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Unusual Course of Reaction of Triphenyl(2-*p*-toluylethyl)phosphonium Bromide with Hydrazine

R. Dzh. Khachikyan

Institute of Organic Chemistry, National Academy of Sciences of Armenia,
ul. Zakaria Kanakertsi 167-A, Yerevan, 375091 Armenia
e-mail: Nara7777@mail.ru

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Abstract—The reaction of triphenyl(2-*p*-toluylethyl)phosphonium bromide with hydrazine hydrochloride yields, along with the hydrazone, 6-*p*-tolyl-2,3-dihydropyridazin-3-one as a minor product.

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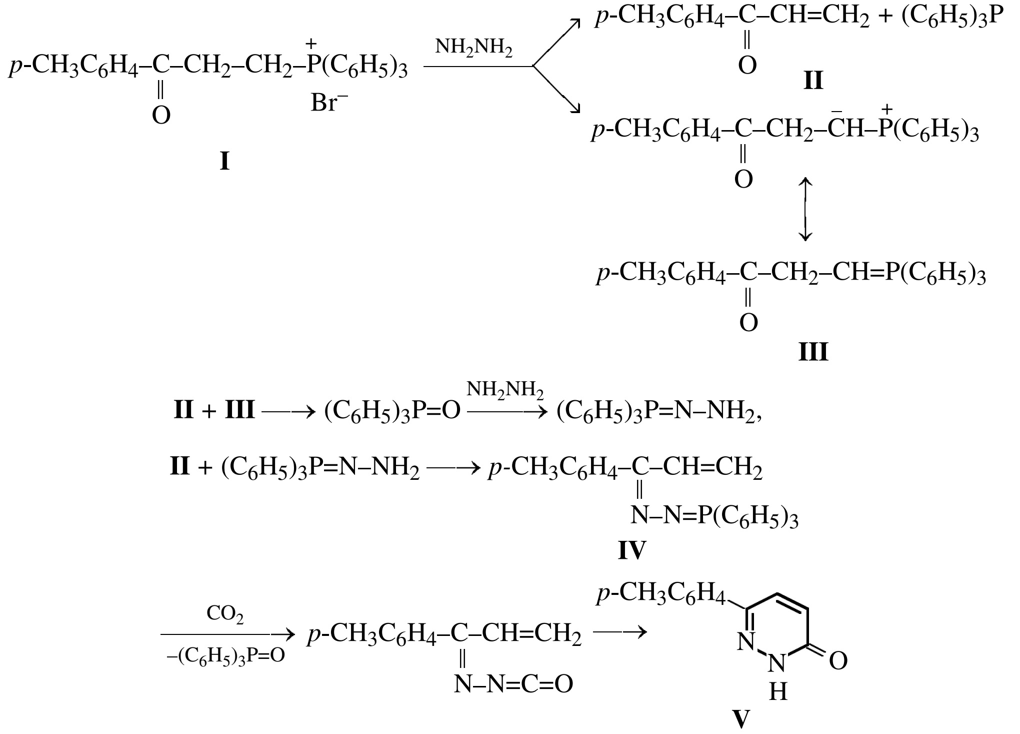
Previously, in a study of functionalization of 2-aroylacrylic acids, we prepared 2-aroylethylphosphonium salt oximes, and also triphenyl-(2-toluyl-1-methoxycarbonylethyl)phosphonium bromide oxime and hydrazone [1].

The reaction of triphenyl-2-toluylethylphosphonium bromide **I** with hydrazine hydrochloride in methanol in the presence of water gave interesting results: As a minor product, together with the expected hydrazone (55%), we unexpectedly isolated 6-*p*-tolyl-2,3-dihydropyridazin-3-one **V** in 18% yield. The ^1H and ^{13}C NMR and mass spectra of the product were identical to those of the authentic sample prepared previously [2, 3].

The by-product is presumably formed by Scheme 1.

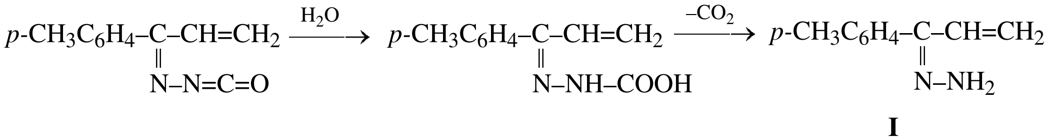
Scheme 1.



