# 1,5-Rearrangement of enol acylates of aryl 1*H*-1,2,4-triazol-1-ylmethyl ketones

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The rearrangement of enol acylates of aryl 1*H*-1,2,4-triazol-1-ylmethyl ketones at 140—150°C in acetic anhydride is studied. The migration of the acyl group to the C(5) atom of the heterocycle is found to be intramolecular. The characteristics of the original and final products are presented. X-ray structural studies of the enol acetates of 2,4-dichlorophenyl 1*H*-1,2,4-triazol-1-ylmethyl ketone and 2,4-dichlorophenyl 5-acetyl-1*H*-1,2,4-triazol-1-ylmethyl ketone are carried out.

**Key words:** enol acetates, enol acylates, 1,5-diketones, ketones, acyl group migration, rearrangement, triazol-1-ylmethyl ketones, X-ray structural analysis

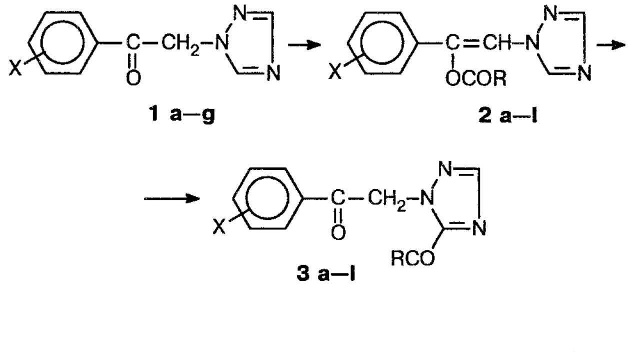
One of the most interesting reactions of enol acylates of ketones is their 1,3-rearrangement (thermal or catalytic) to β-diketones.[1—4] Only a few examples of analogous rearrangements have been described: 1,8-migration of the acyl group to the C(4) atom of the aromatic ring is typical for enol acylates of 2-benzylcyclohexane-1,3-dione,[5] 1,5-rearrangements of esters of *o*-hydroxyacetophenones are also known.[1] A new rearrangement of enol acylates is reported herein.

## Results and Discussion

In choosing the conditions for the acetylation of 2,4-dichlorophenyl 1*H*-1,2,4-triazol-1-ylmethyl ketone (**1f**) by acetic anhydride to enol acetate **2f** at temperatures above 100°C, we discovered (GLC, TLC) conversion of the latter to a new product. Heating the reaction mixture at 140—150°C for 5—6 h afforded it in a 77 % yield (method A). The same compound was also obtained (82 %) when enol acetate **2f** was heated in acetic anhydride under similar conditions (140—150°C, ~5 h) (method B).

On the basis of data from $^1$H NMR spectroscopy, elemental analysis (Table 1), and X-ray diffraction analysis (see below), the product was identified as 2,4-dichlorophenyl 5-acetyl-1*H*-1,2,4-triazol-1-ylmethyl ketone (**3f**).

In view of the observation of such an unexpected direction for migration of the acyl group (the final position is the C(5) atom of the 1,2,4-triazole ring, instead of the vinyl carbon atom of enol acetate **2f**), we became interested in studying this reaction in more detail. It turned out that heating enol acetate **2f** without a solvent or in a diglyme solution at 140—160°C for 6—8 h also produces only the product of 1,5-rearrangement of diketone **3f** in ~50 and ~73 % yields, respectively. However, the most effective procedure is to use acetic anhydride as the solvent and to carry out the reaction out at 140—150°C for 4—5 h. The attempts to lower the temperature for rearrangement of enol acetate **2f** to 80—90°C by using such solvents as $CCl_4$, $CH_3CN$, benzene, or glyme were unsuccessful even when the heating time was increased to 20—24 h: the original enol acetate was recovered in all cases. Similar results (along with the formation of ketone **1f** due to deacetylation of enol


**1 a—g**  **2 a—l**  **3 a—l**

R = Me, X = H (**a**), 2-Br (**b**), 4-Br (**c**), 2-Cl (**e**), 2,4-$Cl_2$ (**f**), 4-Me (**g**); R = $CD_3$, X = 2,4-$Cl_2$ (**h**); R = Et, X = H (**i**), 2,4-$Cl_2$ (**j**); R = $Me_3C$, X = 2,4-$Cl_2$ (**k**); R = $(CH_2)_4Me$, X = 2,4-$Cl_2$ (**l**).

