A NEW RECYCLIZATION OF 2,4,6-TRIETHOXYCARBONYL-1,3,5-TRIAZINE IN THE INTERACTION WITH SEMICARBAZIDE

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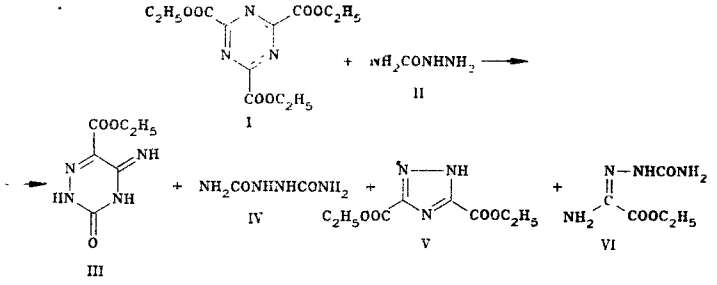
Studying the interaction of 2,4,6-triethoxycarbonyl-1,3,5-triazine (I) with semicarbazide (II) at a ratio I:II = 1:4 in boiling ethanol (1 h), we detected a new reaction — recyclization of the 1,3,5-triazine derivative I to the previously undescribed 3-oxo-5-imino-6-ethoxycarbonyl-2,3,4,5-tetrahydro-1,2,4-triazine (III). Substance III, isolated with a yield of 51%, has mp 261-263°C (from absolute ethanol); IR spectrum: 1645, 1690 (CON, C=NH), 1735 ($COOC_2H_5$), 3130, 3440 cm^{-1} (NH); PMR spectrum (100 MHz, DMSO-D_6): 1.27 (t, 3H) and 4.28 (q, 2H, CH_2CH_3), 7.91 and 8.38 (s, according to 1H, NH, CONH); 12.89 ppm (s, 1H, NH, bonded by an intramolecular hydrogen bond); mass spectrum (70 eV): m/z 184 $[M]^+$, 156 $[M - C_2H_4]^+$, 139 $[M - OC_2H_5]^+$, 112 $[M - COOC_2H_4]^+$, 69 $[M - COOC_2H_4 - CONH]^+$.



The hydrazodicarboxamide (IV) was also isolated from the reaction mass (34%, mp 256-258°C, identified according to the IR spectrum and a mixed melting point test with a known sample [1]), along with 3,5-diethoxycarbonyl-1,2,4-triazole (V) (23%, mp 112-113°C, identical with a known sample [2]) and a previously undescribed amidrazone VI (yield 63%, mp 181-183°C). IR spectrum: 1655, 1680 (CON, C=NH), 1745 ($COOC_2H_5$), 3330, 3360, 3435, 3485 cm^{-1} (NH, NH_2); PMR spectrum (DMSO-D_6): 1.26 (t, 3H) and 4.20 (q, 2H, CH_2CH_3), 6.12 (s, 4H, NH_2), 8.82 ppm (s, 1H, NH); mass spectrum: m/z 174 $[M]^+$, 157 $[M - NH_3]^+$, 131 $[M - NHCO]^+$, 101 $[M - COOC_2H_5]^+$. Substances III and IV were recrystallized from alcohol after cooling, but compound III, in contrast to the hydrazoamide IV, is readily soluble in boiling alcohol. The amidrazone VI was recrystallized from chloroform, while the triazole V was removed chromatographically on a column with silica gel, with elution with a mixture of benzene and ethyl acetate.

The interaction of the symmetrical triazine I with the thiosemicarbazide does not lead to the formation of a nonsymmetrical triazine derivative: in this case only the triazole V arises (yield 50%), along with a previously undescribed thioanalog of compound VI, mp 166-167.5°C (from a mixture of isopropanol and methanol, 1:1). IR spectrum: 1595, 1620 (C=N), 1700 ($COOC_2H_5$), 3300, 3420 (NH, NH_2), 1505 cm^{-1} (C=S); PMR spectrum (DMSO-D_6): 1.30 (t, 3H) and 4.27 (q, 2H, CH_2CH_3), 6.72 (s, 2H, NH_2), 7.24 (s, 1H, NH), 8.09 (s, 1H, NH), 10.90 ppm (s, 1H, NH); mass spectrum: m/z 190 $[M]^+$, 173 $[M - NH_3]^+$, 157 $[M - SH]^+$, 118 $[M - COOC_2H_4]^+$.

All the new compounds had satisfactory analytical characteristics.

LITERATURE CITED

1. J. Thiele, Ann. 271, 127 (1892).
2. N. V. Alekseeva and L. N. Yakhontov, Zh. Org. Khim., 20, 893 (1984).

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