Brief Communications

Selective method for the preparation of 5-chloropentan-2-one

M. G. Vinogradov,[a*] *L. S. Gorshkova,*[a] *V. A. Ferapontov,*[a] *and A. V. Zinenkov*[b]

[a] *N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,*
47 Leninsky prosp., 117913 Moscow, Russian Federation.
Fax: +7 (095) 135 5328
[b] *«Lenneftekhim»,*
40 Zheleznodorozhny pr., 193148 Saint-Petersburg, Russian Federation

A selective method for the preparation of 5-chloropentan-2-one by interaction of 1-methylcyclobutanol with $Ca(OCl)_2$ followed by decomposition of the hypochlorite thus obtained in the presence of Fe^{II} salt is proposed. The selectivity of the ketone formation from the alcohol is 98 %, while the conversion of the alcohol is 35—40 %.

Key words: 5-chloropentan-2-one, 1-methylcyclobutanol, 1-methylcyclobutylhypochlorite, free radical decomposition.

5-Chloropentan-2-one, or γ-acetopropyl chloride (**1**), is an important intermediate of organic synthesis. For instance, it is used in the production of cyclopropyl compounds like methyl cyclopropyl ketone,[1] terpenoids,[2—4] and heterocyclic compounds.[5]

The usual synthesis of ketone **1** by the interaction of α-acetyl-γ-butyrolactone with concentrated HCl is followed by partial resinification of the product.[1] We have carried out a selective synthesis of ketone **1** from 1-methylcyclobutan-1-ol (**3**), which, in turn, was prepared by hydration of methylenecyclobutane, the by-product of isoprene production by the dioxane method.[6,7] Ketone **1** was synthesized by a two-step scheme, which comprised the transformation of alcohol **3** into hypochlorite **2** followed by the decomposition of **2** with the cleavage of the ring.

The decomposition of tertial cycloalkyl hypochlorites is commonly carried out under thermal or photolytic conditions.[8,9] However, in these reactions a mixture of two or more products is formed, and the decomposition of hypochlorite **2** has not been studied. In order to transform hypochlorite **2** into chloroketone **1**, we used a method[10] based on the initiation of the reaction by Fe^{II} ions (Scheme 1).

At the first stage, the choice of the conditions of chlorination is of great importance. When molecular chlorine was used (by bubbling through an alkaline aqueous solution of 1-methylcyclobutanol (see Ref. 11)), the water-unmixable hypochlorite **2** thus formed decomposed spontaneously to give a complex mixture of products. The prolonged passing of chlorine through a solution of sodium alcoxide (prepared by dissolution of sodium in **3**) at 0 °C also failed. In this case, the hypochlorite accumulated too slowly.

The best results were obtained when technical grade calcium hypochlorite was used at the first stage and the

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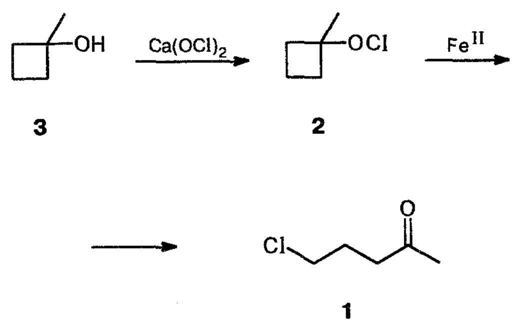
Scheme 1



reaction was carried out in a two-phase water—CCl$_4$ system (this system has been used earlier[10] for the chlorination of 1-methylcycloalkanols with five or more carbon atoms in the cycle). The reaction was monitored following a change in the integral intensity of the signals for the methyl protons of **3** and **2** (δ 1.3 and 1.47, respectively) in the ^{1}H NMR spectrum of the reaction mixture (in CCl$_4$). The solution of **2** in CCl$_4$ thus formed is stable for at least several hours at 0 °C in the dark.

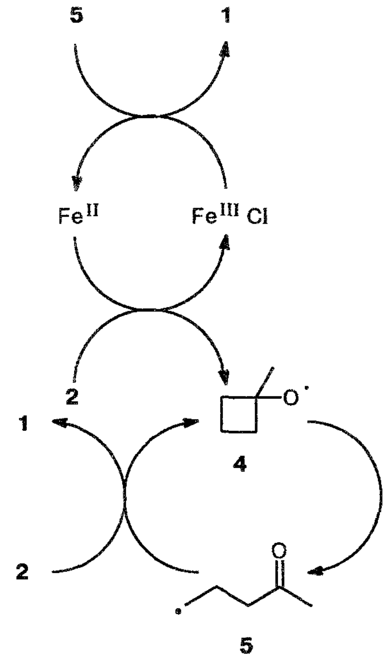
At the stage of the decomposition of **2** in the presence of FeSO$_4$, the selectivity of ketone **1** formation was ~98 % (based on the starting **3**) at 35—40 % conversion of **3**. The ketone **3** remaining intact at the first stage of the reaction can be recycled into the process without isolation from an aqueous solution. The conversion of **3** can be increased by increasing the Ca(OCl)$_2$: **3** molar ratio, but this leads to some decrease in the selectivity of the formation of **1**.

The decomposition of hypochlorite **2** under the effect of Fe^{II} salt probably proceeds as a chain radical process,[10] which comprises the one-electron reduction of **2** at the initial stage of the reaction with the subsequent rearrangement of 1-methylcyclobutoxyl radical (**4**) formed into 4-oxopent-1-yl radical (**5**) (Scheme 2). The latter then abstracts a chlorine atom from a molecule of hypochlorite **2** to afford ketone **1** along with radical **4** (the lower cycle in Scheme 2). One cannot entirely exclude the participation of the Fe^{III} salt formed by the interaction of Fe^{II} with hypochlorite **2** at the stage of chain transfer. In this case, radical **5** is oxidized by the Fe^{III}Cl species to form the end product **1** and to regenerate the Fe^{II} species (the upper cycle in Scheme 2).

