α-Tosyloxylation of fluorosubstituted β-diketones

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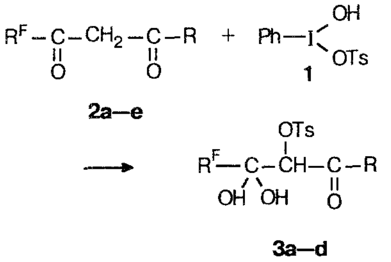
The interaction of fluorinated β-diketones with [hydroxy(tosyloxy)iodo]benzene leads to α-tosyloxy-β-diketones existing in the form of stable hydrates.

Key words: fluorosubstituted β-diketones; α-tosyloxylation; de(perfluoroacyl)ation.

Fluorosubstituted β-diketones are valuable intermediates in organic syntheses because of their rich functional content and high reactivity.[1] The α-functionalization of β-diketones would broaden their synthetic use even more but there are practically no works on this subject. Only the α-acetoxylation of 1-phenyl-4,4,4-trifluorobutan-1,3-dione in 63 % yield is known.[2]

On the other hand, β-diketones of the hydrocarbon series react smoothly with [hydroxy(tosyloxy)iodo]benzene (**1**) to give α-tosyloxy-β-diketones.[3] The purpose of the present work was the investigation of the interaction of fluorosubstituted β-diketones (**2**) with reagent **1**.

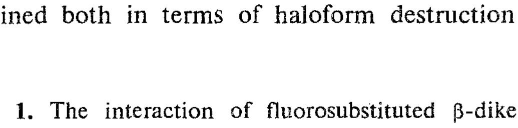
The tosyloxy group was chosen for the functionalization of substance **2** because of the ease of its subsequent nucleophilic substitution as well as the simplicity of the synthesis of reagent **1**. Unlike their hydrocarbon analogs which need heating of the reaction mixture, substances **2a—e** interact with reagent **1** in acetonitrile at room temperature in 1—15 min to give α-tosyloxy-β-diketones in 79—97 % yields (Table 1).



This phenomenon seems to result from the fact that soluted fluorosubstituted β-diketones are actually completely enolized and the primary act of the interaction is the electrophilic attack of the enol double bond by an atom of iodine.[3]

A characteristic feature of the fluorosubstituted α-tosyloxy-β-diketones obtained is that they exist in the form of stable hydrates (**3a—d**), in which the water molecule is bonded, in the form of the *gem*-diol, to the carbonyl group neighboring the fluoroalkyl substituent. This is confirmed by the presence of only one narrow extinction band of the C=O group adjacent to the hydrocarbon substituent in the IR spectra of **3a—d** (Table 2).

In the course of preliminary investigations of the properties of substances **3**, their ability to undergo C—C bond cleavage under the action of alkaline reagents was found. Thus, when the attempt was made to transform the *gem*-dihydroxy group into the 1,3-dioxolane cycle by the method used for fluoroketones,[4] only the α-tosylketones (**4a—c**) were isolated in 83—98 % yields.



Compounds **4a,c** have been obtained earlier by the action of reagent **1** on acetone or acetophenone, correspondingly,[3] and were identical to the products obtained by us. The ease of this cleavage of compounds **3** can be explained both in terms of haloform destruction fol-

Table 1. The interaction of fluorosubstituted β-diketones (**2a—e**) with reagent **1**

Starting compound	R^F	R	Reaction time, t/min	Yield of **3** (%)
2a	CF_3	Me	1	88
2b	CF_3	*t*-Bu	15	79
2c	CF_3	Ph	3	86
2d	n-C_4F_9	Me	8	97
2e	n-C_4F_9	Ph	5	[a]

[a] The reaction product is unstable; it undergoes partial destruction under the reaction conditions giving 1-phenyl-2-tosyloxyethan-1-one (**4c**).

