REACTION OF PYROCATECHOLHALOPHOSPHORANES WITH PHENYLACETYLENE AS A SIMPLE METHOD FOR THE PREPARATION OF FUNCTIONALLY SUBSTITUTED CYCLIC QUASIPHOSPHONIUM YLIDS

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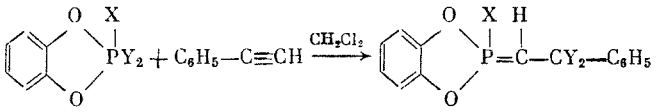
UDC 542.91:547.565.2'118:547.538.241

We have recently shown that pyrocatecholhalophosphoranes undergo addition at the carbonyl group with retention of the coordination of the phosphorus atom [1].

Phosphoranes (I) and (II) also readily undergo addition at the triple bond in phenylacetylene to give functionally substituted quasiphosphonium ylids (III) and (IV), which have been previously obtained only with difficulty. Ylids (III) and (IV) are crystalline compounds with ^{31}P NMR signals at 9 (III) and 18 ppm (IV). The structure of these compounds were also supported by ^{1}H, $^{1}H-\{^{31}P\}$, and ^{13}C NMR spectroscopy. The composition was supported by elemental analysis.



(I), (II) (III), (IV)

X = Y = Br (I), (III), Cl (II), (IV).

Thus, the ^{13}C NMR spectrum of (IV), which is formed as a 7:1 isomer mixture, have signals for the P=CH-CCl_2 fragment at 116.5 ($^{1}J_{PC}$ = 153.7 Hz) and 111.89 ppm ($^{2}J_{PCC}$ = 18 Hz, predominant stereoisomer). The ^{1}H NMR signal for the proton in the P=CH-CBr_2 fragment in (III) is found at 6.22 and 6.18 ppm, $^{2}J_{PCH}$ = 26 and 27 Hz (doublet, converts to a singlet in the $^{1}H-\{^{31}P\}$ DNMR spectrum, the isomer ratio was 1:2). Substitution of the chlorine atom in (IV) using SbF_3 gave quasiphosphonium ylid (V) (X = F, Y = Cl; δP 9 ppm, $^{1}J_{PF}$ = 1064 Hz), while substitution of the bromine atom in (III) gives fluoroylid (VI) (X = F, Y = Br; δP 6.5 ppm, $^{1}J_{PF}$ = 1063, $^{2}J_{PCH}$ = 18.7 Hz and δP 7.5 ppm, $^{1}J_{PF}$ = 1063, $^{2}J_{PCH}$ = 18.7 Hz, 1:2 isomer ratio).

LITERATURE CITED

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0568-5230/90/3906-1319$12.50