As seen from Scheme 1, keto phosphonium salt **I** reacts with hydrazine along two pathways: β-elimination with the formation of ketone **II** and elimination of hydrogen to form ylide which exists in equilibrium with its phosphorane form **III**. Compounds **II** and **III** enter into the Wittig reaction yielding $(C_6H_5)_3P=O$ and a product containing no phosphorus, which we failed to isolate. $(C_6H_5)_3P=O$ reacts with hydrazine to form hydrazone $(C_6H_5)_3P=N–NH_2$, which, in turn, reacts with compound **II** to form azino phosphorane **IV**. The latter compound under the action of atmospheric CO_2 transforms along the Wittig reaction pathway into an isocyanate derivative, which under the reaction conditions closes the ring to form the final compound **V**.

Under the action of water, a part of intermediately forming isocyanate undergoes decarboxylation, and the released carbon dioxide continues the reaction.

Scheme 2.



$$p\text{-}CH_3C_6H_4\text{–}\underset{\substack{\| \\ N\text{–}N=C=O}}{C}\text{–}CH=CH_2 \xrightarrow{H_2O} p\text{-}CH_3C_6H_4\text{–}\underset{\substack{\| \\ N\text{–}NH\text{–}COOH}}{C}\text{–}CH=CH_2 \xrightarrow{-CO_2} p\text{-}CH_3C_6H_4\text{–}\underset{\substack{\| \\ N\text{–}NH_2}}{C}\text{–}CH=CH_2$$

I

The hypothesis that azino phosphorane **IV** enters into Wittig reaction is supported by the results obtained by Bestmann [4] in a study of the reaction with benzaldehyde of the related compound $(C_6H_5)_3P=N–N=C(C_6H_5)_2$. It should be noted that performing this reaction in a CO_2 flow increased the yield of 6-tolyl-2,3-dihydropyridazin-3-one to 34.1%.

EXPERIMENTAL

The ^1H NMR spectra were recorded on a Varian Mercury-300 device with an operating frequency of 300 MHz, internal reference TMS.

Reaction of triphenyl(2-*p*-toluylethyl)phosphonium bromide with hydrazine hydrochloride. *a*. Without CO_2 flow. To a saturated solution of 2 g of triphenyl(2-*p*-toluylethyl)phosphonium bromide in methanol, we added 3.37 g of hydrazine hydrochloride dissolved in a minimal amount of water. The reaction mixture was refluxed on a water bath for 30 h. The precipitate formed was filtered off, washed with water, and dried in a vacuum. 0.14 g (18%) of **6-*p*-tolyl-2,3-dihydropyridazin-3-one** was obtained, mp 240–241°C. Found, %: C 70.5; H 5.51; N 15.1. $C_{11}H_{10}N_2O$. Calculated, %: C 70.97; H 5.37; N 15.05. ^1H NMR spectrum (DMSO-d_6 + CCl_4), δ, ppm: 2.38 s (3H, CH_3), 6.86 d (1H, $C_4N_2H_2$, J 9.9), 7.20 d (2H, C_6H_5, J 8.1), 7.68 d (2H, C_6H_5, J 8.1), 7.80 d (1H, $C_4N_2H_2$, J 9.9), 12.97 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 20.66 (CH_3); 125.14 ($C^{2'}$ and $C^{6'}$); 128.83 ($C^{3'}$ and $C^{5'}$); 129.60 ($C^{1'}$); 130.33 ($C^{4'}$); 131.90 (C^4); 137.87 (C^5); 143.23 (C^6); 159.76 (C=O). Mass spectrum (EI, 70 eV), m/z (I_{rel}, %): 186 $[M]^+$.

The aqueous filtrate was extracted with chloroform, the extract was poured into ether, and the white crystals formed were filtered off and washed with ether. 1.14 g (55%) of **triphenyl(2-*p*-toluylethyl)-phosphonium bromide hydrazone,** mp 221–222°C, was isolated. Found, %: C 66.5; H 5.60; N 5.54; P 6.19; Br 15.3. $C_{28}H_{28}BrN_2P$. Calculated, %: C 66.8; H 5.52; N 5.57; P 6.16; Br 15.9. ^1H NMR spectrum (DMSO-d_6 + CCl_4), δ, ppm: 2.40 s (3H, CH_3), 3.50 m (2H, CH_2), 4.00 m (2H, CH_2), 7.20–8.00 m (15H, $3C_6H_5$, p-C_6H_4). ^{31}P NMR spectrum, δ_P 31.18 ppm.

b. Under CO_2 flow. This experiment was carried out similarly except that, after refluxing for 24 h, CO_2 was passed through the reaction mixture for 1.5–2 h. 0.26 g (34.1%) of **6-*p*-tolyl-2,3-dihydropyridazin-3-one** and 1.3 g (63%) of **triphenyl(2-*p*-toluylethyl)phosphonium bromide hydrazone** were obtained. The melting points, elemental analyses, and ^1H, ^{31}P and ^{13}C NMR spectra coincide with those of the product obtained by procedure *a*.

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