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Novel Organophosphorus Monomers: the 1,1-Diphenyl-3-aryl-4-oxa-5-(2-propenyl)-1-phosphoniacyclohexa-2,5-diene System

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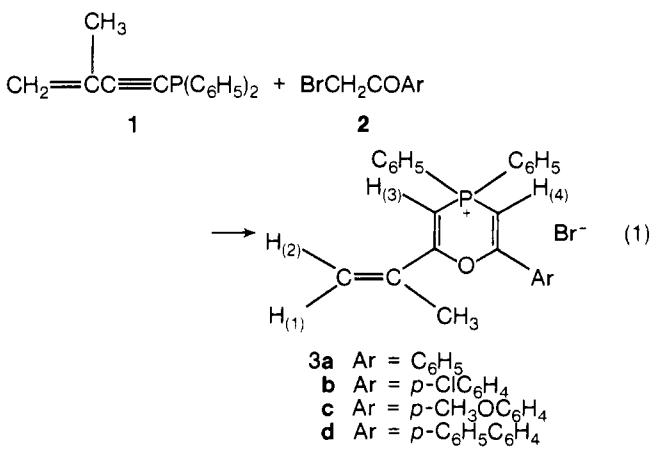
Synthesis of 1,1-diphenyl-3-aryl-4-oxa-5-(2-propenyl)-1-phosphoniacyclohexa-2,5-dienes has been described. These white crystalline phosphonium bromides have been characterized by their IR and NMR spectra.

As a part of our general research program in the synthesis of new monomers and polymers, we wish to report a convenient route to the 1,1-diphenyl-3-aryl-4-oxa-5-(2-propenyl)-1-phosphoniacyclohexa-2,5-diene system **3** (eq 1). The compounds **3** constitute a new class of monomers which have not hitherto been described in the literature. The related syntheses previously reported have not been employed for the preparation of vinyl monomers (*1, 3–5*). We have now found that diphenyl(3-methyl-3-en-1-butynyl)phosphine (**1**) reacts with α-bromo ketones **2** to produce heterocycles **3** in good to excellent yields (eq 1).



(1)

3a Ar = C_6H_5
b Ar = p-ClC_6H_4
c Ar = p-$CH_3OC_6H_4$
d Ar = p-$C_6H_5C_6H_4$

The starting phosphine **1** was prepared by the reaction of 3-methyl-3-en-1-butynyllithium with diphenylphosphinous chloride. The infrared spectrum of **1** exhibited characteristic absorption bands at 1610 cm^{-1} (C=C) and 2170 cm^{-1} (C≡C). The structure of **1** was further supported by its NMR spectrum. The phosphine **1** upon treatment with ketones **2** produced heterocycles **3** as white crystals. The infrared spectra (KBr) of **3** displayed characteristic (C=C) absorption bands at ~1625 and δ ~1605 cm^{-1}. In the NMR spectra of **3a–d**, the signal at δ ~5.75 was assigned to the vinyl proton cis ($H_{(1)}$) to the methyl group while the one at δ ~6.25 was assigned to the vinyl proton trans ($H_{(2)}$) to this methyl group (*2*). The downfield shift (δ ~6.25) of the $H_{(2)}$ signal is probably due to deshielding by the "pseudo aromatic" heterocycle system (*3, 4*). The quartet (J_{HH} = 3, J_{PH} = 6 Hz) at δ ~6.70 was assigned to ring proton $H_{(3)}$, while the quartet (J_{HH} = 3, J_{PH} = 6 Hz) at δ ~7.2 was assigned to $H_{(4)}$; this downfield shift of the $H_{(4)}$ signal is probably due to deshielding by the aryl group.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Model 453 spectrophotometer and the NMR spectra were obtained on a Bruker HX-60 spectrometer; the chemical shifts are described as δ parts per million (ppm) from tetramethylsilane.

