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Reaction of α-Vinylallenylphosphonates with Diazoalkanes

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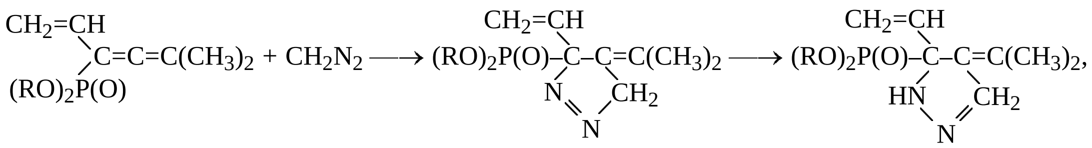
Abstract — Diazomethane reacts with 3-methyl-1-vinyl-1,2-butadienylphosphonates following the scheme of [3 + 2]-cycloaddition at the 1,2-double bond of the allenic fragment. The reaction with diphenyldiazomethane involves the vinyl fragment and yields substituted diphenylcyclopropane.

Phosphorylated allenes are known to react with diazoalkanes at the 1,2-double bond according to the [3 + 2]-cycloaddition pattern [1, 2]. Introduction of a vinyl group into the α-position with respect to the phosphinoyl fragment gives rise to additional unsaturated reaction centers in the dipolarophile: apart from the cumulene triad, conjugated 1,3-diene system and an ethylene group appear.

We have studied addition of diazomethane and diphenyldiazomethane to dimethyl and diethyl 3-methyl-1-vinyl-1,2-butadienylphosphonates **I** and **II**. The IR spectra of the resulting 1 : 1 adducts lack stretching vibation band typical of allene triad (1955–1960 cm^{-1}), indicating that the vinyl group is not involved. The presence of IR absorption at 900 cm^{-1}, typical of out-of-plane bending vibrations of the $=CH_2$ group [3] suggests that the diene system is also retained. The same follows from the ^{1}H NMR spectra of the adducts, which contain multiplets at δ 4.8–5.6 and 6.1–6.5 ppm, typical of vinyl group protons. The presence of an isopropylidene fragment is supported by characteristic signals from methyl groups at a double bond, δ 1.8 ppm. These data led us to conclude that the role of dipolarophile in the reaction with diazomethane is played by the 1,2-double bond of the cumulene triad.

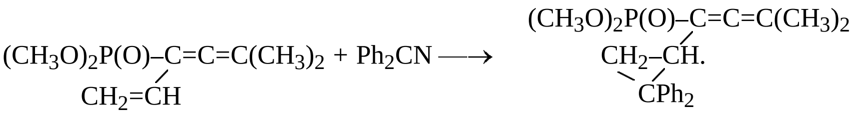


I, II **III, IV** **V, VI**

I, **III**, **V**, R = CH_3; **II**, **IV**, **VI**, R = C_2H_5.

Freshly synthesized adducts **III** and **IV** show in the IR spectra a weak absorption at 3400 (NH) and 1560 cm^{-1} (C=N), whose intensity increases with rise in temperature or on dissolution in proton-donor solvents. Presumably, this is the result of tautomerization of primary products, 4,5-dihydro-3*H*-pyrazoles **III** and **IV**, into the corresponding 1*H*-isomers **V** and **VI**. In the ^{1}H NMR spectra, an olefinic proton signal appears at δ 6.9 ppm (3-H).

Phopsphorylated triene **I** reacts with diphenyldiazomethane less vigorously. Analysis of the IR and ^{1}H NMR spectra of the adduct indicates that the reaction involves the vinyl group of **I**.



VII

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The IR spectrum of **VII** contains a strong absorption band at 1960 cm^{-1} from the cumulene system. In the ^1H NMR spectrum of adduct **VII**, cyclopropane ring protons give a triplet at δ 2.18 ppm (CH) and a doublet at δ 1.38 ppm (CH_2). Signals from the aromatic protons are observed in the region δ 7.0–7.44 ppm.

EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrometer. The ^1H NMR spectra were obtained on a Varian T-60 instrument (60 MHz) in carbon tetrachloride using tetramethylsilane as reference.

3-Dialkoxyphosphinoyl-4-isopropylidene-3-vinyl-4,5-dihydro-3*H*-pyrazoles III and IV. A mixture of 0.01 mol of phosphonate **I** or **II** and 0.015 mol of diazomethane in ether was left to stand for a week at 5°C. The solvent was removed to leave a viscous oily substance.

3-Dimethoxyphosphinoyl-4-isopropylidene-3-vinyl-4,5-dihydro-3*H*-pyrazole (III). Yield 2.3 g (96%), n_D^{20} 1.5370. Found, %: C 50.01; H 6.85; P 12.50. $C_{10}H_{17}N_2O_3P$. Calculated, %: C 49.18; H 6.97; P 12.71.

3-Diethoxyphosphinoyl-4-isopropylidene-3-vinyl-4,5-dihydro-3*H*-pyrazole (III). Yield 2.6 g (97%), n_D^{20} 1.5128. Found, %: C 53.12; H 8.09; P 10.91. $C_{12}H_{21}N_2O_3P$. Calculated, %: C 52.94; H 7.72; P 11.40.

1-Dimethoxyphosphinoyl-1-(2,2-diphenylcyclopropyl)-3-methyl-1,2-butadiene (VII). A mixture of 1.94 g of diphenyldiazomethane and 2 g of phosphonate **I** in 10 ml of petroleum ether was left to stand for 2 weeks at 15°C. The crystals were filtered off and washed with ether. Yield 2.3 g (64%), mp 94–96°C. Found, %: C 72.11; H 7.04; P 7.85. $C_{22}H_{25}O_3P$. Calculated, %: C 71.74; H 6.79; P 8.42.

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REFERENCES

1. Khusainova, N.G., Timoshina, T.V., and Pudovik, A.N., *Zh. Obshch. Khim.*, 1976, vol. 46, no. 11, p. 2624.
2. Khusainova, N.G. and Pudovik, A.N., *Usp. Khim.*, 1978, vol. 47, no. 9, pp. 1507–1527.
3. Bellamy, L.J., *The Infrared Spectra of Complex Molecules*, London: Methuen, 1958.