

LETTERS TO THE EDITOR

Transformation of the Adducts of Acyl Isothiocyanates with (Cyanomethylene)triphenylphosphorane into 1,2,4-Triazole Derivatives

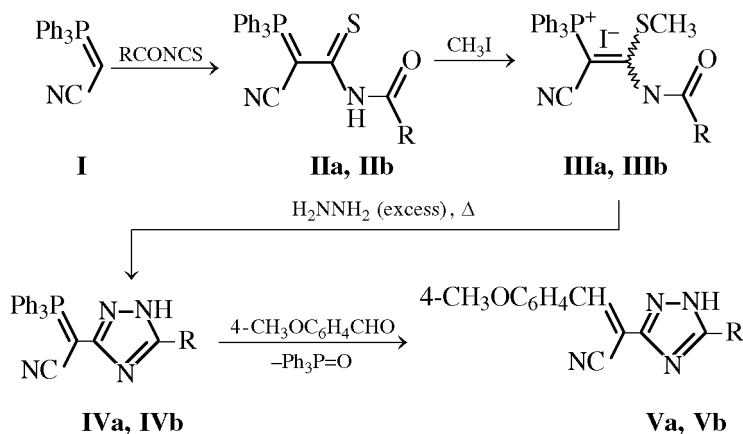
V. D. Bezverkhni, O. B. Smolii, and B. S. Drach

*Institute of Bioorganic and Petroleum Chemistry,
National Academy of Sciences of the Ukraine, Kiev, Ukraine*

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Addition of easily available ylide **I** to acyl isothiocyanates gives compounds **II** which were recently used in the synthesis of phosphorus-containing pyri-

midine derivatives [1]. As shown in the scheme, we have now succeeded in using reagents **II** for preparing two new types of substituted 1,2,4-triazoles.



R = CH₃ (a), 4-CH₃C₆H₅ (b).

Methylation of compounds **II** leads to a mixture of geometric isomers of substituted vinylphosphonic salts **III**, but this has almost no effect on the subsequent cyclocondensation **III** → **IV**. The resulting 1,2,4-triazole ring formation is akin to the well-known cyclization of amidrazones under the action of acylating agents [2]. That compounds **IV** contain an ylide fragment is beyond question, since they readily enter the Wittig reaction with aromatic aldehydes. Stereochemical peculiarities of the transformations **I** → **III** and **IV** → **V**, as well as the implications of prototropy for new 1,2,4-triazole derivatives **IV** and **V** will be discussed in more detail elsewhere.

[Cyano(5-methyl-1,2,4-triazol-3-yl)methylene]triphenylphosphorane (IV). To a solution of 0.01 mol of compound **II** in 150 ml of methanol, 0.01 mol of methyl iodide was added. The mixture was left to stand at 20–25°C for 12 h, and the methanol was removed in vacuo. The residue was dissolved in 50 ml of acetonitrile, 0.03 mol of hydrazine hydrate was added, and the mixture was refluxed for 5 h. The precipitate that formed was filtered off and recrystallized from ethanol. Yield 60%. mp 261–262°C. ¹H NMR spectrum, δ, ppm: 1.92 br.s (3H, CH₃), 7.60–7.70 m (15H, 3C₆H₅), 12.55 br. s (1H,

NH). Found, %: C 72.33; H 5.13; P 8.13. $C_{23}H_{19}N_4P$. Calculated, %: C 72.24; H 5.01; P 8.10.

[Cyano(5-*p*-tolyl-1,2,4-triazol-3-yl)methylene]triphenylphosphorane (IVb) was prepared in a similar way from compound **IIb**. Yield 87%. mp 246–248°C. IR spectrum, ν , cm^{-1} : 2200 ($C\equiv N$), 3400 (NH). 1H NMR spectrum, δ , ppm: 2.45 s (3H, CH_3), 7.08 d ($2H_{arom}$), 7.47 d ($2H_{arom}$), 7.61–7.75 m (15H, $3C_6H_5$), 13.06 br.s (1H, NH). Found, %: C 75.85; H 5.12; P 6.80. $C_{29}H_{23}N_4P$. Calculated, %: C 75.97; H 5.06; P 6.76.

3-[Cyano(*p*-methoxybenzylidene)methyl]-5-methyl-1,2,4-triazole (Va). A suspension of 0.001 mol of compound **IVa** and 0.001 mol of *p*-methoxybenzaldehyde in 10 ml of ethanol was refluxed for 72 h. The precipitate that formed was filtered off and purified by recrystallization from ethanol. Yield 45%. mp 188–190°C. IR spectrum, ν , cm^{-1} : 2220 ($C\equiv N$), 3420 (NH). 1H NMR spectrum, δ , ppm: 2.41 s (3H, CH_3), 3.85 s (3H, CH_3O), 7.13 d ($2H_{arom}$), 8.00 d ($2H_{arom}$), 8.11 s (1H, $CH=CCN$), 13.87 br.s (1H, NH). Found, %: C 64.80; H 5.12; N 23.40.

$C_{13}H_{12}N_4O$. Calculated, %: C 64.99; H 5.03; N 23.32.

3-[Cyano(*p*-methoxybenzylidene)methyl]-5-*p*-tolyl-1,2,4-triazole (Vb) was prepared in a similar way from compound **IVb**. Yield 65%. mp 231–233°C. 1H NMR spectrum, δ , ppm: 2.39 s (3H, CH_3), 3.86 s (3H, CH_3O), 7.15 d ($2H_{arom}$), 7.39 d ($2H_{arom}$), 7.94 d.d ($4H_{arom}$), 8.22 s (1H, $CH=CCN$), ~14.5 br.s (1H, NH). Found, %: C 72.08; H 5.05; N 17.65. $C_{19}H_{16}N_4O$. Calculated, %: C 72.14; H 5.10; N 17.71.

The IR spectra were obtained on a UR-20 spectrometer in KBr pellets. The 1H NMR spectra of compounds **IV** and **V** were recorded on a Bruker-WP (200 MHz) instrument in $DMSO-d_6$ solutions with TMS as internal reference.

REFERENCES

1. Smolii, O.B., Panchishin, S.Ya., and Drach, B.S., *Zh. Obshch. Khim.*, 1993, vol. 63, no. 9, pp. 1990–1994.
2. Nelson, D.G., Roger, R., Heatlie, J.W.M., and Newlands, L.R., *Chem. Rev.*, 1970, vol. 70, no. 1, pp. 151–170.