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LETTERS TO THE EDITOR

One-Step Synthesis of 1,3-Diene Aminophosphonium Salts Based on Buta-1,3-diene-1,4-diylbis(triphenylphosphonium Iodide)

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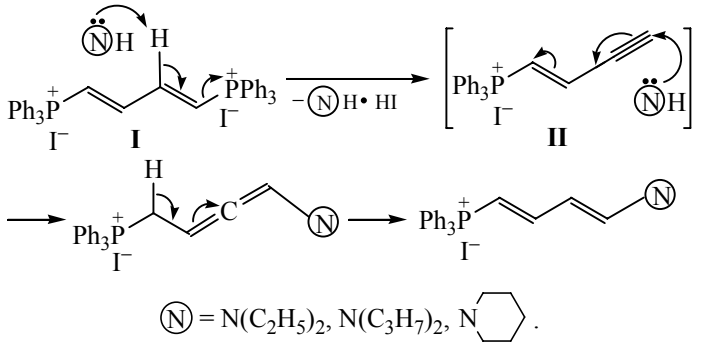
Recently we have reported that buta-1,3-diene-1,4-diylbis(triphenylphosphonium dichloride) undergoes Hofmann elimination at the action of alkaline agents at room temperature to form intermediate monophosphonium salt with a but-1-en-3-ynyl group. The latter undergoes anionotropic α-phenyl migration. Heating the salt in a sealed tube at 100°C in the presence of triethylamine affords the Hofmann elimination product, triphenylphosphine, and a large amount of resin, which is likely the result of condensation of the second product of the elimination, the triphenyl-β-ethynylvinylphosphonium chloride [1].

In continuation of these studies we explored the reaction of buta-1,3-diene-1,4-diylbis(triphenylphosphonium diiodide) **I** with secondary amines: diethyl-, dipropylamine, and piperidine. Indeed, in all cases 4-dialkylaminobuta-1,3-diene-1-yltriphenylphosphonium iodides were obtained in 50–60% yield, the products of nucleophilic addition to triphenyl-β-ethynylvinylphosphonium intermediate **II**. Also triphenylphosphine was isolated (60%) and identified, the second product of the reaction.

The reaction proceeds according to the scheme, which includes an initial formation of intermediate **II**, nucleophilic 1,4-addition of amine, and prototropic isomerization of the resulting β-allenylphosphonium intermediate into the more stable 1,3-dienephosphonium isomer.



N = $N(C_2H_5)_2$, $N(C_3H_7)_2$, N⟨⟩.

The obtained dieneaminophosphonium salt due to the features of its structure may be of interest from both theoretical and practical points of view as a convenient synthon for new functionally substituted phosphonium salts, phosphine oxides, etc.

The ^1H, ^{13}C, and ^{31}P NMR spectra were registered on a Varian Mercury-300 spectrometer operating at 300.077 (^1H), 75.46 (^{13}C), and 121.47 MHz (^{31}P), respectively, at 303 K, internal reference TMS.

Reaction of salt I with secondary amines. To a solution of 2.41 mmol of salt **I** in 30 ml of propanol was added 4.82 mmol of a secondary amine. The mixture was refluxed for 20 h. The solvent was removed. The residue was washed with anhydrous

ether, extracted with water and chloroform. From the ethere extracts triphenylphosphine was isolated, mp 74°C. Dienoamino phosphonium salt was isolated after removal of the solvent from the chloroform extract and recrystallization from ethyl acetate-isopropanol mixture.

4-Diethylaminobuta-1,3-diene-1-yltriphenylphosphonium iodide. Yield 56%, mp 154°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 1.19 t (6H, CH_3, *J* 7.1), 3.30 q (4H, CH_2, *J* 7.1), 5.58 d.d (1H, C*H*CHN, ^1J 12.6, ^2J 11.3), 5.77 d.d (1H, P^+CH, ^1J 21.2, ^2J 15.5), 6.83 d.d.d (1H, P^+CHCH, ^1J 19.4, ^2J 15.5, ^3J 11.3), 7.08 d (1H, NCH, *J* 12.4), 7.60–7.88 m (15H, P^+Ph_3). ^{31}P NMR spectrum (DMSO-d_6), δ_P, ppm: 24.08. Found I, %: 24.72. $C_{26}H_{29}INP$. Calculated I, %: 24.76.

4-Dipropylaminobuta-1,3-diene-1-yltriphenylphosphonium iodide. Yield 60%, mp 165°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 0.93 m (6H, CH_3), 1.61 m (4H, CH_2CH_3), 3.19 m (4H, NCH_2), 5.59 d.d (1H, C*H*CHN, ^1J 12.5, ^2J 11.3), 5.72 d.d (1H, P^+CH, ^1J 21.2, ^2J 15.4), 6.81 d.d.d (1H, P^+CHCH, ^1J 19.3, ^2J 15.4, ^3J 11.3), 7.07 d (1H, NCH, *J* 12.5), 7.61–7.88 m (15H, P^+Ph_3). ^{31}P NMR spectrum (DMSO-d_6), δ_P, ppm: 24.02. Found I, %: 23.52. $C_{28}H_{33}INP$. Calculated I, %: 23.48.

4-Piperidylbuta-1,3-diene-1-yltriphenylphosphonium iodide. Yield 51%, mp 143°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 1.56–1.72 m (6H, $C_5H_{10}N$), 3.33 m (4H, NCH_2), 5.66 d.d (1H, C*H*=CHN, ^1J 12.5, ^2J 11.2), 5.77 d.d (1H, P^+CH, ^1J 21.3, ^2J 15.4), 6.81 d.d.d (1H, P^+CHCH, ^1J 19.5, ^2J 15.4, ^3J 11.2), 7.03 d (1H, NCH, *J* 12.5), 7.60–7.87 m (15H, P^+Ph_3). ^{31}P NMR spectrum (DMSO-d_6), δ_P, ppm: 24.1. Found I, %: 24.14. $C_{27}H_{29}INP$. Calculated I, %: 24.19.

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