SYNTHESIS OF 3-HYDROXY-6-PERFLUOROALKYL-2,3-DIHYDRO-4-PYRONES

V. I. Tyvorskii, L. S. Stanishevskii,
and I. G. Tishchenko

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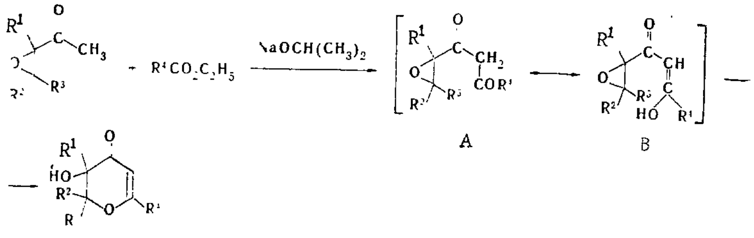
In the reaction of 2-methyl- and 3,3-dimethyl-2-acetyloxirane with ethyl perfluoroacetate and ethyl perfluorobutyrate under the conditions of the Claisen condensation, instead of the expected β-diketones (A) we isolated the products of intramolecular cyclization of their enol form (B) – substituted 3-hydroxy-6-perfluoroalkyl-2,3-dihydro-4-pyrones (I-IV):



I-IV

I $R^1=CH_3$, $R^2=R^3=H$, $R^4=CF_3$; II $R^1=CH_3$, $R^2=R^3=H$, $R^4=n\text{-}C_3F_7$; III $R^1=H$, $R^2=R^3=CH_3$, $R^4=CF_3$; IV $R^1=H$, $R^2=R^3=CH_3$, $R^4=n\text{-}C_3F_7$

The intramolecular cyclization of B proceeds with opening of the epoxide ring on the β-carbon atom side, as confirmed by the presence, according to results of oxidation with periodic acid, in I-IV of an α-ketol grouping. A mixture of 0.2 mole of acetyloxirane and 0.2 mole of perfluoroalkanoic acid ester was added with stirring and cooling to −10° to a suspension of 0.2 mole of sodium isopropoxide in 500 ml of absolute dimethoxymethane. After 30 min, 0.2 mole of glacial acetic acid was added, the solvent was removed by distillation, and the residue was treated with 100 ml of water and extracted with ether. This procedure yielded I (66%), with bp 67° (12 mm), d_4^{20} 1.3581, and n_D^{20} 1.4265; II (54%), with mp 24° (from pentane); III (65%), mp 70° (from hexane); IV (34%), mp 65° (from hexane). IR spectra of I-IV (CCl_4), cm^{-1}: 3500 (OH), 3100 (HC=), 1700 (C=O), and 1630 (C=C). PMR spectra (CCl_4), δ, ppm: I 1.33 (s, CH_3), 3.92 (s, OH), 4.22 and 4.38 (2H, d, J=12 Hz, 2-CH_2), and 5.78 (s, HC); III 1.28 and 1.68 [6H, s, $C(CH_3)_2$], 3.64 (s, OH), 4.20 (s, 3-H), and 5.85 (s, HC=).

The acetylation of I and III was carried out by allowing solutions of them in acetyl chloride to stand for 24 h. Workup gave acetate I (52%), with bp 62° (3 mm), d_4^{20} 1.3287, and n_D^{20} 1.4235, and acetate III (58%), with mp 26° (from pentane). IR spectra of acetates I and III (CCl_4), cm^{-1}: 3100 (HC=), 1760 ($COCH_3$), 1710 (C=O), and 1640 (C=C). PMR spectra (CCl_4), δ, ppm: acetate I 1.53 (s, CH_3), 2.08 (s, $COCH_3$), 4.23 and 5.14 (2H, d, J=12 Hz, 2-CH_2), and 5.83 (s, HC=); acetate III 1.40 and 1.57 [6H, s, $C(CH_3)_2$], 2.18 (s, $COCH_3$), 5.38 (s, 3-H), and 5.83 (s, HC=).

The results of elementary analysis for fluorine were in agreement with the calculated values for all of the compounds obtained.

V. I. Lenin Belorussian State University, Minsk. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, p. 1575, November, 1976. Original article submitted June 15, 1976.