and benzyl radicals (ethylbenzene is the product) and solvolysis (the products are acetic acid and benzylmethyl-d_3 ether)

It was found that during photolysis in a low acoustic field the ratio of the yield of ethylbenzene to the yields of acetic acid and benzylmethyl-d_3 ether increases. The alteration of this ratio by electric power equal $3 \cdot 10^{-3}$ W was 10±3 %.

In our opinion, the alterations observed result from the fact that even small disturbances (excitation of the oscillational degrees of freedom) can influence the relationship of the contributions of the alternative processes, especially when the substance is in a metastable state. These disturbances in this case are acoustic fields, which destroy the solvate shells and thus decrease the contribution of photosolvolysis to the total process. For further investigations and to understand the effects of the acoustic field it will be necessary to study in more detail the processes of the association (complexation) of the starting reagents and the role of small active additives (impurities).

Experimental

Solutions (0.05 mol L^{-1}) of benzylacetate in CD_3OD (degree of deuteration was 98 %) were investigated. The irradiation was carried out in quartz cuvette by the light of a DRSh-500 lamp (working current ~7 A). The low acoustic fields ($W \approx 3 \cdot 10^{-3}$ W; discrete working frequencies f_1 = 200 kHz, f_2 = 5 MHz, f_3 = 10 MHz) were created by a quartz generator. The reaction products were analyzed on BS-567A (100 MHz), MSL-300 (300 MHz), and WM-360 (360 MHz) NMR spectrometers. The results of the measurements were treated by the method of least squares.

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Rearrangement of enol acetates of α-(3,5-dimethyl-1,2,4-triazol-1-yl)-2,4-dichloroacetophenone and α-(1,2,4-triazol-1-yl)-2,4-dichloropropiophenone

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At 140 °C in acetic anhydride enol acetates of α-(3,5-dimethyl-1,2,4-triazol-1-yl)-2,4-dichloroacetophenone and α-(1,2,4-triazol-1-yl)-2,4-dichloropropiophenone undergo 1,3- and 1,5-rearrangement, respectively.

Key words: enol acetates, diketones, ketones, aryl-(1,2,4-triazol-1-yl)methylketones; migration of the acyl group, rearrangement.

1,3-Rearrangements to yield β-diketones are typical of enol acylates of carbonyl compounds.[1,2] We have found previously[3] that under the conditions of thermolysis, enol acylates of aryl-(1,2,4-triazol-1-yl)methylketones undergo 1,5-rearrangement with the migration of the acyl group to the C(5) atom of the triazole ring.

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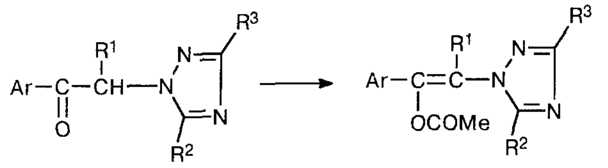
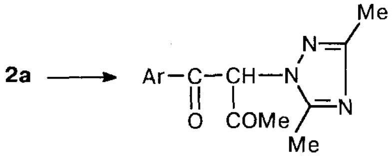
To elucidate the regularities of this type of transformation, one should, first of all, determine whether 1,3-rearrangements of analogous enol acylates are possible.

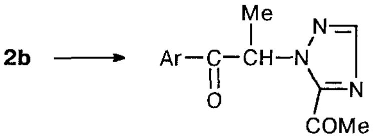
It might be suggested that the presence of a substituent at the C(5) atom of the triazole ring should result in the 1,3-migration of the acyl group. In addition, an increase in the nucleophilicity of the C=C bond of enol acylates (for example, when an H atom of the methylene group is replaced by an electron-donating substituent) should probably also favor the change in the direction of the migration of the acyl group.



1a,b **2a,b**



3



4

$R^1 = H, R^2 = R^3 = Me$ (**a**); $R^1 = Me, R^2 = R^3 = H$ (**b**);
Ar = $2,4\text{-}Cl_2C_6H_3$

In order to verify these suggestions, in the present work we studied the thermal rearrangements of α-(3,5-dimethyl-1,2,4-triazol-1-yl)-2,4-dichloroacetophenone enol acetate (**2a**) and α-(1,2,4-triazol-1-yl)-2,4-dichloropropiophenone enol acetate (**2b**), which contain a methyl group at the C(5) atom of the triazole ring or at the C=C bond, respectively.

Enol acetates **2a,b** were prepared from ketones **1a,b** by treating them with acetic anhydride in the presence of pyridine at 80 °C. Compound **2b** was obtained as a 2 : 3 mixture of geometric isomers, which was used for reactions without separation.