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Table 2. The physicochemical properties of the hydrates of fluorosubstituted α-tosyloxy-β-diketones (**3a—d**)[a]

Compound	M.p./°C	IR, ν/cm^{-1}	^{1}H NMR, δ[b]
5,5,5-Trifluoro-4,4-dihydroxy-3-tosyloxypentan-2-one (**3a**)	82	3378, 3255(O—H); 1730(C=O)	2.43 (s, 3 H, CH_3CO); 2.47 (s, 3 H, CH_3); 4.88 (s, 1 H, CH); 7.59 (m, 4 H, *p*-C_6H_4)
6,6,6-Trifluoro-5,5-dihydroxy-2,2-dimethyl-4-tosyloxyhexan-3-one (**3b**)	89	3430, 3290 (O—H); 1710(C=O)	1.25 (s, 9 H, *t*-Bu); 2.44 (s, 3 H, CH_3); 5.66 (s, 1 H, CH); 7.54 (m, 4 H, *p*-C_6H_4)
4,4,4-Trifluoro-3,3-dihydroxy-1-phenyl-2-tosyloxybutan-1-one (**3c**)	119	3475, 3400(O—H); 1680(C=O)	2.39 (s, 3 H, CH_3); 5.94 (s, 1 H, CH); 7.29—7.99 (m, 9 H, Ph, *p*-C_6H_4)
5,5,6,6,7,7,8,8,8-Nonafluoro-4,4-dihydroxy-3-tosyloxyoctan-2-one (**3d**)	Oil	3450(O—H); 1735(C=O)	2.46 (s, 3 H, CH_3); 3.74 (s, 3 H, CH_3CO); 5.10 (s, 1 H, CH); 7.56 (m, 4 H, *p*-C_6H_4)

[a] For all of the compounds **3a—d** obtained the data of the elemental analysis are within ±0.3 % of the calculated values.

[b] The spectra of **3a,b,d** were registered in $CDCl_3$ + CD_3COOD, the spectrum of **3c** was registered in CD_3COCD_3 + CD_3COOD.

lowed by decarboxylation, and in terms of retro-Claisen destruction with loss of a perfluoroacyl anion.

Experimental

^{1}H NMR spectra were recorded on a Tesla BS-567A instrument at 100 MHz with TMS as the internal standard. IR spectra were registered on a Specord IR-75 spectrometer in vaseline oil.

Reagent **1** was synthesized by the method described earlier.[5]

α-Tosylation of the fluorosubstituted β-diketones 2a—e. A mixture of β-diketone (6 mmol of **2a,b** or 5 mmol of **2c—e**) and 1.96 g (5 mmol) of the reagent **1** in 12.5 mL of MeCN was stirred at room temperature until complete dissolution of the solid. The reaction mixture was filtered and the filtrate was evaporated on a water pump. The oil that formed was diluted with CCl_4 and cooled, and the crystals that precipitated were filtered and washed with cold CCl_4. In the case of compound **2d**, the product was isolated from the reaction mixture by column chromatography on SiO_2 in hexane/ethyl acetate (9 : 4). The reaction time, yields, and physicochemical characteristics of the products obtained are listed in Tables 1 and 2.

The interaction between compound 3b and 2-chloroethanol. 2-Chloroethanol (0.218 mL, 3.25 mmol) and K_2CO_3 (0.449 g, 3.25 mmol) were added to a stirred solution of **3b** (1.25 g, 3.25 mmol) in dry ether (5 mL).The reaction mixture thickened gradually and after 5 h the initial compounds entirely disappeared (TLC monitoring). The reaction mixture was poured into water (50 mL), the ether layer was separated, and the water solution was extracted with ether (2 × 20 mL). The combined ether layers were washed twice with water saturated with NaCl, and dried over $MgSO_4$. The solvent evaporated, the residual oil crystallized during the following drying *in vacuo* to yield 0.77 g (98 %) of 3,3-dimethyl-1-tosyloxybutane-2-one (**4b**), m.p. 46—47 °C. IR, ν/cm^{-1}: 1725 (C=O). ^{1}H NMR ($CDCl_3$, δ): 1.14 (s, 9 H, Bu^t); 2.44 (s, 3 H, CH_3); 4.88 (s, 2 H, CH_2); 7.59 (m, 5 H, Ph).

Compounds **3a,c** were treated with 2-chloroethanol in the presence of K_2CO_3 in the way cited above and compounds **4a** and **4c** were obtained in 95 and 83 % yields, correspondingly.

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