

An immersion study of the composition of the mixture obtained in the nitration of DBC according to Feigenbaum and Miche [2] showed that it consists of 30-40% (I) and 70-60% (II).

### Experimental

A sample of dinitrodibenzo-18-crown-6 was obtained according to Feigenbaum and Miche [2]. Diaminodibenzo-18-crown-6 was obtained according to our previous procedure [1].

The optical properties were studied under an MIN-8 microscope using a long-distance 40x objective and standard IZh-1 immersion liquids in monochromatic, plane-polarized light (589 nm). The refraction indices of the pure compounds were measured by the Becke method with an error of  $\pm 0.002$ . The angular values were measured with an error up to  $1^\circ$ .

### Conclusions

Optical immersion analysis permits the facile and rapid identification of the cis and trans isomers of dinitro- and diaminodibenzo-18-crown-6 as pure compounds and in mixtures.

### LITERATURE CITED

1. V. A. Popova, I. V. Podgornaya, I. Ya. Postovskii, and N. N. Frolov, *Khim.-Farm. Zh.*, 10, No. 6, 66 (1976).
2. W. M. Feigenbaum and R. H. Miche, *J. Polym. Sci.*, 9, No. 3, 817 (1971).

### HYDROLYSIS OF 2-ACETYL-SUBSTITUTED FLUOROALKYL 3-KETOESTERS

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"Acidic" or "ester" cleavage of 2-acyl-3-ketoesters not containing fluorine usually proceeds over the 1,3-diketone bond system. Of the two possible 3-ketoesters, the product with a greater tendency toward enolization is formed [1]. Cleavage at the 3-ketoester fragment has also been reported. Thus, ethyl 2-isobutyrylacetoacetate upon the action of concentrated hydrochloric acid undergoes hydrolysis with decarboxylation to give 5-methyl-1,3-hexanedione [2]. However, there is no information available on the hydrolysis of fluoroalkyl 2-acetyl-3-ketoesters.

In the present work, we studied the hydrolysis of fluoroalkyl 2-acetyl-3-ketoesters (I) and showed that it may proceed at three sites depending on the conditions (see Scheme 1). Thus, heating (I) in water at reflux leads to hydrolysis to give 3-ketoester (IIa) and 1,3-diketone (IIIa) containing heptafluoropropyl substituents in 71 and 13% yields, i.e., with cleavage of the  $C^2-C^4$  and  $C^1-C^2$  bonds, respectively.

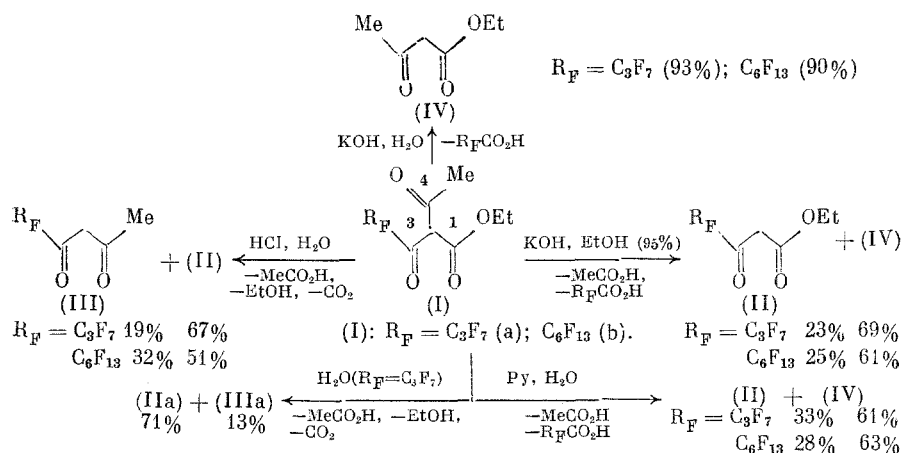
Hydrolysis by the action of aqueous KOH proceeds regioselectively with cleavage of the  $C^2-C^3$  bond, elimination of a fluorocarboxylic acid, and the formation of ethyl acetoacetate (IV) in 90-93% yield (Scheme 1). Ethanolic KOH or aqueous pyridine give a mixture of 3-ketoesters (II) and (IV), i.e., the reaction regioselectivity is lost and the  $C^2-C^4$  and  $C^2-C^3$  bonds are cleaved. Fluoroalkyl 3-ketoesters (II) and 1,3-diketones (III), which are the products of cleavage of the  $C^2-C^4$  and  $C^1-C^2$  bonds are formed upon hydrolysis in hydrochloric acid, similarly to hydrolysis in water.

Thus, the hydrolysis of (I) in alkaline media proceeds either regioselectively at the  $C^2-C^3$  bond or at the  $C^2-C^4$  and  $C^2-C^3$  bonds with the formation of 3-ketoesters. How-

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## Scheme 1



ever, in neutral and acidic aqueous media, this hydrolysis proceeds mainly at the C<sup>2</sup>-C<sup>4</sup> and C<sup>1</sup>-C<sup>2</sup> bonds to give a mixture of fluoroalkyl 1,3-diketone and 3-ketoesters. This reaction pathway may be attributed to the inductive effect of the fluoroalkyl substituents, which enhances the reactivity of C<sup>3</sup> relative to nucleophiles and reduces the nucleophilicity of the oxygen atom at C<sup>3</sup>.

We should note that fluoroalkyl 2-acetyl-3-ketoesters (I), with the exception of the reaction in aqueous KOH, display rather pronounced competitive reactivity of the sites at C<sup>1</sup>, C<sup>2</sup>, and C<sup>3</sup>, which is not characteristic for nonfluorinated 2-acyl-3-ketoesters.

