SIMPLE SYNTHESIS OF 15-HYDROXYPENTADECANOIC ACID FROM 10-UNDECENOIC ACID

L. L. Zakharkin and A. P. Pryanishnikov

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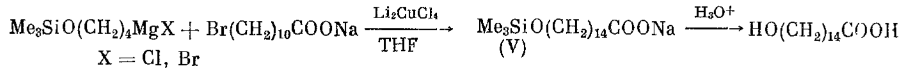
15-Hydroxypentadecanoic acid (I) is the starting compound for obtaining pentadecanolide (tibetolide), a valuable perfume. Many methods are known for the synthesis of acid (I) [1-5] and, in particular, from 10-undecenoic acid (II) via 11-bromoundecanoic acid (III) using the Kolbe electrochemical synthesis [4]. In the present paper a simple new method for obtaining acid (I) from acid (II) via (III) is described. It is based on the use of the method for condensing Grignard reagents with alkyl bromides in the presence of Li_2CuCl_4 [6]. In [7] it was shown that RMgX condenses with $Br(CH_2)_nCOOMgX$ in the presence of Li_2CuCl_4 to give $R(CH_2)_nCOOH$. We found that acid (I) is smoothly obtained by the following scheme:



$$\underset{X = Cl,\ Br}{Me_3SiO(CH_2)_4MgX} + Br(CH_2)_{10}COONa \xrightarrow[THF]{Li_2CuCl_4} \underset{(V)}{Me_3SiO(CH_2)_{14}COONa} \xrightarrow{H_3O^+} HO(CH_2)_{14}COOH$$

Either $Me_3SiO(CH_2)_4Cl$ or $Me_3SiO(CH_2)_4Br$, easily obtained from tetrahydrofuran, and acid (III), the addition product of HBr to acid (II) in the presence of radical initiators, are used in this scheme. Treatment of a suspension of the dry Na salt of 11-bromoundecanoic acid (IV) in THF with $Me_3SiO(CH_2)_4MgCl$ in the presence of Li_2CuCl_4 gives the Na salt of 15-trimethylsiloxypentadecanoic acid (V), the hydrolysis of which with dilute HCl solution gives acid (I) in 85-87% yield, when based on starting acid (III). The salt $Br(CH_2)_{10}COOMgCl$, obtained by treating a solution of acid (II) in THF with the calculated equimolar amount of C_3H_7MgCl, can also be used in this reaction, but this is less convenient than using salt (IV).

EXPERIMENTAL

11-Bromoundecanoic acid (III) was obtained from 10-undecanoic acid (II) as described in [4], 4-chlorobutanol was obtained from THF as described in [8], $MeSiO(CH_2)_4Cl$ was obtained from 4-chlorobutanol as described in [9], and $Me_2SiO(CH_2)_4Br$ was obtained from THF and Me_3SiBr as described in [10].

Sodium Salt of 11-Bromoundecanoic Acid (IV). A solution of 26.5 g (0.1 mole) of acid (III) in 85 ml of either MeOH or EtOH was neutralized with a solution of 2.3 g of Na (or 4 g of NaOH) in 50 ml of either MeOH or EtOH at 10-15°C. To completely remove the alcohol and water the obtained precipitate of salt (IV) was dried in vacuo, then rubbed in a porcelain mortar, and heated in vacuo for 1 h at 50-60°. The yield of the salt was quantitative.