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**Table 1.** Characteristics of diketones **3a—l**

| Compound | Yield * (%) | Mp (°C) | Found/Calculated (%) | | | | Molecular formula | H NMR spectrum ($CDCl_3$), δ (*J*, Hz)*** | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | C | H | N | Hal | | R | $COCH_2$ | ArH | TrlHC(3) |
| **3a** | 84 | 71—72 | 62.09<br>62.87 | 5.09<br>4.84 | 17.95<br>18.33 | — | $C_{12}H_{11}N_3O_2$ | 2.71 | 6.04 | 7.76 | 8.04 |
| **3b** | 79(72) | 116—117 | 46.70<br>46.77 | 3.22<br>3.27 | 12.92<br>13.64 | 26.18<br>25.93 | $C_{12}H_{10}BrN_3O_2$ | 2.72 | 5.93 | 7.49 | 8.02 |
| **3c** | 66 | 158—160 | 46.49<br>46.77 | 3.12<br>3.27 | 13.52<br>13.64 | 26.27<br>25.93 | $C_{12}H_{10}BrN_3O_2$ | 2.72 | 5.93 | 7.50 | 8.02 |
| **3d** | 74(70) | 81—82 | 54.91<br>54.66 | 3.64<br>3.82 | 15.75<br>15.94 | 13.81<br>13.45 | $C_{12}H_{10}ClN_3O_2$ | 2.72 | 5.97 | 7.52 | 8.02 |
| **3e** | 76 | 138—140 | 54.29<br>54.66 | 3.57<br>3.82 | 15.75<br>15.94 | 13.73<br>13.45 | $C_{12}H_{10}ClN_3O_2$ | 2.70 | 6.01 | 7.62 | 8.02 |
| **3f** | 82(77) | 95—96 | 48.05<br>48.34 | 2.95<br>3.04 | 13.91<br>14.09 | 24.12<br>23.79 | $C_{12}H_9Cl_2N_3O_2$ | 2.68 | 5.91 | 7.55 | 7.98 |
| **3g** | 81 | 83—84 | 64.50<br>64.18 | 5.28<br>5.39 | 17.14<br>17.27 | — | $C_{13}H_{13}N_3O_2$ | 2.70 | 6.01 | 7.60 | 8.01 |
| **3h** | 74 | 93—94 | 48.13<br>47.86 | 3.73<br>4.01 | 13.77<br>13.95 | 23.79<br>23.55 | $C_{12}H_6D_3Cl_2N_3O_2$ | — | 5.95 | 7.52 | 8.02 |
| **3i** | 79 | ** | 64.35<br>64.18 | 5.28<br>5.39 | 17.14<br>17.27 | — | $C_{13}H_{13}N_3O_2$ | 1.15 (t, $CH_2C\underline{H}_3$, *J*=7.2);<br>3.17 (q, $C\underline{H}_2CH_3$, *J*=7.2) | 6.03 | 7.65 | 8.04 |
| **3j** | 82(79) | ** | 49.67<br>50.05 | 3.46<br>3.55 | 13.19<br>13.46 | 23.04<br>22.72 | $C_{13}H_{11}Cl_2N_3O_2$ | 1.18 (t, $CH_2C\underline{H}_3$, *J*=7.2);<br>3.19 (q, $C\underline{H}_2CH_3$, *J*=7.2) | 5.96 | 7.66 | 8.00 |
| **3k** | 63 | ** | 53.14<br>52.95 | 4.27<br>4.44 | 12.20<br>12.35 | 21.23<br>20.84 | $C_{15}H_{15}Cl_2N_3O_2$ | 1.42 | 6.05 | 7.72 | 8.02 |
| **3l** | 81 | ** | 54.51<br>54.25 | 4.98<br>4.84 | 11.68<br>11.86 | 19.55<br>20.02 | $C_{16}H_{17}Cl_2N_3O_2$ | 0.92 (t, $CH_3$, *J*=5.8);<br>1.60 (m, $CH_2(C\underline{H}_2)_3CH_3$);<br>3.15 (t, $COCH_2$, *J*=7.2) | 5.94 | 7.55 | 8.10 |

* Yields of diketones prepared according to method B (the values for method A are given in parentheses).

