

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).

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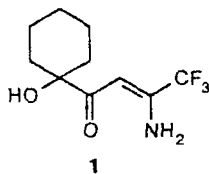
Received February 14, 1997;
in revised form April 21, 1997

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

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Recently, we showed¹ that on long storage, α -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 known² to readily undergo self-condensation under the action of a methanolic solution of KOH. Only reactions with trichloroacetonitrile³ and trifluoroacetonitrile¹ have been described among mixed condensations with participation of this compound as the methylene component. We found that instead of the corresponding α -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

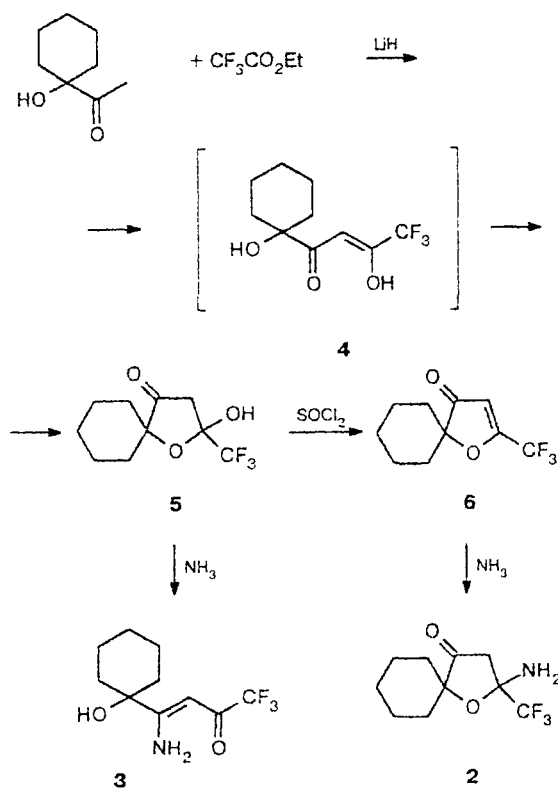
oxygen conjugated to the NH₂ group) intramolecular hydrogen bond in the ketol fragment of α -hydroxyoxoamine 1, which decreases its conformational mobility, has a crucial effect on the difference in stability between compounds 1 and 4.

Dehydration of compound 5 under the action of SOCl₂ and catalytic amount of pyridine gives dihydrofuranone (6) capable of ready addition of aqueous NH₃ with the formation of aminotetrahydrofuranone 2. Treatment of hydroxytetrahydrofuranone 5 with a methanolic solution of NH₃ 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 CF₃COONH₄.

Thus, in its reaction with ammonia, hydroxytetrahydrofuranone 5 behaves analogously to asymmetrical polyfluorinated β -diketones described previously:⁴ 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 CF₃-containing synthons, since it also can be extended to other dialkylacetylcarbinols.

Scheme 1



Compounds 2 and 3 were described previously.¹

5-Hydroxy-2,2-pentamethylene-5-trifluoromethyltetrahydrofuran-3-one (5). Yield 48%, m.p. 53–54 °C (from hexane). Found (%): C, 50.37; H, 5.35. $C_{10}H_{13}F_3O_3$. Calculated (%): C, 50.42; H, 5.50. IR (Vaseline oil), ν/cm^{-1} : 3380 (OH); 1750 (C=O). 1H NMR ($CDCl_3$), δ : 1.64 (m, 10 H, $(CH_2)_5$); 2.77, 2.97 (dd, 2 H, H_A , H_B , $J = 18.7$ Hz); 4.22 (s, 1 H, OH).

2,2-Pentamethylene-5-trifluoromethyldihydrofuran-3-one (6). Yield 77%, b.p. 49–51 °C (4 Torr), n_D^{20} 1.4329. Found (%): C, 54.23; H, 5.27. $C_{10}H_{11}F_3O_2$. Calculated (%): C, 54.55; H, 5.04. IR (thin layer), ν/cm^{-1} : 1725 (C=O); 1635 (C=C). 1H NMR ($CDCl_3$), δ : 1.68 (m, 10 H, $(CH_2)_5$); 5.96 (s, 1 H, =C–H).

This work was financially supported by the Russian Foundation for Basic Research (Project No. 96-03-33373).

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Received February 28, 1997

Sonolysis of HCl in aqueous solutions: the effect of enrichment of the gaseous phase with a volatile component in sonochemical processes

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In this work, the sonochemical decomposition of HCl in aqueous solutions has been studied. The experiments were carried out over a wide range of HCl concentrations (to 12 mol L⁻¹) with various intensities of ultrasonic vibrations at a frequency of 22 kHz under an argon atmosphere at constant temperature (20 °C).

We have established that the formation and accumulation of molecular chlorine in the solution and in the gaseous phase are major results of sonolysis even in diluted HCl solutions, in which the partial pressure of water is 4–5 orders of magnitude higher than the partial pressure of HCl. Hydrogen is another product of sonolysis