15-Hydroxypentadecanoic acid (I). a) With stirring, to a suspension of 28.7 g (0.1 mole) of salt (IV) in 120 ml of dry THF at −20° was added in an N_2 atmosphere a solution of 0.4 g of Li_2CuCl_4 in 7 ml of THF, and then in 30 min was added at −20° a solution of either $Me_3SiO(CH_2)_4MgCl$ or $Me_3SiO(CH_2)_4MgBr$ in THF, which was obtained from either 22 g (0.12 mole) of $Me_3SiO(CH_2)_4Cl$ or 24 g of $Me_3SiO(CH_2)_4Br$ and 3.5 g of Mg in 50 ml of THF. Here salt (IV) dissolved and a homogeneous solution was obtained, which was stirred for 2 h at −20 to −15°. Then, continuing the stirring, the temperature of the solution was raised to 20°, 100 ml of 10% HCl solution was added and after 2 h 50 ml of benzene was added, and the organic layer was separated, washed with water, and dried over $MgSO_4$. The mixture of benzene and THF was distilled off under a slight vacuum, and the solid residue was recrystallized from hexane (heptane) and then repeatedly from benzene. We obtained 21.1 g (87%) of acid (I), mp 82-83°, cf. [4].

b) To a stirred solution of 26.5 g (0.1 mole) of acid (III) in 100 ml of dry THF was gradually added at −20° in an N_2 atmosphere a solution of 0.1 mole of C_3H_7MgCl in 50 ml of THF. The obtained precipitate of the magnesium chloride salt of acid (III) was treated with $Me_3SiO(CH_2)_4MgX$ the same as salt (IV) was treated, and we obtained 18.7 g (78%) of acid (I), mp 82-83°.

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 11, pp. 2604-2605, November, 1982. Original article submitted April 2, 1982.

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CONCLUSIONS

A simple method was proposed for obtaining 15-hydroxypentadecanoic acid from 10-undecenoic acid, which is based on the condensation of the Na salt of 11-bromoundecanoic acid with $Me_3SiO(CH_2)_4MgX$ in the presence of Li_2CuCl_4 as the catalyst.

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ACETYLATION OF RHENIUM AND MANGANESE η^5-INDENYLTRICARBONYL

I. A. Lobanova, V. I. Zdanovich, and N. E. Kolobova

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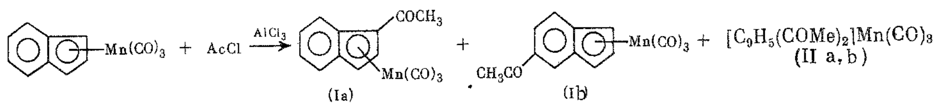
The reactivity of the indenyl complexes of the Group VII metals has received little study. The existing information relates only to the replacement of the CO groups in carbonyl complexes by other n-donor ligands [1, 2]. Data on the reactivity of the π ligand in these complexes is lacking.

In order to study the relative reactivity of the five- and six-membered rings in the η^5-indenyl ligand, we studied the acetylation of the indenyl complexes of Mn and Re under the conditions of the Friedel–Crafts reaction. It proved that the reaction of manganese η^5-indenyltricarbonyl with excess CH_3COCl in the presence of $AlCl_3$ leads to the formation of a mixture of two isomeric monoacetyl derivatives (Ia) and (Ib) in 50-60% yield and small amounts of diacetyl derivatives (IIa) and (IIb):



The (Ia) and (Ib) isomers were separated by chromatography on a Florisil column and were obtained as yellow crystalline compounds that are stable in the solid state and are readily soluble in organic solvents. They have close but slightly different melting points and IR and mass spectra. Both (Ia) and (Ib) are distinctly different in their PMR spectra, and their structure was determined on their basis. The PMR spectrum of (Ia) (δ, ppm, $(CD_3)_2CO$) has a singlet at 2.52 from the protons of the CH_3 group, two doublets at 5.81 and 6.07 from the protons of the five-membered ring, and a multiplet with a center at 8.06 from the protons of the six-membered ring, whereupon the ratio of the intensities of the signals is equal to 3 : 1 : 1 : 4. The PMR spectrum (δ, ppm $(CD_3)_2CO$) of (Ib) has a singlet at 2.61 from the methyl protons, a multiplet with a center at 5.45 from the protons of the five-membered ring, and two singlets at 7.63 and 8.38 from the protons of the six-membered ring, with an intensity ratio of 3 : 3 : 2 : 1.

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow.

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