** Viscous liquid.

*** The center of the multiplet observed for the aromatic protons is given; signals of other protons are singlets unless stated otherwise; Trl is the 1,2,4-triazole radical.

acetate **2f**) were obtained in attempts to carry out the rearrangement under acid catalysis (gaseous HCl, $H_2SO_4$, $BF_3 \cdot Et_2O$). These results indicate that the observed 1,5-rearrangement is a thermal process.

In order to ascertain whether the 1,5-rearrangement is of general character, we synthesized a number of enol acylates of aryl 1*H*-1,2,4-triazol-1-ylmethyl ketones **2a—e**,**g—l** (Table 2). It was found that the optimal conditions for their rearrangement are the same as those for enol acetate **2f**, namely, acetic anhydride, 140—150°C, ~5 h (Table 1). Table 1 indicates that varying the nature of the aryl substituents and the migrating group in the enol acylates does not have any effect on the character of the rearrangement: in all cases the acyl groups migrate only to the C(5) atom of the triazole ring to form the corresponding diketones **3a—e** and **g—l**.

Thus, the reaction discovered is a general reaction for enol acylates of various triazolyl ketones **2** and occurs most efficiently in acetic anhydride. Although the reactivity of 1,2,4-triazoles with respect to electrophiles is known[6,7] to be decreased, the participation of acetic anhydride in the reaction as a coreactant could have been postulated on a formal basis. In order to test this hypothesis, we synthesized $CD_3$-labeled enol acetate **2h** (Table 2) and carried out its rearrangement in acetic anhydride. $CD_3$-labeled diketone **3h** was obtained as the only rearrangement product (Table 1), i.e. unlabeled diketone **3f** was not detected in this product or in filtrate and the mother liquor. This result, along with the absence of this diketone in the products of the rearrangement of enol acylates **2i—l** in acetic anhydride, provides grounds to reject this hypothesis.

