UDC 542.938:547.433'161

V. M. Krokhalev, V. I. Saloutin, and K. I. Pashkevich

Burckenbach et al. showed that triacetylmethane gives acetylacetone upon heating in water at reflux [1]. Cherkasova and Ponomarev [2] have proposed a method of synthesis of furan and thiophene β -diketones by the acylation of copper acetylacetonate using 2-furoyl and 2-thenoyl derivatives with subsequent deacetylation of the triketones obtained. The hydrolysis of tris(trifluoroacetyl)methane leads to hexafluoroacetylacetone and trifluoroacetic acid in 1:1 ratio [3].

Fluoroalkyl-containing β,β' -triketones $R_FCOCH(COCH_3)_2$ (I) are readily available and may be separated in good yield by the acylation of acetylacetone by epoxides of fluoroolefins or fluorocarboxylic acid fluorides [4]. This makes these derivatives promising for the preparation of polyfluorinated β -diketones (II). The hydrolysis of β,β' -triketones (I) under various conditions has been studied in order to develop a synthesis for β -diketones (II). The direction of this reaction depends significantly on the medium. The reaction may proceed at two inequivalent reaction sites C¹ (C¹) or C³.



The hydrolysis of (I) by the action of an equimolar amount of aqueous KOH proceeds regioselectively with cleavage of the C^2-C^3 bond and leads to acetylacetone. The reaction in aqueous pyridine and ethanolic KOH proceeds with cleavage of either the C^2-C^3 or C^1-C^2 bond. Acetylacetone forms in ethanolic alkali, while fluorinated β -diketones (II) are formed in aqueous pyridine with extension of the fluoroalkyl substituent.

Only β -diketones (II) are isolated in the presence of acetamide or trifluoroacetamide and their yield increases sharply with extension of the fluoroalkyl substituent. The hydrolysis in water and dilute hydrochloric acid proceeds regioselectively with cleavage of the C¹-C² bond and leads to fluorinated β -diketones (II).

Thus, the hydrolysis of fluoroalkyl-containing β , β '-triketones in the presence of bases proceeds with cleavage of the C²-C³ or C¹-C² bond. The reaction in water and dilute hydrochloric acid proceeds exclusively with cleavage of the C¹-C² bond. The hydrolysis of triketones (I) by water and aqueous hydrochloric acid may be a preparative method for obtaining fluoroalkyl-containing β -diketones.

EXPERIMENTAL

The gas-liquid chromatographic analysis was carried out on an LMKh-80-2 chromatograph with a katharometer detector and helium as the carrier gas using steel columns packed with 5% SE-30 on Chromaton N-AW-DMCS and 5% XE-60 on Chromaton N-AW-DMCS at 150°C. Triketones (Ia) and (b) were obtained according to our previous procedure [4], β -diketones (IIa, b) and their copper chelates were obtained according to [5]. Copper chelates (IIa, b), and (III) were identified by thin-layer chromatography on Silufol UV-254 plates.

<u>1. Hydrolysis in Aqueous Medium</u>. A mixture of 10 mmoles (Ia) or (Ib) and 1.8 ml (100 mmoles) water was stirred for 1.5 h at 70°C. After cooling, the reaction mass was treated with saturated aqueous $Cu(OAc)_2$ and extracted with ether. The extracts were dried over MgSO₄. After removal of the solvent, the residue was subjected to chromatography on a

Institute of Chemistry, Urals Branch, Academy of Sciences of the USSR, Sverdlovsk. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 9, pp. 2177-2179, September, 1988. Original article submitted October 15, 1987. 300×20 mm silica gel column in chloroform. The solution of the copper chelate was evaporated and the residue was evaporated in vacuum. The yields of the copper chelates of (IIa) and (IIb) were 1.60 g (68.1%) and 2.59 g (77.3%), respectively.

