Chemistry

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1961

SovietRxiv

Abstract

Full Text

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SYNTHESIS OF MONOHYDRIC SATURATED AND ACETYLENIC TERTIARY ALCOHOLS OF THE FERROCENE SERIES

The possibility of obtaining dihydric tertiary alcohols of the ferrocene series on the basis of carbonyl-containing derivatives of ferrocene—respectively, diacetyl- and dibenzoylferrocene, as well as the dimethyl ester of ferrocenedicarboxylic acid—has already been shown by Riemschneider and Helm (1) and by A. N. Nesmeyanov et al. (2). In the present work, for the first time, the synthesis of monohydric saturated and acetylenic tertiary alcohols of the ferrocene series has been carried out by condensation of monoacetyl- and monobenzoylferrocenes with magnesium- and sodium-organic compounds.

Saturated tertiary alcohols were synthesized by condensation of acetylferrocene and benzoylferrocene with Grignard reagents obtained from saturated alkyl halides. To obtain alcohols with acetylenic radicals, acetylene magnesium bromide prepared according to Jones (3) was used (we were unable to carry out the synthesis of this type of alcohol by the Favorskii reaction). Sodium acetylide was also prepared according to Normant (4) at −15°, and was introduced into condensation with acetyl- and benzoylferrocene. It was found that 3-methyl-3-ferrocenyl-3-hydroxypropyne-1 can be obtained by two methods (via C_2HMgBr and C_2HNa), whereas 3-phenyl-3-ferrocenyl-3-hydroxypropyne-1 is synthesized only by the first method.

It is interesting to note that the disubstituted organometallic acetylenic reagent (Iosich' s reagent) no longer reacts either with acetylferrocene or with benzoylferrocene.

The properties of the synthesized tertiary alcohols of the ferrocene series are presented in Table 1.

Table 1

Properties of tertiary alcohols of the ferrocene series

Compound	Yield, %	M.p., °C	Found, % C	Found, % H	Found, % Fe	Empirical formula	Calculated, % C	Calculated, % H	Calculated, % Fe
α-Hydroxyisopropylferrocene	58	56—58	64.01 64.10	6.39 6.40	22.20	$C_{13}H_{16}OFe$	63.97	6.56	22.90
α-Hydroxy-α-phenylethylferrocene	32	110—111	70.62 70.68	6.59 6.47	18.70	$C_{18}H_{18}OFe$	70.59	5.88	18.26
α-Hydroxy-α-phenylpropylferrocene	60	87—88	71.45 71.29	6.91 6.85	17.10	$C_{19}H_{20}OFe$	71.28	6.25	17.46
α-Hydroxy-α-phenylamylferrocene	72	65—66	72.52 72.40	6.70 6.75	16.68	$C_{21}H_{24}OFe$	72.41	6.91	16.10
3-Methyl-3-ferrocenyl-3-hydroxypropyne-1 *	5	—	66.25 66.05	6.58 6.68	—	$C_{14}H_{14}OFe$	66.14	5.51	22.04
3-Methyl-3-ferrocenyl-3-hydroxypropyne-1 **	5	112—114	65.38 65.56	5.77 5.56	22.85	$C_{14}H_{14}OFe$	66.14	5.51	22.04
3-Phenyl-3-ferrocenyl-3-hydroxypropyne-1 *	16	89—90	72.02 71.92	5.33 5.36	17.33	$C_{19}H_{16}OFe$	72.19	5.10	17.67

* For the synthesis, acetylene magnesium bromide prepared according to Jones ([3]) was used.

** For the synthesis, sodium acetylide prepared according to Normant ([4]) was used.

Experimental Part

Saturated tertiary alcohols were synthesized according to the scheme:

$$\mathrm{Fc{-}C(=O){-}R + R'MgX \rightarrow Fc{-}C(OH)(R)(R')}$$

$$R = \mathrm{CH_3},\ \mathrm{C_6H_5} \qquad R' = \mathrm{CH_3},\ \mathrm{C_2H_5},\ \text{n-}\mathrm{C_4H_9}$$

The synthesis was carried out under the conditions indicated in (1). Acetyl- or benzoylferrocene was added to the Grignard reagent in benzene solution, and the reaction mixture was stirred for 1 hour at 60°. The mixture was then decomposed with a saturated solution of NH_4Cl. After preliminary purification with activated charcoal, the reaction product was recrystallized from dilute ethyl alcohol. The yield of the reaction products was 58–72%. The following were obtained: α-hydroxyisopropylferrocene, α-hydroxy-α-phenylethylferrocene, α-hydroxy-α-phenylpropylferrocene, and α-hydroxy-α-phenylamylferrocene.

The synthesis of acetylenic alcohols is represented by the scheme:

$$\mathrm{Fc{-}C(=O){-}R + HC{\equiv}CX \rightarrow Fc{-}C(OH)(R){-}C{\equiv}CH}$$

$$R = \mathrm{CH_3},\ \mathrm{C_6H_5};\quad \mathrm{X = MgBr,\ Na}$$

Acetylenylmagnesium bromide was prepared by the method of (3). To it, at room temperature, a solution of acetylferrocene in THF was added. After stirring for 12 hours, the reaction mixture was decomposed with a saturated solution of NH_4Cl, extracted with ether, and the ether extract was dried over Na_2SO_4. The residue after removal of the solvent (a dark-red liquid) was dissolved in hexane and boiled with activated charcoal. The precipitated crystals were purified by recrystallization from dilute alcohol.

In an analogous manner, acetylenylmagnesium bromide was condensed with benzoylferrocene. Sodium acetylide was prepared according to Normant (4) at −15°. To the reagent obtained, a solution of acetylferrocene in THF was added at −10°. The reaction product was decomposed with a solution of NH_4Cl, extracted with ether, dried over Na_2SO_4, and after removal of the solvent was chromatographed on Al_2O_3. A fraction with m.p. 112–114°, characterized as an acetylenic alcohol, was isolated.

The following were obtained: 3-methyl-3-ferrocenyl-3-hydroxypropyne-1 (by two methods–via C_2HMgBr and C_2HNa) and 3-phenyl-3-ferrocenyl-3-hydroxypropyne-1.

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Received
2 XII 1960

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Note: Figure translations are in progress. See original paper for figures.

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