**Table 2.** Characteristics of enol acylates **2a—l**

| Compound | Yield (%) | Mp (°C) | Found (%)<br>Calculated | | | | Molecular formula | $^1$H NMR spectrum (CDCl$_3$), δ (*J*, Hz)* | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | C | H | N | Hal | | R | =CH | ArH | TrlHC(3) | TrlHC(5) |
| **2a** | 46 | 110—111 | $\underline{62.72}$<br>62.87 | $\underline{4.81}$<br>4.84 | $\underline{18.52}$<br>18.33 | — | $C_{12}H_{11}N_3O_2$ | 2.35 | 7.27 | 7.53 | 8.02 | 8.43 |
| **2b** | 83 | 84—85 | $\underline{46.63}$<br>46.77 | $\underline{3.12}$<br>3.27 | $\underline{13.49}$<br>13.64 | $\underline{26.19}$<br>25.93 | $C_{12}H_{10}BrN_3O_2$ | 2.28 | 7.05 | 7.46 | 8.04 | 8.58 |
| **2c** | 37 | 130 | $\underline{46.51}$<br>46.77 | $\underline{3.04}$<br>3.27 | $\underline{13.91}$<br>13.64 | $\underline{26.27}$<br>25.93 | $C_{12}H_{10}BrN_3O_2$ | 2.36 | 7.26 | 7.51 | 8.03 | 8.42 |
| **2d** | 82 | 103—104 | $\underline{54.35}$<br>54.66 | $\underline{3.61}$<br>3.82 | $\underline{16.27}$<br>15.94 | $\underline{13.60}$<br>13.45 | $C_{12}H_{10}ClN_3O_2$ | 2.27 | 7.07 | 7.42 | 8.02 | 8.57 |
| **2e** | 54 | 122 | $\underline{54.39}$<br>54.66 | $\underline{3.69}$<br>3.82 | $\underline{16.19}$<br>15.94 | $\underline{13.23}$<br>13.45 | $C_{12}H_{10}ClN_3O_2$ | 2.37 | 7.15 | 7.41 | 8.02 | 8.43 |
| **2f** | 77 | 137—138 | $\underline{48.58}$<br>48.34 | $\underline{3.07}$<br>3.04 | $\underline{14.27}$<br>14.09 | $\underline{23.63}$<br>23.79 | $C_{12}H_9Cl_2N_3O_2$ | 2.28 | 7.02 | 7.39 | 8.03 | 8.56 |
| **2g** | 44 | 118—119 | $\underline{64.13}$<br>64.18 | $\underline{5.62}$<br>5.39 | $\underline{17.61}$<br>17.27 | — | $C_{13}H_{13}N_3O_2$ | 2.33; 2.36<br>($CH_3Ar$) | 7.11 | 7.30 | 8.01 | 8.41 |
| **2h** | 45 | 134—135 | $\underline{47.54}$<br>47.86 | $\underline{3.64}$<br>4.01 | $\underline{14.19}$<br>13.95 | $\underline{23.93}$<br>23.55 | $C_{12}H_6D_3Cl_2N_3O_2$ | — | 7.05 | 7.37 | 8.02 | 8.55 |
| **2i** | 54 | — | $\underline{64.31}$<br>64.18 | $\underline{5.24}$<br>5.39 | $\underline{17.41}$<br>17.27 | — | $C_{13}H_{13}N_3O_2$ | 1.16 (t, $CH_2C\underline{H}_3$, *J*=7.2);<br>2.53 (q, $CO\underline{C}H_2$, *J*=7.2) | 7.27 | 7.52 | 8.02 | 8.45 |
| **2j** | 51 | — | $\underline{49.57}$<br>50.05 | $\underline{3.49}$<br>3.55 | $\underline{13.15}$<br>13.46 | $\underline{23.01}$<br>22.72 | $C_{13}H_{11}Cl_2N_3O_2$ | 1.19 (t, $CH_2C\underline{H}_3$, *J*=7.2);<br>2.58 (q, $CO\underline{C}H_2$, *J*=7.2) | 7.04 | 7.39 | 8.02 | 8.55 |
| **2k** | 58 | — | $\underline{52.65}$<br>52.95 | $\underline{4.12}$<br>4.44 | $\underline{12.02}$<br>12.35 | $\underline{20.62}$<br>20.84 | $C_{15}H_{15}Cl_2N_3O_2$ | — | 7.02 | 7.37 | 8.04 | 8.57 |
| **2l** | 52 | — | $\underline{53.87}$<br>54.25 | $\underline{5.05}$<br>4.84 | $\underline{11.55}$<br>11.86 | $\underline{19.60}$<br>20.02 | $C_{16}H_{17}Cl_2N_3O_2$ | 0.87 (t, $C\underline{H}_3CH_2$, *J*=5.8);<br>1.21 (m, $(C\underline{H}_2)_3CH_3$);<br>2.49 (t, $CO\underline{C}H_2$, *J*=7.2) | 7.01 | 7.35 | 8.01 | 8.55 |

* The integrated intensity of each signal corresponds to the number of protons in the fragment indicated; the center of the multiplet observed for the aromatic protons is given; the signals of the other protons are singlets unless stated otherwise; Trl is the 1,2,4-triazole radical.

To elucidate whether the process observed is intra- or intermolecular, we carried out a "cross" experiment with enol acetate **2a** and enol propionate **2j**. These enol acylates rearrange with approximately equal rates and can be easily separated (along with diketones **3a, f, i,** and **j**) by GLC (see Experimental). An equimolar mixture of these enol acylates was heated in acetic anhydride at 140°C. After 3 h the extent of conversion of each substrate was equal to 90—92 %, and the reaction mixture contained (according to GLC) products of the "normal" reaction, that is, diketones **3a** and **3j**, and did not contain the cross diketones **3f** and **3i**, which would have been formed in the case of intermolecular acyl exchange. These results, as well as those which we previously[8] obtained when we investigated the kinetics of the rearrangement of enol acetate **2f**, attest to an intramolecular mechanism for the process.