The rearrangement of enol acetates **2a,b** was carried out by a procedure similar to that described previously,[3] *i.e.*, in acetic anhydride at 140 °C. It turned out that under these conditions, enol acetate **2a** reacted very slowly, and its conversion was no more than 25—30 % (according to ^1H NMR spectroscopy and TLC) even after 18 h. The reaction product was isolated in an ~18 % yield, along with a 1 : 1 mixture of the starting enol acetate **2a** and triazolylketone **1a** (yield 56 %), and identified as β-diketone **3** (see Experimental). Thus, as we expected, enol acetate **2a** undergoes 1,3-rearrangement, which occurs with a lower degree of conversion than the 1,5-rearrangement[3] of triazolylketone enol acylates containing no substituents at the C(5) atom of the triazole ring. At 200 °C, the complete conversion (TLC data) of enol acetate **2a** was achieved within 2 h, however, this rearrangement was accompanied by substantial resinification, and β-diketone **3** was isolated in only a ~43 % yield.

The reaction of enol acetate **2b** in acetic anhydride at 140 °C occurs much more quickly than that of **2a**, and its conversion is as high as 80 % even after 12 h. Analysis of the reaction mixture (data of ^1H NMR spectroscopy and TLC) indicates that 1,5-diketone **4** was formed as the only product. Thus, in this case, too, in spite of the presence of the electron-donating methyl group at the C=C bond of enol acetate **2b**, only the 1,5-rearrangement with the migration of the acetyl group to the C(5) atom of the triazole ring occurs.

Thus, the results of the present work and the literature data[3] indicate that the presence of the triazole ring at the double bond of enol acetate results in a decrease in its nucleophilic activity, and, consequently, thermolysis yields only the products of 1,5-rearrangement. The reaction considered is apparently common to triazolylketones that contain no substituents at the C(5) atom of the ring. However, enol acylates of triazolylketones containing a substituent at the C(5) atom of the triazole ring undergo 1,3-rearrangement, which occurs with much more difficulty and with a lower degree of conversion.

Experimental

The course of the reactions and the purity of the individual compounds were monitored by TLC on Silufol UV-254 plates in an acetone—chloroform (1 : 9) system. Reaction products were isolated by preparative TLC on 24×24 cm^2 plates (a 2 mm thick unfixed Silpearl layer) using chloroform (for enol acetate **2a** and diketones **3** and **4**) or an isopropanol—chloroform (1 : 8) system (for enol acetate **2b**) as eluents. The ^1H NMR spectra were recorded on a Bruker AC-80 spectrometer using TMS as the internal standard.

Triazolylketones 1a,b were prepared from 2,4-dichlorophenacyl bromide and 4-amino-3,5-dimethyl-1,2,4-triazole and from α-bromo-2,4-dichloropropiophenone and 4-amino-1,2,4-triazole, respectively by the known method.[4,5] 4-Amino-3,5-dimethyl-1,2,4-triazole was prepared according to the previously described[6] procedure.

α-(3,5-Dimethyl-1,2,4-triazol-1-yl)-2,4-dichloroacetophenone (1a). Yield 83 %; m.p. 105—107 °C, m.p. of the salt with HNO_3 125—127 °C. Found (%): C, 50.94; H, 4.12; Cl, 25.23; N, 14.95. $C_{12}H_{11}Cl_2N_3O$. Calculated (%): C, 50.72; H, 3.90; Cl, 24.96; N, 14.79. ^1H NMR ($CDCl_3$), δ: 2.31 and 2.35 (both s, 6 H, 2 Me); 5.39 (s, 2 H, CH_2); 7.17—7.66 (m, 3 H, Ar).

α-(1,2,4-Triazol-1-yl)-2,4-dichloropropiophenone (1b). Yield 78 %; oil, m.p. of the salt with HNO_3 108—109 °C. Found (%): C, 48.76; H, 3.24; Cl, 26.51; N, 15.43. $C_{11}H_9Cl_2N_3O$. Calculated (%): C, 48.91; H, 3.36; Cl, 26.25; N, 15.56. ^1H NMR ($CDCl_3$), δ: 1.64 (d, 3 H, Me, J = 7.2 Hz); 5.86 (q, 1 H, CH, J = 7.2 Hz); 7.06—7.38 (m, 3 H, Ar); 7.80 (s, 1 H, H(3), triazole); 8.19 (s, 1 H, H(5), triazole).