2. Hydrolysis by Aqueous Potassium Hydroxide. A sample of 0.84 g (15 mmoles) KOH in 2.7 ml water was added to 15 mmoles (Ia) or (Ib) and left at 20°C for 24 h. The reaction mixture was acidified by the addition of dilute hydrochloric acid to pH ~ 5 and extracted with three 10-ml portions of ether. The extracts were shaken with saturated aqueous $Cu(OAc)_2$. The precipitate was separated, washed with water and a small amount of ether, and dried in vacuum. The yield of copper acetylacetonate was 1.02 g (51.9%) from (Ia) and 0.92 g (46.9%) from (Ib).

<u>3. Hydrolysis in Aqueous Pyridine</u>. A mixture of 15 mmoles (Ia) or (Ib), 1.19 g (15 mmoles) pyridine, and 2.70 ml water was stirred at 70°C for 20 min [in the case of (Ia)] or 2 h [in the case of (Ib)]. After cooling, the reaction mixture was acidified by the addition of dilute hydrochloric acid to pH ~ 5 and extracted with three 10-ml portions of ether. The extracts were treated with saturated aqueous $Cu(OAc)_2$. The residue was separated and treated as in procedure 2. The yield of copper acetylacetonate was 0.90 g (45.8%) in the case of (Ia) and 0.37 g (18.8%) in the case of (Ib). After removal of the precipitate, the ethereal solution was treated as in procedure 1. The yield of the copper chelate of (IIa) was 0.06 g (1.7%) and the yield of the copper chelate of (IIb) was 1.71 g (34.0%).

<u>4. Hydrolysis in Ethanolic KOH</u>. A mixture of 20 mmoles (Ia) or (Ib), 1.12 g (20 mmoles) KOH in 7.5 ml ethanol was maintained at 20°C for 24 h. The reaction mass was treated as in procedure 3. The yield of copper acetylacetonate was 0.66 g (25.2%) for (Ia) and 0.74 g (28.3%) for (Ib). The yield of the copper chelate of (IIa) was 0.61 g (13.0%).

5. Hydrolysis in the Presence of Acetamide. A mixture of 0.1 mole (Ia) or (Ib), 5.91 g (0.1 mole) CH_3CONH_2 , and 18.0 ml water was stirred at 70°C for 30 min, cooled, and extracted with three 50-ml portions hexane. The extracts were dried over MgSO₄. After removal of the solvent, the residue was distilled in vacuum to give 1.61 g (7.9%) (IIa) and 15.39 g (50.6%) (IIb). Gas-liquid chromatographic analysis indicated that these samples were identical to those obtained according to Park et al., [5].

<u>6. Hydrolysis in the Presence of Trifluoroacetamide</u>. By analogy to procedure 5, a mixture of 0.1 mole (Ia) or (Ib), 5.7 g (0.05 mole) CF_3CONH_2 , and 18.0 ml water gave 3.57 g (17.5%) (IIa) or 18.67 g (61.4%) (IIb). Gas-liquid chromatographic analysis indicated that these samples were identical to those obtained according to Park et al., [5].

7. Hydrolysis by Hydrochloric Acid. a) A mixture of 16 mmoles (Ia) or (Ib), 1.5 ml concentrated hydrochloric acid, and 1.5 ml water was maintained for 50 min at 70°C. The reaction mass was treated as in procedure 1 to give 2.75 g (73.2%) copper chelate of (IIa) and 4.52 g (84.4%) copper chelate of (IIb).

b) A mixture of 27.35 g (79 mmoles) (Ib), 7 ml concentrated hydrochloric acid, and 7 ml water was stirred at 70°C for 1.5 h. The reaction mass was treated as in procedure 5 to give 18.73 g (78.0%) (IIb). Gas-liquid chromatographic analysis indicated that the product was identical to a sample obtained according to Park et al. [5].

CONCLUSIONS

1. The regioselective hydrolysis of 3-perfluoroacylpentane-2,4-diones in aqueous neutral and acid media may serve as a preparative method for obtaining fluoroalkyl-containing β -diketones.

2. The hydrolysis of 3-perfluoroacylpentane-2,4-diones in the presence of bases proceeds with the loss of the perfluoroacyl and acetyl groups to form acetylacetone and fluoroalkyl-containing β -diketones.

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