The conformations of enol acylates **2** also favor such a rearrangement pathway, as was established by an X-ray structural investigation of enol acetate **2f** and diketone **3f** (Fig. 1, Experimental). The angle between the triazole ring plane and the plane specified by the C(4)—C(7)—C(8)—C(1) fragment in the molecule of enol acetate **2f** is equal to 22.2°. The relatively low value of this angle is evidently due to the π-interaction between the triazole ring and the C(7)—C(8) double bond. This π-system is expanded to some extent due to involvement of the benzene ring, whose plane forms a 45.3° angle with the plane of the C(7)—C(8)—C(1) fragment. However, closer approach of the plane of the triazole ring to the plane of the C(7)—C(8)—C(1) fragment is prevented by an intimate intramolecular contact between the O(1) and C(9) atoms (the distance is 2.77 Å). The distance between the C(9) and C(11)

**Table 3.** Bond lengths (*d*) and bond angles (ω) in molecules **2f** and **3f**

| Bond | *d* (Å) | | Angle | ω (deg) | |
|---|---|---|---|---|---|
| | **2f** | **3f** | | **2f** | **3f** |
| Cl(1)—C(2) | 1.76(1) | 1.76(2) | C(7)—O(1)—C(11) | 116.6(8) | |
| Cl(2)—C(4) | 1.74(1) | 1.71(2) | N(2)—N(1)—C(8) | 124.8(10) | 118.7(16) |
| O(1)—C(7) | 1.43(1) | 1.19(2) | N(2)—N(1)—C(9) | 109.7(10) | 113.2(15) |
| O(1)—C(11) | 1.39(1) | — | C(8)—N(1)—C(9) | 125.3(10) | 128.0(16) |
| O(2)—C(11) | 1.19(2) | 1.14(2) | N(1)—N(2)—C(10) | 109.1(11) | 102.5(15) |
| N(1)—N(2) | 1.35(2) | 1.33(2) | C(9)—N(3)—C(10) | 116.0(13) | 104.8(16) |
| N(1)—C(8) | 1.41(1) | 1.48(3) | C(2)—C(1)—C(6) | 119.6(11) | 118.4(15) |
| N(1)—C(9) | 1.34(1) | 1.33(2) | C(2)—C(1)—C(7) | 124.0(10) | 123.7(14) |
| N(2)—C(10) | 1.32(2) | 1.39(3) | C(6)—C(1)—C(7) | 116.2(10) | 117.6(14) |
| N(3)—C(9) | 1.31(2) | 1.34(2) | Cl(1)—C(2)—C(1) | 122.5(9) | 119.0(12) |
| N(3)—C(10) | 1.33(2) | 1.39(3) | Cl(1)—C(2)—C(3) | 115.5(19) | 118.5(12) |
| C(1)—C(2) | 1.36(2) | 1.39(2) | C(1)—C(2)—C(3) | 121.7(11) | 122.3(15) |
| C(1)—C(6) | 1.39(2) | 1.39(2) | C(2)—C(3)—C(4) | 115.7(12) | 118.1(15) |
| C(1)—C(7) | 1.48(2) | 1.51(2) | Cl(2)—C(4)—C(3) | 116.9(10) | 119.7(13) |
| C(2)—C(3) | 1.40(2) | 1.36(2) | Cl(2)—C(4)—C(5) | 118.7(10) | 118.8(13) |
| C(3)—C(4) | 1.37(2) | 1.40(2) | C(3)—C(4)—C(5) | 124.2(12) | 121.3(15) |
| C(4)—C(5) | 1.35(2) | 1.36(2) | C(4)—C(5)—C(6) | 118.6(12) | 119.4(15) |
| C(5)—C(6) | 1.38(2) | 1.39(2) | C(1)—C(6)—C(5) | 119.6(11) | 120.0(15) |
| C(7)—C(8) | 1.29(2) | 1.57(2) | O(1)—C(7)—C(1) | 116.3(9) | 122.7(15) |
| C(11)—C(12) | 1.50(2) | 1.45(3) | O(1)—C(7)—C(8) | 119.4(10) | 122.1(16) |
| C(9)—C(11) | — | 1.48(2) | C(1)—C(7)—C(8) | 124.1(11) | 114.4(14) |
| | | | N(1)—C(8)—C(7) | 126.9(11) | 109.3(15) |
| | | | N(1)—C(9)—N(3) | 101.9(11) | 108.7(15) |
| | | | N(1)—C(9)—C(11) | — | 125.5(15) |
| | | | N(3)—C(9)—C(11) | — | 125.6(16) |
| | | | N(2)—C(10)—N(3) | 103.0(11) | 110.6(17) |
| | | | O(1)—C(11)—O(2) | 122.4(10) | — |
| | | | O(1)—C(11)—C(12) | 109.6(10) | — |
| | | | O(2)—C(11)—C(12) | 127.8(11) | 124.5(18) |
| | | | O(2)—C(11)—C(9) | — | 122.1(8) |
| | | | C(9)—C(11)—C(12) | — | 113.2(16) |