Enol acetate 2a. A mixture of ketone **1a** (2.84 g, 10 mmol), Ac_2O (10.2 g, 100 mmol), and pyridine (0.79 g, 10 mmol) in 100 mL of CCl_4 was boiled for 15 h, diluted with 200 mL of $CHCl_3$, washed with a 2 % aqueous solution of $NaHCO_3$ and water, and dried with Na_2SO_4. The solvent was removed. Preparative TLC gave 2.63 g (80.7 %) of enol acetate **2a** as an oil. Found (%): C, 51.35; H, 4.29; Cl, 22.14; N, 12.96. $C_{14}H_{13}Cl_2N_3O_2$. Calculated (%): C, 51.55; H, 4.02; Cl, 21.73; N, 12.88. ^1H NMR (acetone-d_6), δ: 2.19 and 2.21 (both s, 6 H, 2 Me); 2.49 (s, 3 H, OMe); 7.21 (s, 1 H, CH); 7.30—7.70 (m, 3 H, Ar).

Enol acetate 2b. Compound **2b** was prepared similarly to enol acetate **2a**. Yield 78 %; a syrup-like mass; n_D^{25} 1.5686 (*cf.* Ref. 7: n_D^{25} 1.5690). Found (%): C, 49.77; H, 3.68; Cl, 23.20; N, 13.65. $C_{13}H_{11}Cl_2N_3O$. Calculated (%): C, 50.02; H, 3.54; Cl, 22.71; N, 13.46. ^1H NMR (acetone-d_6), δ (signals for two stereoisomers are given; the ratio between their integral intensities was 3/2): 2.06/2.18 (both s, 3 H, Me); 2.10/2.25 (both s, 3 H, OMe); 7.09—7.49 (m, 3 H, Ar); 7.57/7.88 (both s, 1 H, H(3), triazole); 7.75/8.36 (both s, 0.6 H + 0.4 H, H(5), triazole).

2-(3,5-Dimethyl-1,2,4-triazol-1-yl)-1-(2,4-dichlorophenyl)-1,3-butanedione (3). *A*. A solution of ketone **1a** (0.57 g, 2 mmol) in 4 mL of acetic anhydride was boiled at ~140 °C for 18 h. Then the mixture was concentrated *in vacuo*, and 80 mL of ethyl acetate was added to the residue. The resulting solution was washed with water, with a 2% aqueous solution of $NaHCO_3$, and again with water and dried with Na_2SO_4. The solvent was evaporated. Preparative TLC gave 0.32 g (56 %) of a mixture (~1 : 1) of enol acetate **2a** and ketone **1a** and 0.11 g (17.7 %) of diketone **3** as an oil. Found (%): C, 51.80; H, 3.94; Cl, 22.20; N, 12.64. $C_{14}H_{13}Cl_2N_3O_2$. Calculated (%): C, 51.55; H, 4.02; Cl, 21.73; N, 12.88. ^1H NMR (acetone-d_6), δ: 2.18 (s, 3 H, Me); 2.54 (s, 6 H, Me and COMe); 6.96 (s, 1 H, CH); 7.43—7.59 (m, 3 H, Ar).

B. Enol acetate **2a** (1.63 g, 5 mmol) was kept in an Ar atmosphere for 2 h at 200 °C. The resulting resinous mass was dissolved in $CHCl_3$ and chromatographed to give 0.70 g (42.9 %) of diketone **3** and 0.81 g of a resin.

α-(5-Acetyl-1,2,4-triazol-1-yl)-2,4-dichloropropiophenone (4). A solution of enol acetate **2b** (1.30 g, 4 mmol) in 15 mL of acetic anhydride was boiled (~140 °C) for 12 h. Then the reaction mixture was diluted with water (100 mL), neutralized with a 10% aqueous solution of KOH, and extracted with ethyl acetate. The extract was treated in the same way as in the synthesis of diketone **3** (method *A*). Preparative TLC gave 0.92 g (71.3 %) of diketone **4** as a syrup-like mass and 0.20 g (15 %) of the starting enol acetate **2b**. Found (%): C, 50.28; H, 3.72; Cl, 23.05; N, 13.31; $C_{13}H_{11}Cl_2N_3O$. Calculated (%): C, 50.02; H, 3.54; Cl, 22.71; N, 13.46. ^1H NMR ($CDCl_3$), δ: 1.82 (d, 3 H, Me, J = 7.2 Hz); 2.74 (s, 3 H, COMe); 6.66 (q, 1 H, CH, J = 7.2 Hz); 7.15—7.60 (m, 3 H, Ar); 8.00 (s, 1 H, H(3), triazole).

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