Preparation of Diphenyl(3-methyl-3-en-1-butynyl)phosphine (1). Freshly distilled 3-methyl-3-en-1-butyne (13.2 g, 0.2 mol) was dissolved in 500-mL of anhydrous diethyl ether and placed under nitrogen in a 2-L three-necked flask. The flask was cooled with dry ice and a 2.4 M hexane solution (85 mL) of *n*-butyllithium was added slowly (30 min) with continuous stirring. The reaction mixture was stirred for 1 h and then diphenylphosphinous chloride (44.0 g, 0.2 mol) was added dropwise with continuous stirring. The reaction mixture was stirred at this temperature for 2 h and then allowed to warm up to 0 °C. Saturated ammonium chloride solution (100 mL) was added to the reaction mixture, and the layers were separated. The aqueous layer was extracted with two 50-mL portions of diethyl ether; the combined extracts were washed with sodium bicarbonate solution and dried over anhydrous sodium sulfate. The dried solution was filtered and ether was evaporated to obtain 45 g of light brown oily product. Vacuum distillation was attempted using a portion of the product but rapid polymerization occurred at about 100 °C and no distillate could be obtained. The infrared spectrum ($CHCl_3$) of the product displayed strong absorption bands at 2920, 2170 (C≡C), 1610 (C=C), 1430 (P–C_6H_5), 1270, 1120, 1090, 980, and 900 cm^{-1}; the NMR spectrum exhibited a pair of doublets (J = 1 Hz, δ 1.78, 3 H, CH_3), a quartet (J = 1 Hz, δ 5.15, 1

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H, cis (CH=C)), a quartet ($J \simeq 1$ Hz, δ 5.30, 1 H, trans CH=C), and a multiplet at δ 6.93–7.92 (10 H, aromatic protons).

Synthesis of 1,1-Diphenyl-3-aryl-4-oxa-5-(2-propenyl)-1-phosphoniacyclohena-2.5-dienes (3a–d). General. The starting bromo ketone **2** (0.01 mol) was dissolved in 100 mL of toluene and 0.01 mol of alkynylphosphine **1** was added to this solution. The reaction mixture was placed in an oil bath at 65 °C for 1 h and then allowed to cool to room temperature; white crystals started separating even before the reaction mixture cooled to room temperature. The reaction mixture was allowed to stay overnight at room temperature and then it was filtered to obtain the desired product in 60–70% yield. The product was recrystallized from acetone; the melting points, infrared (KBr), and NMR ($CDCl_3$) data are listed below. **3a:** mp 228–230 °C; IR, strong absorption bands at 2980, 1630, 1605, 1580, 1440, 1290, 1130, 1120, 1110, 840, 750, 690, and 520 cm^{-1}; NMR, broad singlet (δ 2.27, 3 H, CH_3), narrowly split quartet (δ 5.75, $H_{(1)}$), broad singlet (δ 6.25, $H_{(2)}$), quartet ($J = 3$ Hz, δ 6.70, $H_{(3)}$), quartet ($J = 3$ Hz, δ 7.20, $H_{(4)}$), and a multiplet at δ 7.52–8.17 (15 H, aromatic). **3b:** mp 233–235 °C; IR, strong absorptions at 2990, 1630, 1605, 1490, 1440, 1290, 1275, 1115, 1105, 1095, 1010, 840, 830, 820, 755, 715, 690, and 515 cm^{-1}; NMR: broad singlet (δ 2.20, 3H, CH_3), narrowly split multiplet (δ 5.70, $H_{(1)}$), broad singlet (δ 6.20, $H_{(2)}$), quartet ($J = 3$ Hz, δ 6.70, $H_{(3)}$), quartet ($J = 3$ Hz, δ 7.25, $H_{(4)}$), and a multiplet at δ 7.33–8.28 (14 H, aromatic). **3c:** mp 243–246 °C, IR, strong absorption at 2985, 1630, 1600, 1575, 1515, 1540, 1290, 1270, 1180, 1130, 1120, 835, 690, and 530 cm^{-1}; NMR, broad singlet (δ 2.25, 3 H, CH_3C), singlet (δ 3.88, 3 H, CH_3O), multiplet (δ 5.70, $H_{(1)}$), multiplet (δ 6.22, $H_{(2)}$), quartet ($J = 3$ Hz, δ 6.55, $H_{(3)}$), quartet ($J = 3$ Hz, δ 6.87, $H_{(4)}$), doublet ($J = 9$ Hz, 2 H, aromatic proton ortho to the methoxy group), and multiplet at δ 7.77–8.17 (12 H, aromatic). **3d:** mp 282–285 °C; IR, strong absorptions at 2970, 1630, 1605, 1440, 1305, 1120, 840, 765, 745, 725, 700, 685, and 530 cm^{-1}; NMR, broad singlet (δ 2.23, 3 H, CH_3), multiplet (δ 5.73, $H_{(1)}$), multiplet (δ 6.25, $H_{(2)}$), quartet (J = Hz, δ 6.60, $H_{(3)}$), quartet ($J = 3$ Hz, δ 7.10, $H_{(4)}$), and a multiplet at δ 7.33–8.25, (19 H, aromatic).