### Experimental

The gas-liquid chromatographic analysis was carried out on an LKhM-8MD chromatograph with a katharometer detector and helium as the gas carrier using a 2 m × 4 mm steel column packed with 5% SE-30 silicon on Chromaton N-AW-DMCS and 5% XE-60 silicon on Chromaton N-AW-DMCS at 150°C. The product compositions were determined using calibration curves plotted for authentic sample mixtures.

Samples of (Ia) and (Ib) were obtained according to our previous procedure [3], while (IIa) was obtained according to Hauptstein [4] and (IIIa) was obtained according to Barkley and Levine [5]. Ethyl 4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluoro-3-oxononanoate (IIb) was obtained according to a standard procedure [6] in 52% yield. Found, %: C 30.10, H 2.56, F 56.67. C<sub>11</sub>H<sub>7</sub>O<sub>3</sub>F<sub>13</sub>. Calculated, %: C 30.43, H 1.63, F 56.89. IR spectrum (ν, cm<sup>-1</sup>): 1770 (keto C=O), 1740 (enol CO<sub>2</sub>C<sub>2</sub>H<sub>5</sub>), 1640 (C=C), 3120 (OH). PMR spectrum (δ, ppm, 50% in CCl<sub>4</sub>): 3.78 q (CH<sub>2</sub>), 3.59 s (=CH), 1.25, 1.33 t (CH<sub>3</sub>), 11.92 s (OH).

5,5,6,6,7,7,8,8,9,9,10,10,10-Tridecafluoro-2,4-decanedione (IIIb) was obtained according to Henne et al. [7] in 23% yield. Found, %: C 29.56, H 1.32, F 59.83. C<sub>10</sub>H<sub>2</sub>O<sub>2</sub>F<sub>13</sub>. Calculated, %: C 29.72, H 1.25, F 61.11. IR spectrum (ν, cm<sup>-1</sup>): 1595 (C=O), 2600-3500 (OH), PMR spectrum (δ, ppm, 50% in CCl<sub>4</sub>): 2.10 s (CH<sub>3</sub>), 6.10 s (=CH), 14.90 s (OH).

**Hydrolysis in Aqueous Medium.** A sample of 0.03 mole (Ia) in 100 ml distilled water was heated at reflux. The mixture was cooled to about 20°C and extracted with ether. The extract was dried over MgSO<sub>4</sub> and ether was distilled off to give 7.04 g of a mixture of (IIa) and (IIIa), which were identified using gas-liquid chromatographic comparison with authentic samples.

**Hydrolysis by Aqueous KOH.** A sample of 0.03 mole KOH in 100 ml water was added to 0.03 mole (Ia) or (Ib) and maintained for 24 h. Then, the mixture was acidified by the addition of dilute sulfuric acid to pH ~ 5 and extracted with ether. The extract was washed with water and dried over MgSO<sub>4</sub>. Ether was distilled off to give (IV) (3.63 g from (Ia) and 3.51 g from (Ib)), which was identified by gas-liquid chromatographic comparison with an authentic sample. The hydrolysis in 95% aqueous ethanol was carried out by analogy.

Hydrolysis in the Presence of Pyridine. A mixture of 0.03 mole (Ia) or (Ib) and 0.03 mole pyridine in 50 ml distilled water was heated at reflux for 3 h. After cooling to about 20°C, the mixture was acidified to pH ~ 5 by the addition of dilute sulfuric acid and extracted with ether. The extract was dried over MgSO<sub>4</sub> and ether was distilled off to give 7.22 g of a mixture of (IIa) and (IV) from (Ia) and 10.90 g of a mixture of (IIb) and (IV). The analysis was carried out by gas-liquid chromatographic comparison with authentic samples.

Hydrolysis by Hydrochloric Acid. A mixture of 0.03 mole (Ia) or (Ib), 25 ml concentrated hydrochloric acid, and 25 ml distilled water was heated at reflux for 3 h and cooled to about 20°C. Then, 50 ml water was added and the mixture was extracted with ether. The extract was washed with water and dried over MgSO<sub>4</sub>. Distillation of the solvent gave 7.16 g of a mixture of (IIa) and (IIIa) from (Ia) and 10.52 g of a mixture of (IIb) and (IIIb) from (Ib), which were identified by gas-liquid chromatographic comparison with authentic samples.

### Conclusions

Fluoroalkyl 2-acetyl-3-ketoesters are hydrolyzed by a) aqueous KOH regioselectively with cleavage of the C<sup>2</sup>-C<sup>3</sup> bond, b) aqueous ethanolic KOH and aqueous pyridine with cleavage of the C<sup>2</sup>-C<sup>3</sup> and C<sup>2</sup>-C<sup>4</sup> bonds, and c) in neutral aqueous and acid media with cleavage of the C<sup>1</sup>-C<sup>2</sup> and C<sup>2</sup>-C<sup>4</sup> bonds.

### LITERATURE CITED

1. M. Viscontini and N. Mercling, *Helv. Chim. Acta*, 35, 2280 (1952).
2. L. Bouveault, *Comptes Rendus Acad. Sci.*, 131, 45 (1900).
3. V. M. Krokhaliev, V. I. Saloutin, and K. I. Pashkevich, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 421 (1987).
4. M. Hauptstein and R. A. Brauer, *J. Am. Chem. Soc.*, 77, 4930 (1955).
5. B. L. Barkley and R. Levine, *J. Am. Chem. Soc.*, 73, 4625 (1951).
6. I. L. Knunyants and G. G. Yakobson (eds.), *Syntheses of Organofluorine Compounds [in Russian]*, Khimiya, Moscow (1973), pp. 60-61.
7. A. L. Henne, M. S. Newman, L. L. Quill, and R. A. Stanforth, *J. Am. Chem. Soc.*, 69, 1819 (1947).