Ring Expansion of 9-Substituted 9-Phosphafluorenes to 9,10-Dihydro-9-phosphaphenanthrene 9-Oxides

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RECENTLY it was shown[1] that triarylphosphines react with phenylacetylene and water in boiling diethylene glycol to give the phosphine oxide (I; R = Ph). The corresponding reaction using methyl propiolate in place of phenylacetylene occurs under much milder conditions (ether at room temperature) and in an almost quantitative yield to give the corresponding compound (I; R = CO_2Me, Ar = Ph).

$Ar_2P(O){\cdot}CHAr{\cdot}CH_2R$ (I)

In order to achieve a ring expansion of a 9-phosphafluorene to a 9-phosphaphenanthrene, use was made of the 1,2-aryl shift in the above reactions. 9-Methyl-9-phosphafluorene,[2] methyl propiolate, and water in tetrahydrofuran gave a product, m.p. 145—148°, which has been shown to be 9-methyl-10-methoxycarbonylmethyl-9,10-dihydro-9-phosphaphenanthrene 9-oxide (II; R = Me). Two alternative structures were considered, the 9-phosphafluorene oxide (III) which would result from migration of the methyl group, and the biphenylphosphine oxide (IV) which would result from ring opening.

The n.m.r. spectrum showed resonances at τ 1·75–2·80 (m; 8H aryl), 6·36 (s; 3H methoxyl), 5·6—7·2 (complex; 3H methine and methylene) and 8·67 (d; 3H methyl J_{PH} 13 c./sec.). The ultraviolet absorption spectra of the product, 9-methyl-9-phosphafluorene 9-oxide,[3] 2-biphenyldimethylphosphine oxide,[2] and 9,9-diphenyl-9,10-dihydro-9-phosphoniaphenanthrene bromide[4] are given in the Figure. The comparison shows the chromophore of the product to resemble that of the 9-phosphoniaphenanthrene and not that of the 9-phosphafluorene or the biphenylphosphine oxide. A satisfactory elemental analysis was obtained.

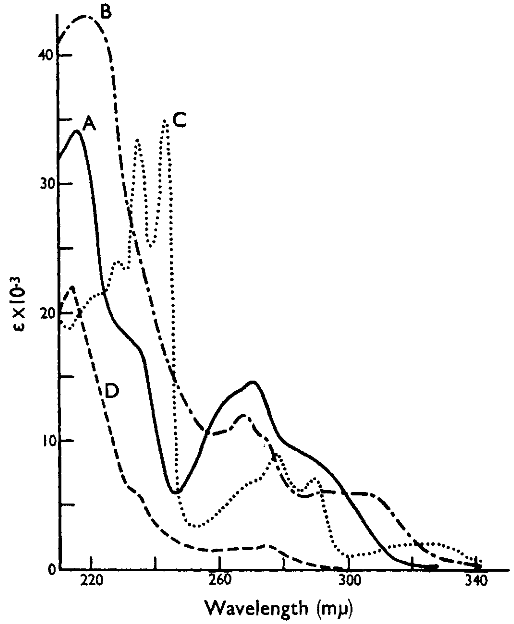
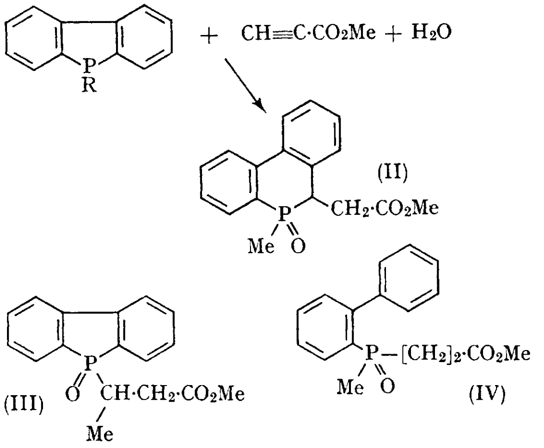


FIGURE. *The ultraviolet absorption spectra of* A, *the product* (II); B, 9,9-*diphenyl*-9,10-*dihydro*-9-*phosphoniaphenanthrene bromide*; C, 9-*methyl*-9-*phosphafluorene* 9-*oxide*; D, 2-*biphenyldimethylphosphine oxide.*

Preliminary results indicate that this reaction may be used even when the phosphorus substituent (R) might be expected to compete in the 1,2-migration, *i.e.*, R = Ph or $PhCH_2$. 9-Benzyl-9-phosphafluorene (b.p. 162° at 0·3 mm. Hg) was prepared by a modification of the 9-phenyl-9-phosphafluorene preparation.[5]



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[5] G. Wittig and A. Maercker, *Chem. Ber.*, 1964, **97**, 747.