, 11.3, 11.3; P, 10.8, 10.7. Calc. for $C_{15}H_{32}NO_2P$: C, 62.2; H, 11.2; P, 10.7%), together with the unreacted starting compounds and a small amount of polymeric materials.

Piperidine hydrochloride accelerates this reaction and catalytic addition takes place already at 120-130° but is complicated by the dealkylation of the starting and end products and the formation of polymers due to prolonged heating of reagents.

Piperidine addition to vinyldi-butylphosphine (II) proceeds much less readily. In the absence of a catalyst (30 hours at 145-160°) no addition is observed. In the presence of piperidine hydrochloride the yield of β-piperidinoethyldibutylphosphine amounts under similar conditions to 14% (b.p. 128-128.5°/3 mm; n_D^{20} 1.4891; d_4^{20} 0.8854; MR_D 83.92. Calc. MR_D 83.45. Found: C, 70.1, 70.0; H, 12.7, 12.6; P, 11.8, 12.0. Calc. for $C_{15}H_{32}NP$: C, 70.0; H, 12.5; P, 12.0%), the remainder accounting for the unreacted starting compounds.

The structure of addition products obtained was proved as follows:



(1) Aminophosphonite (III) is converted to dibutyl piperidinoethylphosphonate with active manganese dioxide in petrol ether (b.p. 153-154°/2 mm;

n_D^{20} 1.4604; d_4^{20} 0.9939; MR_D 84.24. Calc. MR_D 84.08. Found: C, 59.0, 59.3; H, 10.5, 10.5; P, 9.8, 10.1. Calc. for $C_{15}H_{32}NO_3P$: C, 59.0; H, 10.6; P, 10.1%).

Dioxalate of dibutyl piperidinoethylphosphonate (m.p. 155.5-156° [from dioxan]. Found: C, 51.4, 51.3; H, 8.4, 8.6; P, 7.5, 7.6. Calc. for $C_{17}H_{34}NO_7P$: C, 51.6; H, 8.7; P, 7.8%), proved to be similar to the dioxalate of dibutyl-β-piperidinoethylphosphonate (V) prepared from sodium dibutylphosphite and β-chloroethylpiperidine (VI) (m.p. 155.0-155.5°, mixed m.p. 155.5-156°).

(2) By sulphur addition aminophosphonite (III) is converted to dibutyl piperidinoethylthiophosphonate (b.p. 140-141°/1.5 mm; n_D^{20} 1.4870; d_4^{20} 1.0038; MR_D 92.10. Calc. MR_D 91.57. Found: C, 55.8, 55.9; H, 10.1, 10.1; P, 9.9, 9.7; S, 10.1, 10.1. Calc. for $C_{15}H_{32}NO_2PS$: C, 56.0; H, 10.0; P, 9.6; S, 10.0. Hydrochloride: m.p. 151-151.5° (from benzene). Found: C, 49.9, 49.9; H, 9.0, 9.0; P, 8.8, 9.0. Calc. for $C_{15}H_{33}ClNO_2PS$: C, 50.3; H, 9.3; P, 8.7%). The hydrochloride shows no depression of the mixed melting point with the hydrochloride of dibutyl-β-piperidinoethylthiophosphonate (VII) produced from sodium dibutylthiophosphite and β-chloroethylpiperdine (VI).

(3) Starting from dibutylphosphite, acetaldehyde, and piperidine we prepared, following Fields[3], dibutyl-α-piperidinoethylphosphonate (IX). (Chloroplatinate: m.p. 154-154.5° [from alcohol]. Found: C, 35.5, 35.6; H, 6.6, 6.5; N, 2.9, 2.9; Cl, 21.3, 21.6. Calc. for $C_{30}H_{66}Cl_6NO_3PPt$: C, 35.3; H, 6.5; N, 2.8; Cl, 20.8%). The melting point of this compound differs from that of the chloroplatinate of dibutyl-β-piperidinoethylphosphonate (V).(m.p. 144-145° [from acetone]. Found: C, 35.2, 35.3; H, 6.6, 6.6; N, 3.2, 3.1; Cl, 20.4, 20.4). The mixed melting point was 119-125°.

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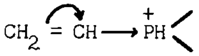
[3] E.K. Fields, J. Amer. Chem. Soc. 74, 1528 (1952).

(4) Piperidinoethylbutylphosphine, prepared by piperidine addition to vinyldibutylphosphine is oxidized with active manganese dioxide into piperidinoethyldibutylphosphine oxide (b.p. 158.5-159°/1.5 mm; m.p. 34-35°. Found: C, 66.0, 66.1; H, 11.8, 11.9; P, 11.3, 11.0. Calc. for $C_{15}H_{32}NOP$: C, 65.9; H, 11.8; P, 11.8%. Oxalate: m.p. 122-123.5°[from tetrahydrofuran]. Found: C, 53.2, 53.1; H, 8.6, 8.7; P, 7.5, 7.3; N, 3.4, 3.3. Calc. for $C_{15}H_{32}NOP \cdot 1^1/_2\ C_2O_4H_2$: C, 52.9; H, 8.6; P, 7.6; N, 3.4%).

The mixed melting point showed the oxalate of this phosphine oxide to be identical with that of β-piperidinoethyldibutylphosphine oxide (VIII) prepared from dibutyl-β-piperidinoethylphosphonite (III) by the action of butylmagnesium bromide followed by oxidation with active manganese dioxide and piperidine addition to vinyl butylphosphine oxide (X).

The reason for β-orientation of the addition of piperidine (nucleophilic reagent) to vinyl compounds of trivalent phosphorus has not yet been elucidated. It is however, possible to make two suggestions:

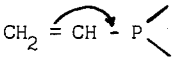
(1) The addition of the remainder of piperidine is preceded by proton addition to form the system



$$CH_2 = CH \longrightarrow \overset{+}{P}H\lt$$

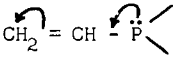
in which β-orientation is due to the inductive effect;

(2) β-addition results from π-d-interaction of the double bond electrons with the vacant d-orbital of the atom of trivalent phosphorus



$$CH_2 = CH - P\lt$$

In any case no conjugation of the type



$$CH_2 = CH - \ddot{P}\lt$$

requiring α-addition is observed.