atoms, which directly participate in the rearrangement, is equal to 2.94 Å, and they thus occupy sterically favorable positions for migration of the acetyl C(11) atom to the C(9) atom. The changes in the bonding scheme occurring during the rearrangement (the conversion of the C(7)—C(8) double bond into a single bond and the formation of the C(7)—O(1) bond) greatly weaken the π-interaction between the triazole ring and the C(7)C(8)C(1) fragment with resultant rotation of these fragments relative to each other (the angle between their planes in diketone **3f** is 81.4°) and in removal of the steric hindrances observed in the original enol acetate **2f**. The acetyl group in diketone **3f** is located nearly in the same plane with the triazole ring (the angle between them equals only 5°), while the benzene ring is rotated 75.1° relative to the central C(7)C(8)O(1) fragment of the molecule.

**Table 4.** Crystallographic parameters and data from the X-ray structural experiments and the refinement of structures **2f** and **3f**

| Parameter | **2f** | **3f** | Parameter | **2f** | **3f** |
|---|---|---|---|---|---|
| Space group | $P2_12_12_1$ | $P2/n$ | γ (deg) | 90 | 97.88(3) |
| *a* (Å) | 11.452(7) | 7.519(3) | *V* (Å$^3$) | 1312(1) | 1316(1) |
| *b* (Å) | 7.462(5) | 8.395(3) | *Z* | 4 | 4 |
| *c* (Å) | 15.354(8) | 21.048(5) | Radiation | Cu $K_\alpha$ | Mo $K_\alpha$ |
| α (deg) | 90 | 90 | Number of measured reflections with $I > 2\sigma$ | 1113 | 784 |
| β (deg) | 90 | 90 | | | |
| | | | *R* | 0.086 | 0.082 |

**Table 5.** Atomic coordinates (x $10^4$) for structures **2f** and **3f**

| Atom | **2f** | | | **3f** | | |
|---|---|---|---|---|---|---|
| | *x* | *y* | *z* | *x* | *y* | *z* |
| Cl(1) | −2853(3) | 6355(7) | −3419(2) | 2416(6) | 2875(7) | 3667(3) |
| Cl(2) | −7276(3) | 6599(6) | −2317(3) | 8058(7) | 958(7) | 4876(2) |
| O(1) | −1372(6) | 7015(10) | −1862(5) | 4365(16) | 3000(15) | 2174(6) |
| O(2) | −1569(8) | 9089(12) | −790(5) | 18(18) | 1724(19) | 2187(6) |
| N(1) | −712(8) | 4379(13) | −601(6) | 2750(21) | 521(21) | 1444(8) |
| N(2) | −315(11) | 2835(18) | −236(8) | 3840(19) | 180(21) | 977(8) |
| N(3) | 1030(12) | 709(20) | −276(9) | 1442(23) | 1324(22) | 600(3) |
| C(1) | −3455(9) | 6150(15) | −1700(7) | 5020(20) | 1463(20) | 3075(7) |
| C(2) | −3818(9) | 6353(18) | −2540(7) | 4424(19) | 2012(21) | 3651(7) |
| C(3) | −5008(10) | 6504(20) | −2756(8) | 5289(21) | 1838(21) | 4207(7) |
| C(4) | −5775(10) | 6431(18) | −2068(9) | 6878(20) | 1133(21) | 4190(8) |
| C(5) | −5449(10) | 6335(21) | −1222(2) | 7523(21) | 597(21) | 3634(7) |
| C(6) | −4272(9) | 6155(19) | −1028(8) | 6554(22) | 703(23) | 3074(7) |
| C(7) | −2218(10) | 5886(15) | −1440(22) | 4161(22) | 1733(22) | 2439(8) |
| C(8) | −1866(9) | 4660(17) | −900(7) | 3212(28) | 153(25) | 2110(8) |
| C(9) | 165(9) | 5580(15) | −651(9) | 1337(19) | 1184(21) | 1236(7) |
| C(10) | 796(10) | 3039(14) | −19(7) | 3014(23) | 712(26) | 437(9) |
| C(11) | −1091(9) | 8610(16) | −1444(8) | −66(26) | 1736(25) | 1643(8) |
| C(12) | −124(10) | 9546(20) | −1932(9) | −1463(25) | 2364(25) | 1283(8) |

The interatomic distances and bond angles in **2f** and **3f** have typical values and are presented in Table 3.

