Deamination and Rearrangement of a 2-Aminoethylphosphine Oxide

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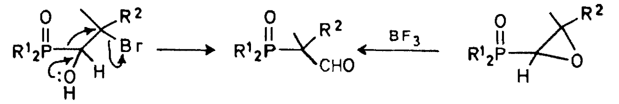
Summary Deamination of a 2-aminoethylphosphine oxide gives products in which a diphenylphosphinyl group has migrated by a Wagner–Meerwein 1,2-shift.

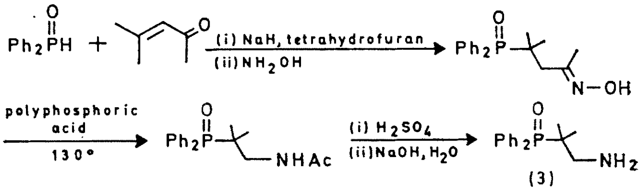
REARRANGEMENTS involving 1,2-phosphyl†[1] migration have previously been restricted to situations where *n*-participation by an oxygen atom provides the driving force for the reaction. The halohydrin rearrangement of (**1**) is of this kind.[2] Better known examples are the Baeyer–Villiger and Schmidt reactions of α-ketophosphonates,[3] and the BF_3-catalysed rearrangement of epoxyphosphonates (**2**).[4]



(1; R^1 = OH, R^2 = H) (2; R^1 = EtO, R^2 = Me)

In all these cases phosphyl migration seems to be preferred to hydride, alkyl, or aryl migration, and it has been claimed[4] that the $R^1{}_2P(O)$ group has a high migratory aptitude. We now report a Wagner–Meerwein phosphyl migration, unassisted by *n*-participation, in the deamination of a 2-aminoethylphosphine oxide (**3**).

The crystalline amine (**3**) was synthesised as shown in Scheme 1. Diazotisation with nitrous acid in water, or with isopentyl nitrite in anhydrous acetonitrile gave a mixture of five products separated by t.l.c. (Table). In each case *ca.* 5% of the amine was recovered.



SCHEME 1

Diazotisation of $Ph_2P(O)CMe_2{\cdot}CH_2{\cdot}NH_2$

Percentage yield of product (based on amine consumed) ±3%	Conditions HONO in water[a]	iso-$C_5H_{11}ONO$ in MeCN[b]
(A)	25	48
(B)	8	12
(C)	38	8
(D)	6	8
(E)	14	7

[a] 2 mmol amine and 250 mg H_2SO_4 in 0·75 ml water, 2 mmol $NaNO_2$ added over ½ h at 0°. Kept at 0° for 3 h.

[b] 2 mmol amine and 3 mmol iso-$C_5H_{11}ONO$ in 2 ml dry acetonitrile, refluxed 8 h.

Compound (D) was identified as the unrearranged alcohol (**4**) and was synthesised from diphenylethoxyphosphine (**5**)

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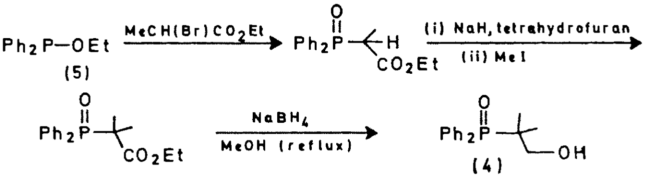
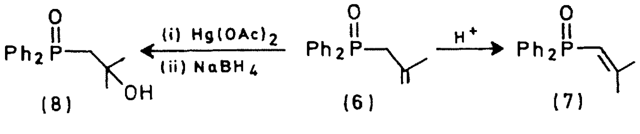
† "Phosphyl" includes all $R^1{}_2$ P(O) groups, where R^1 = alkyl, aryl, or R^2O (ref. 1).

(Scheme 2). Compounds (A) and (B) were isomeric olefins: synthesis of (A) from (**5**) and 2-methylallyl iodide showed

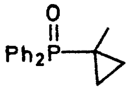


SCHEME 2

that it was the methylallylphosphine oxide (**6**).[5] (B) was the dimethylvinylphosphine oxide (**7**), formed when a solution of (**6**) in concentrated sulphuric acid was quenched with water.

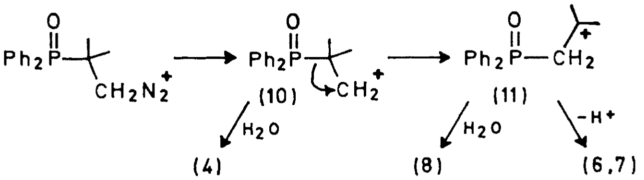


(C), the major product of deamination in aqueous solution, was an alcohol isomeric with (**4**). Synthesis from the olefin (**6**) by Brown's mercuration–reduction sequence[6] showed that it was the rearranged alcohol (**8**). The remaining product, (E), was tentatively identified as the cyclopropane (**9**).



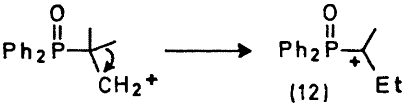
(**9**)

No products of complete methyl migration were detected, and all the rearranged products (**6**, **7**, and **8**) can be logically derived from the cation (**11**) formed from the primary cation (**10**) by phosphyl migration. The appearance of nonconjugated phosphine oxide (**6**) as the major olefinic product is initially puzzling since the acid-catalysed isomerisation of (**6**) to (**7**) shows that the conjugated



structure (**7**) is the more stable. However, deamination notoriously produces "hot" cations,[7] and much of this excess of energy is presumably left in the rearranged cation (**11**). An irreversible statistical deprotonation would then lead to a 3 : 1 ratio of (**6**) to (**7**), close to that observed. The acid-catalysed isomerisation, through the same cation (**11**) this time with no excess of energy, is reversible and gives the thermodynamic product.

We suggest that exclusive phosphyl migration does not necessarily indicate a high migratory aptitude for the $R^1_2P(O)$ group, but is rather a consequence of the unattractive alternatives. In this case, if methyl migration were to occur in cation (**10**), an unstable α-phosphinyl cation would be produced (**12**). Rate studies[‡] alone can decide this question and we are studying the solvolysis of the toluene-*p*-sulphonate of the unrearranged alcohol (**4**) to this end.



All compounds were identified by i.r., 100 MHz n.m.r., and mass spectra.

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[‡] Rate studies cannot be carried out on the deamination since the rate-determining step occurs during the diazotisation (ref. 8).

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