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Comments on the Preparation of α-Halogeno-*sec.*-alkyl Esters

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The preparation of α,β-dichloro-*sec.*-propyl acetate and butyrate, and α, β, β′-trichloro-*sec.*-propyl acetate from the acid chlorides and chloroacetones in the presence of anhydrous zinc chloride was reported recently by Euranto and Kujanpää.[1] Attempts to prepare α-chloro-*sec.*-propyl acetate by the above method or by treating *sec.*-propenyl acetate with hydrogen chloride or *sec.*-propyl acetate with chlorine failed. At the same time, however, a patent description was published [2] where the preparation of α-halogeno-*sec.*-alkyl esters from acid halides and ketones in the presence of stronger condensing agents such as aluminium chloride and boron trifluoride was described. As examples, α-bromo-*sec.*-propyl acetate and α-chlorocyclohexyl acetate were mentioned, but only the preparation and properties of the first-mentioned compound were described.

Attempts were made to prepare α-bromo-*sec.*-propyl acetate by closely following the procedure described in the patent. Fractions were collected with a somewhat higher boiling point (*e.g.*, 48°C/11 torr) than that given in the patent (43—44°C/13 torr). The fractions could be analysed by conductometric measurement and argentometric titration by making use of the different hydrolysis rates of acetyl bromide (estimated half-life 0.5 s at 25°C in acetone-water containing 50 g of water per litre), α-bromo-*sec.*-propyl acetate (90 s), and 2-methyl-2-bromopentanone-4 (more than 100 days), which were found among the reaction products. Even the fractions richest in α-bromo-*sec.*-propyl acetate contained only about 1 % of that compound. The main product was found to be 2-methyl-2-bromopentanone-4 by measuring conductometrically the rate of hydrolysis at 25°C in acetone-water containing 300 g of water per litre. The first-order rate coefficient was found to be 1.6×10^{-5} s^{-1}, whereas the ketone (b.p. 49°C/10 torr, lit.[3] 52—53°C/11 torr) prepared from mesityl oxide and hydrogen bromide [3] gave a value of 1.8×10^{-5} s^{-1} (the corresponding value for *tert.*-butyl bromide was found to be 6.1×10^{-4} s^{-1}; both values are in accord with those expected on the basis of the structures of these tertiary bromides). The same ketone (b.p. 46—47°C/11 torr) was prepared also from acetyl bromide and mesityl oxide. The formation of 2-methyl-2-bromopentanone-4 in the attempted synthesis of α-bromo-*sec.*-propyl acetate may thus be explained by assuming that mesityl oxide is formed from acetone and acid halide [1] and that hydrogen bromide derived from acetyl bromide then adds to the double bond of mesityl oxide.

Aluminium chloride proved to be a good catalyst in the preparation of α-chloro-*sec.*-alkyl esters from ketones and acid chlorides even in cases where zinc chloride was ineffective or led to other products. Boron trifluoride was found to be a much weaker catalyst than aluminium chloride. Several esters were prepared by the following method. Equimolar amounts of freshly distilled acid chloride and ketone, which had been dried with anhydrous potassium carbonate and distilled, were mixed and a small amount of anhydrous aluminium chloride was added. The reaction mixture became slightly warm (in the case of α-chlorocyclohexyl acetate initial cooling of the reaction mixture was needed) and turned yellow or reddish. After it had stood overnight at room temperature, excess of ketone and acid chloride was evaporated at a temperature below 20°C, the crude ester was distilled rapidly at

25—45°C (in the case of α-chlorocyclohexyl acetate at 33—73°C) at diminished pressure and redistilled in an efficient distillation assembly. The resulting esters were colourless liquids which decomposed during a few hours or days to the acid chloride and ketone and turned yellow (it was found by a kinetic method that, *e.g.*, *ca.* 20 % of a sample of α-chloro-*sec.*-propyl acetate decomposed in 6 h at room temperature and *ca.* 70 % in 48 h at 0°C). It was not possible to distil all of them in a Todd distillation assembly and usually even the purest samples contained acid chloride and ketones as impurities. These impurities, however, did not interfere in the kinetic experiments (to be published later) for which the esters were prepared. The esters were in general more stable the larger the alkyl component and the smaller the acyl component.