## Experimental

GLC was carried out on a Chrom-5 chromatograph with a flame ionization detector and a glass column (1.2 × 0.003 m) packed with 5 % GE-XE-60 on Chromaton N-AW-DMCS (0.16—0.20 mm), helium (40 $cm^3$ $min^{-1}$) as carrier gas, a column temperature starting from 150° (2 min) with a subsequent increase to 220°C at a rate of 10 deg $min^{-1}$ and detector and evaporator temperatures of 250°C. TLC was performed on Silufol UV-254 plates in a 1:18 acetone—chloroform solvent system. The melting points were determined on a Boetius hot-stage apparatus. The $^1$H NMR spectra were recorded on a Bruker AC-80 (80 MHz) spectrometer in $CDCl_3$ with tetramethylsilane as an internal standard. Ketones **1a—g** were synthesized by a known procedure[9], enol acetates **2a** and **c—g** were prepared by treating ketones **1a** and **c—g** with acetic anhydride at 80°C in the presence of pyridine, and enol acylates **2b** and **h—l** were obtained by treating ketones **2a, b,** and **f** with sodium hydride and the corresponding acyl chlorides at −40°C to −50°C (see Ref.[10, 11]). Their characteristics are given in Table 2.

**Preparation of diketones 3. Method A.** A solution of 0.01 mol of triazolyl ketone **1** in 20 mL of acetic anhydride was refluxed (140—150°C) for 5—6 h (with monitoring by GLC and TLC). Acetic anhydride was then evaporated *in vacuo*, the residue was diluted with 70—80 mL of ether, the resulting solution was washed successively with water, 2 % aqueous

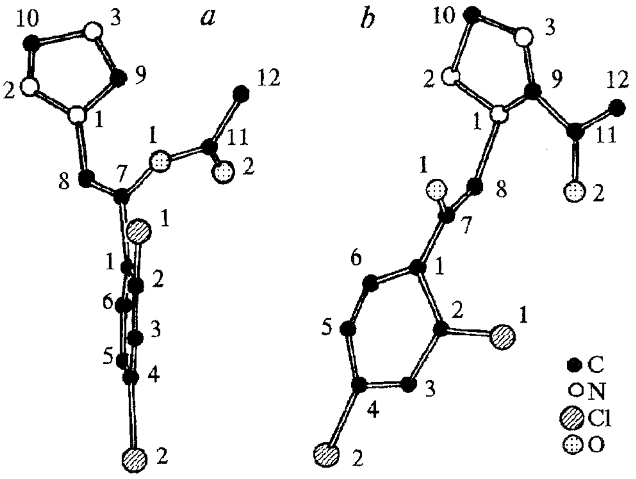

**Fig. 1.** Molecular structure of enol acetate **2f** (*a*) and diketone **3f** (*b*).

$NaHCO_3$, and water, and dried with $Na_2SO_4$. The solvent was evaporated and diketone **3** was isolated by chromatography ($SiO_2$, 1:18 acetone—chloroform) or by crystallization from 2-propanol (see Table 1).

**Method B.** A solution of 0.002 mol of enol acylate **2** in 5—6 ml of acetic anhydride was refluxed (140—150°C) for ~5 h. Acetic anhydride was evaporated *in vacuo*, and diketone **3** was isolated from the residue. The yields, mp, and data from the elemental analysis and $^1H$ NMR spectra of diketones **3a—l** are given in Table 1.

X-ray structural investigations of enol acetate **2f** and diketone **3f** were carried out on DAR-UMB and RED-4 automatic diffractometers, respectively (Table 4). The structures were solved by the direct method with the MULTAN program and refined by the least-squares method in the anisotropic approximation for the nonhydrogen atoms. The coordinates of the hydrogen atoms were calculated geometrically and not refined.

All calculations were performed on an SM-4 computer with the XTLSM system of programs. General views of molecules **2f** and **3f** are shown in Figure 1, the atomic coordinates are listed in Table 5, and the interatomic distances and bond angles are given in Table 3.

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