

## Letters to the Editor

### 10,10-Diethoxy-9-oxa-10-sila-9,10-dihydrophenanthrene as a source of heterocyclic silanone

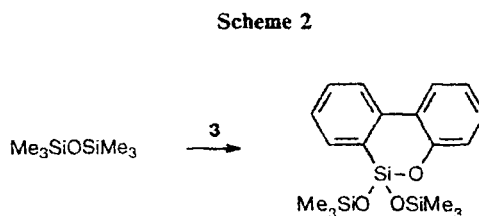
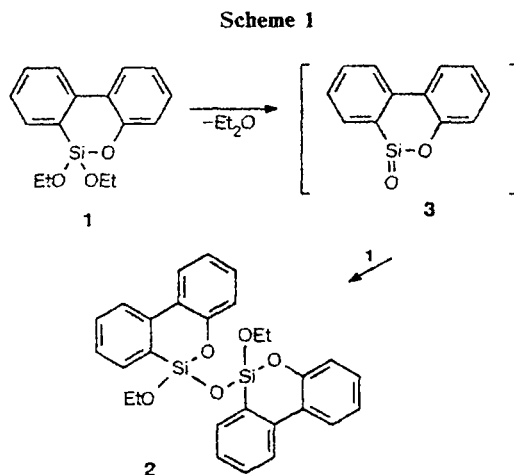
T. L. Krasnova,\* E. A. Chernyshev, A. P. Sergeev, and E. S. Abramova

M. V. Lomonosov Moscow State Academy of Fine Chemical Technology,  
86 prosp. Vernadskogo, 117571 Moscow, Russian Federation.  
Fax: 007 (095) 430 7983

Previously,<sup>1</sup> we reported the generation of silanones functionalized with different substituents at the Si atom in liquid phase at high temperature in the presence of catalytic amounts of a cation-exchange resin KU-23 or Lewis acids. In the present work, data concerning the catalytic thermolysis of 10,10-diethoxy-9-oxa-10-sila-9,10-dihydrophenanthrene (1) in the presence of 5 mol. % FeCl<sub>3</sub> are reported. The identification of products formed was performed by GLC.

It was established that the thermolysis of compound 1 at 160 °C results after 2 h in the formation of diethyl ether and 10,10'-diethoxy-9,9'-dioxo-10,10'-disila-9,9',10,10'-tetrahydro-10,10'-oxydiphenanthrene (2). Under these conditions, the conversion of compound 1 is 22%. In our opinion, the formation of disiloxane 2 under the reaction conditions may be explained by the insertion of 9-oxa-10-sila-9,10-dihydrophenanthren-10-one (3), an intermediate that formed upon elimination of diethyl ether from the initial compound 1, at the Si—O(Et) bond of the latter (Scheme 1).

To prove the generation of intermediate 3 from compound 1, hexamethyldisiloxane (HMDS) was used as a scavenger. The reaction mixture obtained when the process was carried out in the presence of 5 mol. % FeCl<sub>3</sub> at 110 °C contained, along with the initial 1 and HMDS, 10,10-bis(trimethylsiloxy)-9-oxa-10-sila-9,10-



dihydrophenanthrene, a product of the insertion of intermediate 3 at the Si—O bond of HMDS (Scheme 2), and disiloxane 2, a product of the insertion of intermediate 3 at the Si—O bond of the initial 1 according to Scheme 1, the conversion of compound 1 being 36%.

Thus, we obtained data attesting to the possibility of generating unstable intermediates with the Si=O bond, in which the silicon atom is involved in the heterocyclic system, in catalytic thermolysis.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 96-03-33268).

### Reference

1. E. A. Chernyshev, T. L. Krasnova, A. P. Sergeev, and B. V. Molchanov, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 1577 [*Russ. Chem. Bull.*, 1996, **45**, 1504 (Engl. Transl.)].

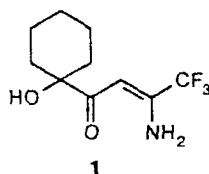
Received February 14, 1997;  
in revised form April 21, 1997

## Ring-chain isomerism in the series of $\alpha$ -hydroxy-1,3-diketones. Synthesis and some properties of 5-hydroxy-2,2-pentamethylene-5-trifluoromethyltetrahydrofuran-3-one

V. Ya. Sosnovskikh,\* M. Yu. Mel'nikov, and V. A. Kutsenko

A. M. Gor'kii Ural State University,  
51 prosp. Lenina, 620083 Ekaterinburg, Russian Federation.  
Fax: 007 (343 2) 61 5978

Recently, we showed<sup>1</sup> that on long storage,  $\alpha$ -hydroxyoxoamine (1), obtained by condensation of 1-acetylcyclohexanol with trifluoroacetonitrile, undergoes initially a spontaneous cyclization to 5-amino-2,2-pentamethylene-5-trifluoromethyltetrahydrofuran-3-one (2), which then isomerizes to 4-amino-5-hydroxy-5,5-pentamethylene-1,1,1-trifluoro-3-penten-2-one (3). In this work, we describe a simpler procedure for the synthesis of compounds 2 and 3, based on the reaction of 1-acetylcyclohexanol with ethyl trifluoroacetate.



1-Acetylcyclohexanol is known<sup>2</sup> to readily undergo self-condensation under the action of a methanolic solution of KOH. Only reactions with trichloroacetonitrile<sup>3</sup> and trifluoroacetonitrile<sup>1</sup> have been described among mixed condensations with participation of this compound as the methylene component. We found that instead of the corresponding  $\alpha$ -hydroxy-1,3-diketone (4), its cyclic form, 5-hydroxy-2,2-pentamethylene-5-trifluoromethyltetrahydrofuran-3-one (5) is formed in the interaction of 1-acetylcyclohexanol with ethyl trifluoroacetate in ether in the presence of LiH (Scheme 1). The stronger (due to the increased basicity of the carbonyl

oxygen conjugated to the  $\text{NH}_2$  group) intramolecular hydrogen bond in the ketol fragment of  $\alpha$ -hydroxyoxoamine 1, which decreases its conformational mobility, has a crucial effect on the difference in stability between compounds 1 and 4.

Dehydration of compound 5 under the action of  $\text{SOCl}_2$  and catalytic amount of pyridine gives dihydrofuranone (6) capable of ready addition of aqueous  $\text{NH}_3$  with the formation of aminotetrahydrofuranone 2. Treatment of hydroxytetrahydrofuranone 5 with a methanolic solution of  $\text{NH}_3$  at room temperature gives hydroxyaminoenone 3; its yield does not exceed 45% since the reaction is accompanied by partial transformation of compound 5 into starting 1-acetylcyclohexanol and  $\text{CF}_3\text{COONH}_4$ .

Thus, in its reaction with ammonia, hydroxytetrahydrofuranone 5 behaves analogously to asymmetrical polyfluorinated  $\beta$ -diketones described previously:<sup>4</sup> their interaction with ammonia and primary amines involves the carbonyl group not bonded to the polyfluoroalkyl substituent.

The sequence of the reactions described is of interest for synthesizing new highly reactive  $\text{CF}_3$ -containing synthons, since it also can be extended to other dialkylacetylcarbinols.