A FACILE S_Ni' REARRANGEMENT: THE FORMATION OF

1,2-ALKADIENYLPHOSPHONATES FROM 2-ALKYNYL PHOSPHITES

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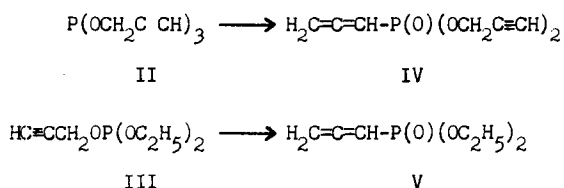
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WHEN the conventional procedure for the preparation of trialkyl phosphites (i.e. phosphorus trichloride, alcohols and a tertiary amine) was applied in the synthesis of 2-alkynyl phosphites (I) - needed for a separate study - fresh solutions of the preparations contained the expected phosphites in high yield and purity, as indicated by infrared and P^{31} nuclear magnetic resonance spectroscopy. Thus the freshly prepared solution of tris-(2-propynyl) phosphite (II) in ether contained in its infrared spectrum the diagnostic acetylenic modes at 3.02 (spC-H stretching) and 4.71 μ (HspC-spC stretching) and so significant absorption at 8.0 μ (P $\rightarrow$ O mode); the NMR spectrum exhibited only one peak, δ_{p31}-135 p.p.m., which is characteristic of trialkyl phosphites.[1] Re-examination of the solution after standing overnight at room temperature indicated extensive changes: the infrared spectrum acquired several additional bands, comprising strong maxima at 5.11 and 8.00 μ, and the P^{31} NMR spectrum indicated the presence of only one phosphorus species, at -17.9 p.p.m.

Similar behavior was observed also with the mixed phosphite, diethyl 2-propynyl phosphite, $(C_2H_5O)_2POCH_2C\equiv CH$ (III): the acetylenic modes

[1] J. Van Wazer, C.F. Callis, J.N. Shoolery and R.C. Jones, J. Amer. Chem. Soc. 78, 5715 (1956); N. Muller, P.C. Lauterbur and J. Goldenson, Ibid. 78, 3557 (1956).

present in the fresh sample disappeared on standing and gave rise to bands at 5.15 and 8.00 μ, and the P^{31} resonance peak shifted from -137 to -14.4 p.p.m.

The changes in the P^{31} NMR spectra thus indicate that the P^{III} ester on standing rearranges to a P^{IV} (quadruply connected) phosphonate ester; the changes in the infrared spectra indicate that the $P^{III} \longrightarrow P^{IV}$ rearrangement is accompanied by the disappearance of one $H-C \equiv C-CH_2-O-P$ moiety and the formation of the $H_2C=C=CH-P \longrightarrow O$ structure. The following transformations are thus indicated:

$$P(OCH_2C\,CH)_3 \longrightarrow H_2C=C=CH-P(O)(OCH_2C\equiv CH)_2$$
$$\qquad\qquad II \qquad\qquad\qquad\qquad\qquad IV$$

$$HC\equiv CCH_2OP(OC_2H_5)_2 \longrightarrow H_2C=C=CH-P(O)(OC_2H_5)_2$$
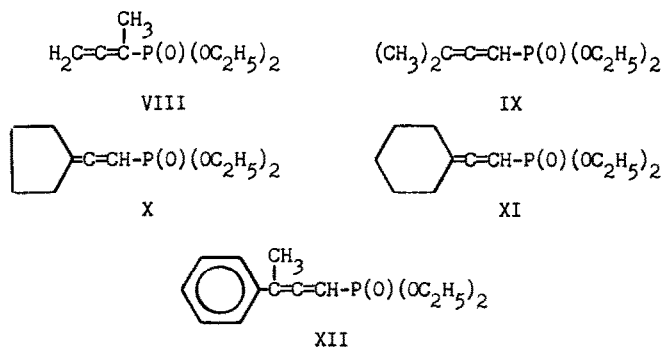$$\qquad\qquad III \qquad\qquad\qquad\qquad\qquad V$$

Subsequent work established that the rearrangement of the phosphorous esters of 2-alkynols to the allenic structures is a general reaction and that variations in both the acetylenic alcohol and the trivalent phosphorus moiety are feasible.