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Some 2,5- and 5,6-Dihalonicotinic Acids and Their Precursors. 5

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The preparation of 2-bromo-5-chloro-, 2-bromo-5-iodo-, 6-bromo-5-chloro-, and 6-bromo-5-iodonicotinic acid by oxidation of the appropriate dihalopicoline is described. The syntheses of the dihalopicolines are also presented. Experimental and spectral data for all compounds are reported.

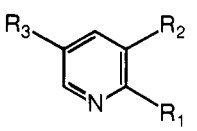
Compounds possessing hypolipidemic activity are the subject of extensive pharmaceutical research. Halo and dihalonicotinic acids and their derivatives have received attention as potential hypolipidemic agents (*1–4*), and in this communication we wish to report the preparation and characterization of four new dihalonicotinic acids as an extension of our previous work (*5–8*).

Dihalonicotinic acids IV, V, IX, and X were generated by oxidation of dihalopicolines II, III, VII, and VIII, respectively. 2-Bromo-5-chloro-3-picoline (II) and 2-bromo-5-iodo-3-picoline (III) were obtained by diazotization of 5-amino-2-bromo-3-picoline (I) (*9, 10*). 6-Bromo-5-chloro-3-picoline (VII) and 6-bromo-5-iodo-3-picoline (VIII) were prepared in analogous fashion from 5-amino-6-bromo-3-picoline (VI) (*9, 10*).

Elemental analyses (C, H, N) for all new compounds in agreement with theoretical values were obtained and submitted for review. Experimental and physical data for compounds reported herein are presented in Table I.

Experimental Section

Elemental analyses were performed by Heterocyclic Chemical Corp., Harrisonville, Mo. Melting points were taken on a Mel-Temp apparatus and are uncorrected. Infrared spectra were



I, R_1 = Br; R_2 = CH_3; R_3 = NH_2
II, R_1 = Br; R_2 = CH_3; R_3 = Cl
III, R_1 = Br; R_2 = CH_3; R_3 = I
IV, R_1 = Br; R_2 = CO_2H; R_3 = Cl
V, R_1 = Br; R_2 = CO_2H; R_3 = I
VI, R_1 = Br; R_2 = NH_2; R_3 = CH_3
VII, R_1 = Br; R_2 = Cl; R_3 = CH_3
VIII, R_1 = Br; R_2 = I; R_3 = CH_3
IX, R_1 = Br; R_2 = Cl; R_3 = CO_2H
X, R_1 = Br; R_2 = I; R_3 = CO_2H

obtained on a Perkin-Elmer 337 spectrophotometer with samples prepared as KBr disks. Proton nuclear magnetic resonance spectra were obtained at 60 MHz on a Jeolco C-60 HL instrument with tetramethylsilane as an internal standard.

2-Bromo-5-chloro-3-picoline (II). A stirred solution of 5-amino-2-bromo-3-picoline (I) (1.85 g, 0.01 mol) (*9, 10*) in a mixture of concentrated hydrochloric acid (8 mL) and water (4 mL) was diazotized at 0 °C by the slow, dropwise addition of a solution of sodium nitrite (2.0 g) in water (5 mL) over a period of 15 min. Copper powder (8 g) was cautiously added to the freshly diazotized solution, and the resulting mixture was neutralized with 25% sodium hydroxide (9 mL). Indirect steam distillation of the orange neutral suspension afforded the dihalopicoline II as a white volatile solid. Further purification was achieved by recrystallization (Table I).

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