Russian Journal of General Chemistry, Vol. 71, No. 6, 2001, pp. 981–982. Translated from Zhurnal Obshchei Khimii, Vol. 71, No. 6, 2001, pp. 1043–1044.

LETTERS TO THE EDITOR

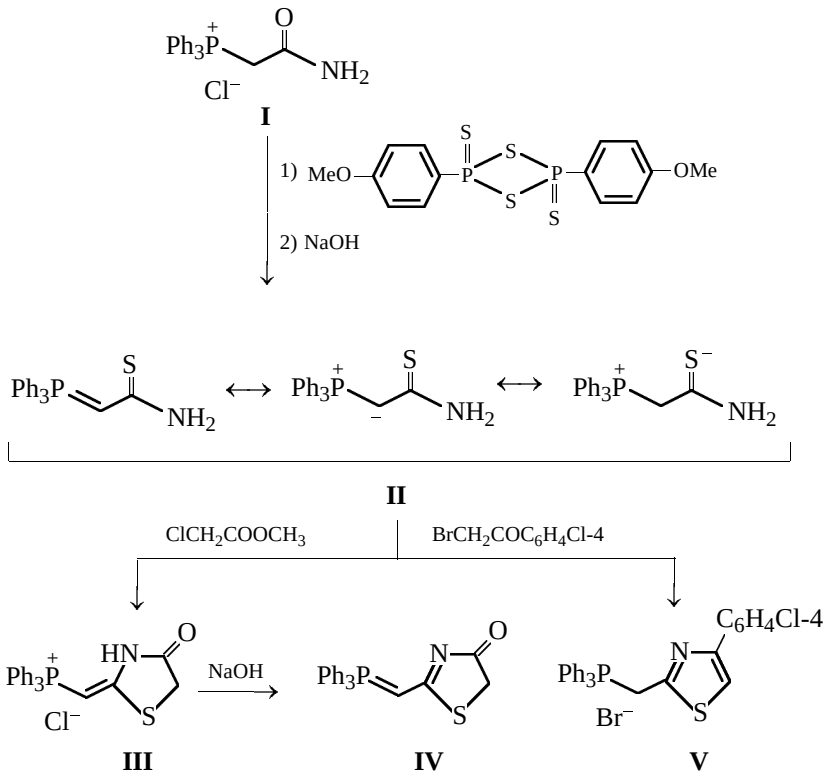
Triphenyl(thiocarbamoylmethylene)phosphorane, a Promising Reagent for Heterocyclizations

O. B. Smolii, V. D. Bezverhnii, and B. S. Drach

Institute of Bioorganic Chemistry and Petrochemistry, National Academy of Sciences of Ukraine, Kiev, Ukraine

Received August 24, 2000

The available phosphonium salt **I** via a series of simple reactions was converted to a new phosphorus-containing mesomeric reagent **II** which can be described by three canonical structures: phosphinomethylene, ylide, and betaine. The contrubution of the latter structure is the most significant, since compound **II** readily reacts with α-halocarbonyl compounds without participation of the ylide center (see scheme).



The electronic structure and heterocyclizations of triphenyl(thiocarbamoylmethylene)phosphorane (**II**) will be described in detail in further publications. Here we would only like to note that this reagent is a parental representative of a series of stabilized phosphonium ylides containing a thiocarbamoyl group (cf. [1]).

Triphenyl(thiocarbamoylmethylene)phosphorane (II). To a suspension of 0.01 mol of phosphonium salt **I** [2] in 50 ml of toluene, 0.01 mol of Lawesson reagent was added. The resulting mixture was stirred for 3 h at 110°C and then left for 12 h at 20–25°C. The toluene was decanted, and the residue was treated with acetone for crystallization. The

1070-3632/01/7106-0981 $25.00

precipitate was filtered off and crystallized from ethanol. Then it was dissolved in a minimum of ethanol at 20–25°C and treated with a solution of 0.006 mol of sodium hydroxide in 15 ml of water. The mixture was left for 15 min at 20–25°C, the precipitate was filtered off and crystallized from acetonitrile. Yield 35%, mp 182–185°C. Found, %: C 71.39; H 5.28; P 9.40; S 9.63. $C_{20}H_{18}NPS$. Calculated, %: C 71.62; H 5.41; P 9.23; S 9.56.

(4-Oxo-4,5-dihydrothiazol-2-ylidenemethylene)triphenylphosphonium chloride (III). To a solution of 0.01 mol of reagent **II** in 40 ml of ethanol, 0.01 mol of methyl chloroacetate was added. The resulting mixture was kept for 24 h at 20–25°C, the precipitate was filtered off and crystallized from ethanol. Yield 50%, mp 273–275°C. ^{1}H NMR spectrum, δ, ppm: 3.90 s (2H, CH_2), 6.09 d (1H, CH, $^3J_{HP}$ 11.6 Hz), 7.40–7.90 m (15 H, $3C_6H_5$), 12.99 br.s (1H, NH). Found, %: C 64.10; H 4.51; P 7.48; S 7.68. $C_{22}H_{19}$·ClNOPS. Calculated, %: C 64.15; H 4.65; P 7.52; S 7.78.

(4-Oxo-4,5-dihydrothiazol-2-ylmethylene)triphenylphosphorane (IV). To a solution of 0.005 mol of compound **III** in 10 ml of methanol, 0.005 mol of sodium methoxide in 5 ml of absolute methanol was added. The resulting mixture was left for 15 min at 20–25°C, the methanol was removed in a vacuum, and the residue was crystallized from acetonitrile. Yield 45%, mp 232–235°C. ^{1}H NMR spectrum, δ, ppm: 3.61 s (2H, CH_2), 4.19 d (1H, CH, $^3J_{PH}$ 22.0 Hz) 7.61–7.70 m (15H, $3C_6H_5$). Found, %: C 70.21; H 4.71; P 8.19; S 8.60. $C_{22}H_{18}NOPS$. Calculated, %: C 70.38; H 4.83; P 8.25; S 8.54.

[4-(*p*-Chlorophenyl)thiazol-2-ylmethyl]thiophenylphosphonium bromide (V) was prepared from reagent **II** and *p*-chlorophenacyl bromide under the same conditions as compound **III**. Yield 54%, mp 268–270°C ^{1}H NMR spectrum, δ, ppm: 5.91 d (2H, CH_2, $^3J_{HP}$ 15.6 Hz), 7.42 d and 7.60 d (4H, C_6H_4), 7.70–7.90 m (15H, $3C_6H_5$), 8.16 s (1H, C^5–H). Found, %: C 59.88; H 3.89; P 5.57; S 5.92. $C_{28}H_{22}BrClNPS$. Calculated, %: C 61.05; H 4.03; P 5.62; S 5.82.

The ^{1}H NMR spectra of compounds **III**–**V** were recorded on a Bruker WP spectrometer (200 MHz) in DMSO-d_6 against TMS.

REFERENCES

1. Smolii, O.B., Panchishin, S.Ya., Romanenko, E.A., and Drach, B.S., *Zh. Obshch. Khim.*, 1995, vol. 65, no. 4, pp. 583–586.
2. Ger. Patent 943 648, 1956, *Chem. Abstr.*, 1958, vol. 52, 16 292e.