The Reaction of Pentaoxyphosphoranes with Acetonitrile to give Oxazolines

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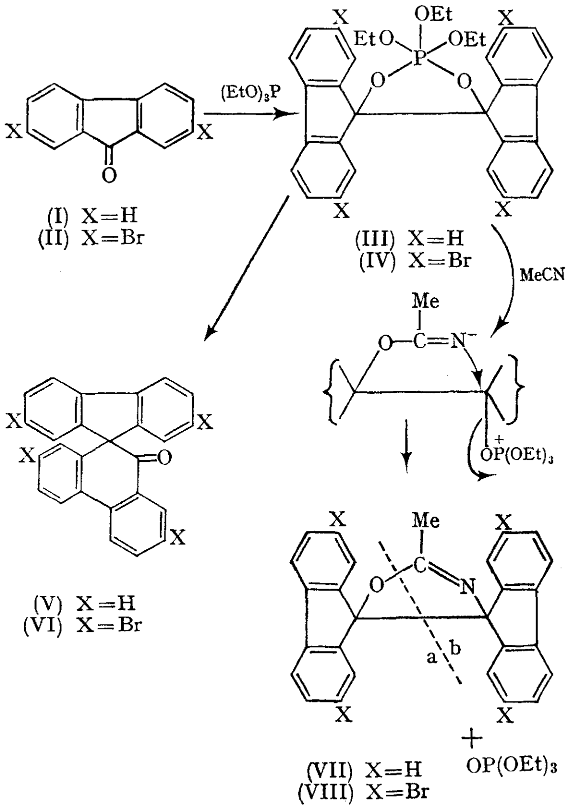

(I) X=H
(II) X=Br

(III) X=H
(IV) X=Br

(V) X=H
(VI) X=Br

(VII) X=H
(VIII) X=Br

WE have recently shown that fluorenone (I) or 2,7-dibromofluorenone (II) react with triethyl phosphite to give the 2,2,2-triethoxy-1,3,2-dioxaphospholans (III) or (IV).[1,2] When the phospholans are heated they rearrange to give the correspondng fluorene-9-spiro-9′-phenanthrenones (V) and (VI). We now find that if (III) is dissolved in anhydrous acetonitrile at 43—46° for 20 hr., it gives (V) (71%), triethyl phosphate, and the oxazoline (VII), (17%) m.p. 249·0—249·5° [C=N at 1655 cm.$^{-1}$ in the infrared; ^{1}H n.m.r. Me : aryl ratio was 3 : 16 for τ 7·45 (singlet) and τ 2·40 (centre of multiplet) relative to Me_4Si]. The suspension of (IV) in acetonitrile under similar conditions gives (VI) (31%) and (VIII), (54%), m.p. 273—274·5° [1655 cm^{-1}; ^{1}H n.m.r. Me : aryl ratio was 3 : 12 for τ 7·33 (singlet) and τ 2·54 (centre of multiplet)].

Confirmation of the proposed structure for (VII) is obtained from its mass spectrum at 75 ev which exhibits major peaks at: 385 (parent), 342 ($P-CH_3CO$), 205 ($C_{15}H_{11}N^{+\cdot}$, b), 180 ($C_{13}H_8O^{+\cdot}$, a), 164 ($C_{13}H_8$, "fluorenyl$^{+\cdot}$"), and 152 ($C_{12}H_8$, "biphenylene$^{+\cdot}$"). Metastable peaks are observed at: $m^* = 304$ (calc. 304 for $385^+ \rightarrow 342^+ + CH_3CO$), 131 (calc. for $205^+ \rightarrow 164^+ + CH_3CN$), 128 (calc. for $180^+ \rightarrow 152^+ + CO$) and 109 (calc. for $385^+ \rightarrow 205^+ + C_{13}H_8O$). A similar fragmentation pattern is observed for (VIII) with a parent peak at 701 *m/e*.

An oxazoline structure for (VII) is established by the loss of MeCO. Such fragmentation is not compatible with the isomeric isoxazoline (–O–N=C–Me) structure. The loss of CH_3CO may actually be occurring *via* an acetyl aziridine which is formed from (VII) upon electron impact. The thermal rearrangement of oxazolines to *N*-acylaziridines has been postulated.[3]

Oxazoline formation represents a new reaction of pentaoxyphospholanes with a triply-bonded species. It may proceed as shown.

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[1] I. J. Borowitz and M. Anschel, *Tetrahedron Letters*, 1967, 1517, 5032.

[2] The formation of (III) and related phospholanes has also been noted by F. Ramirez and C. P. Smith, *Chem. Comm.*, 1967, 662.

[3] H. L. Wehrmeister, *J. Org. Chem.*, 1965, **30**, 664.