For analysis, the esters were hydrolysed in water and the total amount of liberated acids was determined by titration with sodium hydroxide and the amount of the chloride ion by potentiometric titration with silver nitrate. The amounts are given as percentages of the theoretical amount. The yields of the esters varied from 5 (α-chloro-*sec.*-propyl esters) to 17 % (α-chlorocyclohexyl acetate). The following esters were prepared:

α-Chloro-sec.-*propyl acetate.* From acetone (E. Merck AG., *pro analysi*) and acetyl chloride (BDH, Laboratory Reagent). B.p. 29—30°C/12 torr, n_D^{20} 1.4152, d_4^{20} 1.0662, $[R]_D$ 32.09 (calc. 31.59), acid 98 %, chloride 94 %.

α-Chloro-sec.-*propyl propionate.* From acetone and propionyl chloride (BDH, Laboratory Reagent). B.p. 28—30°C/6 torr, n_D^{20} 1.4205, d_4^{20} 1.0326, $[R]_D$ 36.95 (calc. 36.24), acid 94 % chloride 97 %.

α-Chloro-sec.-*butyl acetate.* From methyl ethyl ketone (Fluka AG., *puriss.*) and acetyl chloride. B.p. 31—34°C/6 torr, n_D^{20} 1.4247, d_4^{20} 1.0375, $[R]_D$ 37.09 (calc. 36.24), acid 90 %, chloride 89 %.

1-Chloro-1-ethylpropyl acetate. From diethyl ketone (BDH, Laboratory Reagent) and acetyl chloride. B.p. 50—52°C/7 torr, n_D^{20} 1.4293, d_4^{20} 1.0452, $[R]_D$ 40.63 (calc. 40.89), acid 98.1 %, chloride 97.8 %.

1-Chloro-1-methylbutyl acetate. From methyl propyl ketone (BDH, Laboratory Reagent) and acetyl chloride. B.p. 33—34°C/2 torr, n_D^{20} 1.4271, d_4^{20} 1.0261, $[R]_D$ 41.20 (calc. 40.91), acid 97.7 %, chloride 98.7 %.

1-Chloro-1,2-dimethylpropyl acetate. From methyl isopropyl ketone (BDH, Laboratory Reagent) and acetyl chloride. B.p. 38—39°C/4.5 torr, n_D^{20} 1.4309, d_4^{20} 1.0309, $[R]_D$ 41.33 (calc. 40.92), acid 93.7 %, chloride 93.6 %.

α-Chlorocyclohexyl acetate. From cyclohexanone (BDH, technical) and acetyl chloride. B.p. 62—63°C/3 torr, n_D^{20} 1.4635, d_4^{20} 1.1208, $[R]_D$ 43.45 (calc. 43.37), acid 98.1 %, chloride 98.2 %.

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Favorsky Rearrangements

I. A New Synthesis of Isocrotonic Acid

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The preparation of isocrotonic acid has hitherto been a rather troublesome synthesis. The best method described was stereospecific *cis*-hydrogenation of tetrolic acid using a palladium catalyst [1] but, as many other acetylenic compounds, tetrolic acid is not simply prepared.[2,3]

de Simó and McAllister [4] reported in a patent that when 1,3-dichlorobutanone-2 was treated with a boiling saturated solution of sodium carbonate a mixture of crotonic and isocrotonic acids could be isolated in 46.6 % yield. This is an example of the Favorsky rearrangement of a dihalogeno ketone. The authors did not separate the isomers.

Other examples of the above rearrangement were reported by Wagner and Moore who, in addition to other bromo ketones, treated 1,3-dibromo-3-methylpentanone-2