The nature of the rearrangement was studied with the use of substituted 2-propyn-1-ols. The phosphite, $HC \equiv C-CH(CH_3)-OP(OC_2H_5)_2$ (VI), (λ characteristic: 3.02 and 4.72 μ) on rearrangement yielded a phosphonate (VII), (λ diagnostic: 3.12, 5.13 and 8.05 μ; δ_{p31}: -14.8 p.p.m.) which was hydrogenated to a diethyl butylphosphonate ester, identical (by direct comparison of its physical and spectral constants) with authentic diethyl n-butylphosphonate and different from diethyl s-butylphosphonate. The H' NMR spectrum of VII showed the presence of one methyl group in the C_4 fragment and thus, together with the infrared, P^{31} NMR and hydrogenation data, indicated the following rearrangement:

$$CH_3$$
$$HC\equiv C-CH-O-P(OC_2H_5)_2 \longrightarrow CH_3-C=C=CH-P(O)(OC_2H_5)_2$$
$$\overset{H}{}$$

　　　　　　VI　　　　　　　　　　　　　　　　　　VII
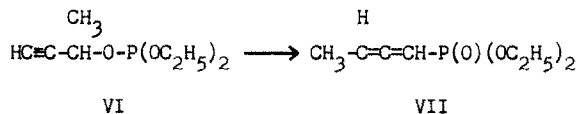
By similar methods the structures of the phosphonates VIII-XII were derived from the phosphites of 2-butyn-1-ol, 2-methyl-3-butyn-2-ol, 1-ethynylcyclopentanol, 1-ethynylcyclohexanol and ethynyl methyl phenyl carbinol, respectively:

$$CH_3$$
$$H_2C=C=C-P(O)(OC_2H_5)_2 \qquad (CH_3)_2C=C=CH-P(O)(OC_2H_5)_2$$

　　　　　VIII　　　　　　　　　　　　　　　　IX

$$\square\!=\!C=CH-P(O)(OC_2H_5)_2 \qquad \bigcirc\!=\!C=CH-P(O)(OC_2H_5)_2$$

　　　　　　X　　　　　　　　　　　　　　　　　XI

$$CH_3$$
$$\bigcirc\!\!\!-\!C=C=CH-P(O)(OC_2H_5)_2$$

　　　　　　　　　　XII

The 2-alkynyl phosphite $\rightarrow$ 1,2-alkadienylphosphonate transformation can be rationalized by an internal 1,3-rearrangement ($S_N i'$ mechanism). The observed relative order of ease of rearrangement of the phosphites: (alcohol given)

$$CH_3 \qquad CH_3$$
$$HC\equiv C-\underset{CH_3}{\overset{|}{C}}-OH > HC\equiv C-\overset{|}{CH}-OH > HC\equiv C-CH_2-OH \ (and > CH_3C\equiv C-CH_2-OH)$$
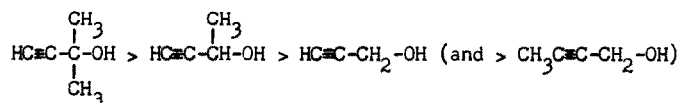
parallels the decreasing order of carbonium ion stabilities (and, hence, their ease of formations) and thus lends support to the internal ($S_N i$) mechanism, for which the importance of the carbonium ion character of the participant alkyl group was emphasized.[2]

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[2] D.J. Cram, J. Amer. Chem. Soc. 75, 332 (1953).