Experimental

1-Methylcyclobutanol was prepared by the known method.[1] GLC was carried out on a Biokhrom-1 chromatograph with a 0.24 mm × 50 m capillary column pretreated with HClO$_4$ using XE-60 as the stationary phase. NMR spectra were recorded on a Bruker AC-200P spectrometer.

Scheme 2



5-Chloropentan-2-one (1). A cooled solution of technical grade calcium hypochlorite (0.05 g-at. of active chlorine) in a mixture of water (200 mL) and acetic acid (24 mL) was mixed with a solution of 1-methylcyclobutanol (10.3 g, 0.1 mol) in CCl$_4$ (50 mL) at 0 °C in the dark. The reaction mixture was stirred at 0 °C until the test of the aqueous layer for active chlorine (KI) became negative. After the end of the reaction (~4 h), the organic layer was separated from the aqueous layer, which contained the unreacted **3**, and washed with water. Finely powdered FeSO$_4 \cdot 7H_2O$ (10 g, 0.036 mol) was added to the washed organic layer with stirring at room temperature under an inert atmosphere. The mixture was stirred for an additional 30 min, during which period the hypochlorite was entirely decomposed (negative reaction with KI) and the coloration of the solution faded. According to the GLC analysis, the reaction mixture (CCl$_4$ solution) contained more than 98 % ketone **1**. The solution was filtered, the precipitate was washed subsequently with CCl$_4$ and water and then dried, the solvent was removed, and the residue was distilled *in vacuo* to afford 5.4 g of compound **1** (98 % yield based on **3** reacted; the conversion of **3** was 38 %). B.p. 65 °C (15 Torr), n_D^{24} 1.4375 (*cf.* Ref. 1: b.p. 70—72 °C (20 Torr), n_D^{25} 1.4371). ^{1}H NMR, δ: 1.9—2.05 (m, CH$_2$); 2.14 (s, MeCO); 2.63 (t, CH$_2$CO); 3.57 (CH$_2$Cl). ^{13}C NMR (CDCl$_3$), δ: 25.55, 28.80, 39.15, 43.55, 206.25.

The aqueous layer from the first stage and the aqueous extract from the second stage of the process were combined and extracted with ether, the extract was dried over MgSO$_4$, the solvent was removed, and the residue was distilled to give 6.4 g of starting **3**, b.p. 34—35 °C (15 Torr) (*cf.* Ref. 6: b.p. 38—39 °C (17 Torr)).

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Synthesis of *closo*-3,3-(η^3,η^2-tricyclo[5.2.1.$0^{2,6}$]deca-4,8-diene-3-yl)-1-(hydroxymethyl)-3,2,1-dicarbollylrhodium and the crystal structure of its dimer with the O—H...Rh bond

I. T. Chizhevsky, T. V. Zinevich, P. V. Petrovskii, V. I. Bregadze, F. M. Dolgushin, A. I. Yanovsky, and Yu. T. Struchkov*

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

Protonation of the [*closo*-3,3-(η^4-$C_{10}H_{12}$)-1-(CH_2OH)-3,1,2-$RhC_2B_9H_{10}$]$^-$ PPN^+ ($C_{10}H_{12}$ — dicyclopentadiene, PPN^+ — bis(triphenylphosphine)iminium cation) at the ethylene bond of the norbornene moiety yields the neutral *closo*-3,3,3-(η-$C_{10}H_{13}$)-1-(CH_2OH)-3,1,2-$RhC_2B_9H_{10}$ with an agostic C—H...Rh bond. On prolonged storage in EtOH, the latter complex is converted into *closo*-3,3-($\eta^{3,2}$-$C_{10}H_{11}$)-1-(CH_2OH)-3,1,2-$RhC_2B_9H_{10}$ with π-allylolefinic type coordination. Its crystal structure as dimeric aggregates with O—H...O and O—H...Rh bonds was determined by X-ray diffraction.

Key words: rhodacarboranes, dicyclopentadiene, O—H...Rh bond, X-ray structure analysis.

The majority of metallacarboranes of transition metals with five-electron ligands belong to the group of η^5-alkylcyclopentadienyl[1] and η^5-indenyl[2] π-complexes. Known examples of (π-dienyl)metallacarboranes with η^3,η^2-allylolefinic type bonds are ruther scanty so far and limited to complexes with either endocyclic η^3-allylic and exocyclic η^2-olefinic[3] or, *vice versa*, endocyclic η^2-olefinic and exocyclic η^3-allylic metal—hydrocarbon ligand coordination.[4] In the present work, we report the first example of *closo*-rhodacarborane, in which the rhodium atom is coordinated by the tricyclic dienyl ligand *via* endocyclic η^3,η^2-allylolefinic binding.

We have found that the anionic complex [*closo*-3,3-(η^4-$C_{10}H_{12}$)-1-(CH_2OH)-3,1,2-$RhC_2B_9H_{10}$]$^-$$PPN^+$ [**1**, $C_{10}H_{12}$ — dicyclopentadiene, PPN^+ — bis(triphenylphosphine)iminium cation] obtained from the dicarbollide-dianion [*nido*-7-(CH_2OH)-7,8-$C_2B_9H_{10}$]$^{2-}$ and the [(η^4-$C_{10}H_{12}$)RhCl]$_2$ dimer under the conditions

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