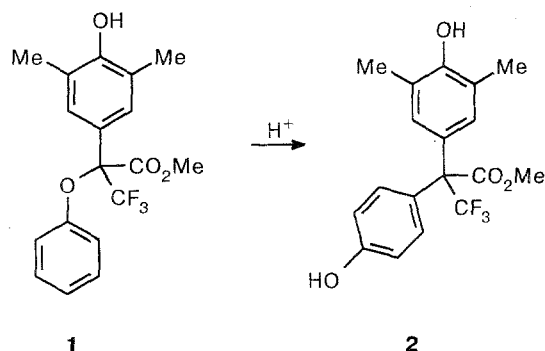


# Rearrangement of methyl $\beta,\beta,\beta$ -trifluoro- $\alpha$ -(4-hydroxy-3,5-dimethylphenyl)- $\alpha$ -phenoxypropionate

V. I. Dyachenko,\* A. F. Kolomiets, and A. V. Fokin

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,  
28 ul. Vavilova, 117813 Moscow, Russian Federation.  
Fax: +7 (095) 135 5085

We found that methyl  $\alpha$ -(4-hydroxy-3,5-dimethylphenyl)- $\beta,\beta,\beta$ -trifluoro- $\alpha$ -phenoxypropionate (**1**), obtained by the Claisen reaction from the corresponding benzyl halide and phenol, completely rearranges to bisphenol **2** in  $\text{CF}_3\text{COOH}$  at 20 °C for 5–6 h.



The closest structural analogy to this rearrangement is the conversion of phenyl benzyl ether to benzylphenols in the presence of Zn or Cu or without these catalysts.<sup>1</sup> However, the above-mentioned process occurs only at 250 °C to give a mixture of 2- and 4-mono- and 2,4-dibenzylphenols in a low yield; this process is attended by decomposition and resinification of the reac-

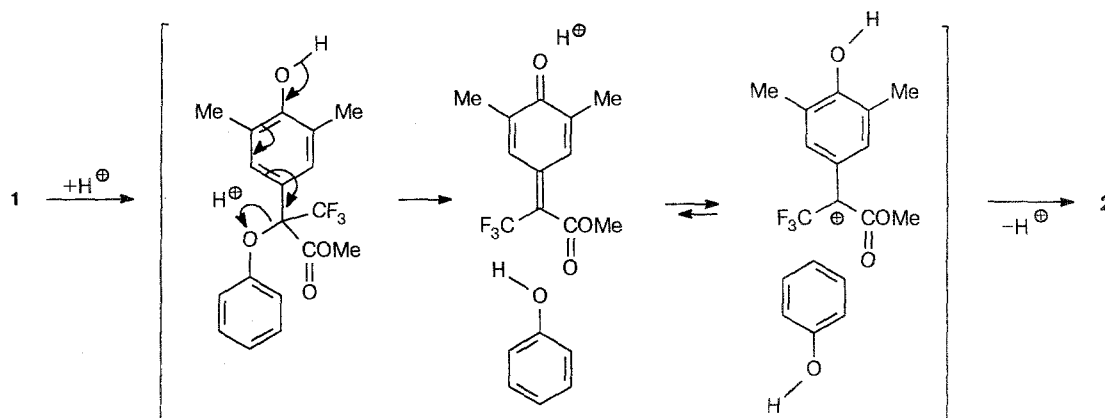
tion mass. Apparently, the rearrangement that we found has a different typology and proceeds with an intermediate formation of methylenequinone and phenol under the action of the acid (Scheme 1).

In this connection it is pertinent to note that when equimolar amounts of phenol and 7-trifluoro-7-methoxycarbonyl-2,6-dimethylmethylenequinone, which was obtained previously,<sup>2</sup> were mixed in  $\text{CF}_3\text{COOH}$  at 20 °C, the same product **2** was obtained with the identical high degree of selectivity and in the same yield as in the case of the rearrangement of ester **1**. Moreover, it was demonstrated in a special experiment that this methylenequinone actually occurs in the  $\text{CF}_3\text{COOH}$  solution, and, therefore, this compound may be an intermediate in the case of the rearrangement of ester **1**.