The ease of rearrangement is probably the result of a very favorable, planar transition state between the acetylenic and allenic end structures through which the molecule passes with only small changes in the bond angles.[3] The driving force of the reaction is apparently provided by the
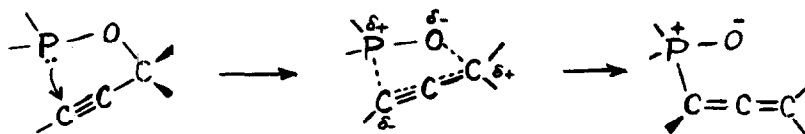
energy gain associated with the $P^{III} \longrightarrow P^{IV}$ transformation.[4]

Although very reactive, the allenyl phosphonates are readily isolable and characterizable compounds. Some of the characteristic constants include (compound, b.p. ^{o}/mm, n_D^{25}, δ_{p31}): IV, 117/0.3, 1.4842, -17.9; V, 89/0.4, 1.4544, -14.4; VII, 105/1.0, 1.4497, -14.8; VIII, 73/0.1, 1.4587, -17.3; IX, 95/0.8, 1.4588, -15.0; X, 123/0.2, 1.4738, -17.3).[5]

The rather wide scope of the reaction can be illustrated also by variations in the phosphorus moiety, some of which are shown in examples XIII-XV:

$$H_2C=C=CH-P(O)[N(CH_3)_2]_2 \qquad H_2C=C=CH-P(O)(SCH_3)_2 \qquad H_2C=C=CH-P(O)(CH_3)_2$$

XIII   XIV   XV
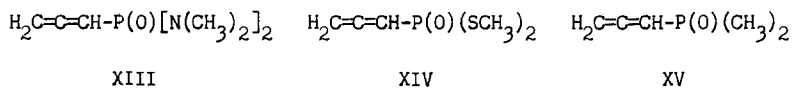
with the constants: XIII, 85/0.17, 1.5046, -23.9; XIV, 102/0.3, 1.5840, --; XV,[6] m.p. 58-60°, δ_{p31}: -41.0 (aqueous solution).

Due to the facility of the rearrangement, the formation of alkadienyl-

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[3] Allyl phosphites, for which no similar planar transition state can be constructed, are stable under comparable conditions.

[4] The alkynyl phosphite-alkadienylphosphonate rearrangements are usually highly exothermic; in the absence of solvents or adequate cooling the reaction can become uncontrollably violent.

[5] All of the compounds gave satisfactory elemental analyses.

[6] While present work was being concluded the formation of diphenyl propadienyl phosphine oxide from 2-propynol and diphenylchlorophosphine was reported by R.C. Miller, Abstracts of Papers presented at Chicago, September 3-8, 1961, Division of Organic Chemistry of the American Chemical Society, Paper No. 80, p. 43Q.

phosphonates could have escaped detection. A cursory perusal of the litera-
ture indicated for instance the description of propargyl esters of alkylphos-
phonous acids.[7] Repeating the experimental procedure with ethylphosphonous
dichloride yielded a product, b.p. $108°/0.3$ mm, n_D^{25} 1.5071, δ_{p31} -45.3 p.p.m.
(reported constants: b.p. $126-7°/6$ mm, n_D^{12} 1.5015), the infrared spectrum
of which indicated it to be 2-propynyl ethyl(propadienyl)phosphinate (XVI),
instead of the reported di-2-propynyl ethylphosphonite (XVII):

$$CH_3CH_2-\overset{O}{\underset{O}{P}}\begin{smallmatrix}-CH=C=CH_2\\ \diagdown CH_2-C\equiv CH\end{smallmatrix}$$

$$CH_3CH_2-P(OCH_2C\equiv CH)_2$$

              XVI   XVII

    The ease of rearrangement was established by the infrared spectrum
of the reaction mixture taken immediately after the combination of the
reactants: strong bands at 5.11 and 7.92 μ indicated the presence of the
allenyl and phosphoryl modes, respectively. It is very likely that the
other compounds described as alkylphosphonous esters[7] also have the allenyl-
phosphinate structures.

[7] G. Kamai and E.A. Gerasimova, Trudy Kazan. Khim. Tekhnol. Inst. im. S.M.
Kirova 23, 138-142 (1957); Chem. Abstr. 52, 9946 (1958).