1,4-REARRANGEMENT OF THE ENOL ACETATE OF 2,4-DICHLOROPHENYL 1,2,4-TRIAZOL-1-YLMETHYL KETONE

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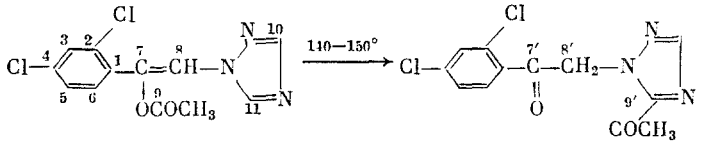
UDC 542.952.1:547.792.5

The enol acetates of carbonyl compounds undergo 1,2-rearrangement with the formation of 1,3-diketones [1, 2]. The 1,4-migration of the acetyl group of the 1,2,4-triazole ring to C^5 and formation of 1,5-diketone (II) was shown for the enol acetate of 2,4-dichlorophenyl 1,2,4-triazol-1-ylmethyl ketone (I) obtained according to our previous procedure [3]. This rearrangement proceeds upon heating of enol acetate (I) or its solution in diglyme, DMSO, or acetic anhydride at 140-150°C for 4-5 h. The yield of diketone (II) was 70-80%. To our knowledge, this is the first example of the 1,4-rearrangement of ketone enol acetates.



(I) (II)

Enol Acetate of 2,4-Dichlorophenyl 1,2,4-Triazol-1-ylmethyl Ketone (I), mp 137-138°C (from 2-propanol). PMR spectrum in CD_3CN (δ, ppm): 2.25 s (3H, CH_3), 7.18 s (1H, =CH), 7.36-7.54 m (3H, ArH), 7.98 s (1H, $C^{10}H$), 8.58 s (1H, $C^{11}H$). ^{13}C NMR spectrum in CD_3CN (δ, ppm): 21.0 (CH_3), 117.3 (C^8), 128.2 (C^2), 130.7 (C^3), 131.8 (C^7), 132.8 (C^6), 133.9 (C^2), 136.2 (C^1), 137.2 (C^4), 145.0 (C^{10}), 152.4 (C^{11}), 168.2 (C^9).

2,4-Dichlorophenyl 5-Acetyl-1,2,4-triazol-1-ylmethyl Ketone (II), mp 95-96°C (from 2-propanol). PMR spectrum in CD_3CN (δ, ppm): 2.63 s (3H, CH_3), 5.87 s (2H, CH_2), 7.5-7.8 m (3H, ArH), 8.02 s (1H, $C^{10}H$). ^{13}C NMR spectrum in CD_3CN (δ, ppm): 28.3 (CH_3), 61.1 ($C^{8'}$), 129.1 (C^5), 132.2 (C^3), 132.6 (C^6), 134.0 (C^2), 135.2 (C^1), 139.7 (C^4), 147.1 (C^{10}), 151.9 (C^{11}), 191.6 ($C^{9'}$), 183.8 ($C^{7'}$). The elemental analysis data for (I) and (II) corresponded to the calculated values.

LITERATURE CITED

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Institute of Chemistry, Academy of Sciences of the Moldavian SSR, Kishinev. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 6, p. 1454, June, 1990. Original article submitted February 1, 1990.

0568-5230/90/3906-1317$12.50