**Methyl  $\beta,\beta,\beta$ -trifluoro- $\alpha$ -(4-hydroxy-3,5-dimethylphenyl)- $\alpha$ -phenoxypropionate (**1**)**, yield 68.2 %,  $n_D^{20} = 1.5270$ ,  $R_f = 0.51$  (1:3 acetone- $\text{CCl}_4$ ).  $^1\text{H}$  NMR ( $\delta$ , acetone- $d_6$ ): 7.75 (s, 1 H, OH); 7.30 (s, 2 H, H-2, H-6); 7.25 (m, 2 H, H-3, H-5); 7.07 (d.d, 1 H, H-4); 6.90 (m, 2 H, H-2, H-6); 3.75 (s, 3 H, OMe); 2.25 (s, 6 H, OMe).  $^{19}\text{F}$  NMR ( $\delta$ , acetone- $d_6$ ): -3.9.

**Methyl  $\beta,\beta,\beta$ -trifluoro- $\alpha$ -(4-hydroxy-3,5-dimethylphenyl)- $\alpha$ -(4-hydroxyphenyl)propionate (**2**)**, yield 94 %, m.p. 156–158 °C ( $\text{C}_6\text{H}_6$ ),  $R_f = 0.36$  (1:2 acetone- $\text{CCl}_4$ ). Found (%): C, 65.58; H, 4.31; F, 13.89.  $\text{C}_{22}\text{H}_{17}\text{F}_3\text{O}_4$ . Calculated (%):

Scheme 1



C, 65.67; H, 4.23; F, 14.18.  $^1\text{H}$  NMR ( $\delta$ , J/Hz): 7.50 (s, 1 H, OH); 7.30 (s, 1 H, OH); 7.01 (d, 2 H, H-2, H-6,  $^3J = 8.1$ ); 6.85 (s, 2 H, H-2', H-6'); 6.81 (d, 2 H, H-3, H-5,  $^3J = 8.1$ ); 3.75 (s, 3 H, OMe); 2.20 (s, 6 H, 2 Me).

The work was supported by the Russian Foundation for Basic Research (Project No. 93-07-22696).

## References

1. O. Behaghel, H. Freisenhner, *Chem. Ber.*, 1934, **67**, 1368.
2. V. I. Dyachenko, A. F. Kolomiets, and A. V. Fokin, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 1631 [*Russ. Chem. Bull.*, 1994, **43**, 1543 (Engl. Transl.)].

Received April 18, 1995;  
in revised form June 15, 1995

# Synthesis of fluoroalkyl-containing bis- $\beta$ -diketones of aromatic and heterocyclic series

V. G. Ratner, D. L. Chizhov, and K. I. Pashkevich\*

Institute of Organic Synthesis, Ural Branch of the Russian Academy of Sciences,  
20 ul. Kovalevskoi, 620219 Ekaterinburg.  
Fax: +7 (343 2)44 5944

A huge number of fluoroalkyl-containing  $\beta$ -diketones, widely used in both organic synthesis and practice,<sup>1</sup> are presently known. At the same time there is only one example of fluoro-containing bis- $\beta$ -diketones in which two  $\beta$ -diketone fragments are bound by the saturated fluoroaliphatic chain,<sup>2</sup> whereas aliphatic bis- $\beta$ -diketones have for a long time drawn the attention of investigators.<sup>3</sup>

We have synthesized for the first time fluoroalkyl-containing bis- $\beta$ -diketones (**1**), in which diketone fragments are separated by aromatic cycle or heterocycle with a consequent considerable extension of  $p$ - $\pi$ -conjugation in the chain (Scheme 1).

Claisen condensation of a methyl polyfluorocarboxylate with a diacetyl derivative was applied for this synthesis. Compounds **1a–c** exist as bis-enols **2a–c**, which is typical for fluoro-containing diketones.

**5-Acetyl-1,3-di-(4,4,4-trifluoro-1,3-dioxobut-1-yl)benzene (1a).** 1,3,5-Triacetylbenzene (2.04 g, 0.01 mol), LiH (0.3 g, 0.036 mol), and dry methyltrifluoroacetate (25 mL) were placed in a 100-ml three-neck flask. The reaction mixture was stirred and refluxed for 20 h. The solvent was distilled off, water (20 mL) was added to the reaction mixture, and the pH was brought to 3–4 by dilute HCl. The aqueous solution was extracted with ether (4 $\times$ 30 mL), and the extracts were washed with water and shaken with an aqueous solution of  $\text{Cu}(\text{OAc})_2$  (3 $\times$ 50 mL). Then ether was distilled off, and the residue was

Scheme 1

