Fragrant Esters of 3-Cyclohexylbutanoic Acid

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 $\mathbf{3}$ -Cyclohexylbutanoic acid can be obtained by using the following procedure:



Thus, the acid is not too easily available, but remarkable fragrant properties of its esters raise the interest in its production. The first four stages of its synthesis have been described previously.¹⁻⁴ Prins's reaction of α -methylstyrene with formaldehyde yields 4-methyl-4-phenyl-1,3-dioxane.

The reaction is carried out at temperatures about 80°C and can be catalyzed with sulfuric acid, acid ion exchangers, and the like. Hydrogenolysis of dioxane thus obtained, carried out under rather hard reaction conditions (200°C, 10 MPa) and catalyzed with Adkins's catalysts, gives rise to 3-phenyl-1-butanol in a high yield. The latter is hydrogenated in the ring using an Ni catalyst at 180-200°C and 6.5-10 MPa to 3-cyclohexyl-1-butanol. Dehydrogenation of the latter in the gaseous phase at 240-250°C using a catalyst based on CuO-ZnO-Al₂O₃ gives rise to 3-cyclohexylbutanal. This compound is oxidized with air at 120°C; the aldehyde is almost totally converted to 3-cyclohexylbutanoic acid already within two hours, with spontaneous oxidation being comparatively fast even at room temperature. The total yield of 3-cyclohexylbutanoic acid related to α -methylstyrene is 54%.

Esters of 3-cyclohexylbutanoic acid, with the exception of methyl ester, were obtained by the classic esterification with the corresponding alcohols; the reaction equilibrium was displaced by azeotropic distillation of water with toluene. p-Toluenesulfonic acid was used as the catalyst. The yields varied around 90%; allyl ester was obtained in a yield of 78.3%. Methyl ester was obtained in the absence of toluene, water and methanol were removed by distillation during the reaction, and pure methanol was added to the reaction mixture. The yield of methyl ester was also 90%.

Table I. Physico-chemical constants of alkyl esters of 3-cyclohexylbutanoic acid			
Alkyl	B.p. (°C) at 1.87 kPa	n ²⁰	
methyl	104-105	1.4555	
ethyl	110-111	1.4532	
propyl	120.5-122.5	1.4537	
isopropyl	115	1.4500	
allyl	122-124	1.4643	
butyl	141-142	1.4550	
isobutyl	132	1.4530	
amyl	146-147	1.4561	
isoamyl	140-142	1.4550	

Table II. Organoleptic characteristics of alkyl esters of 3-cyclohexylbutanoic acid

A	lkyl	Fragrance characteristics
'n	nethyl	fruit, apricot-type or peach-type
6	thyl	fruit, resembling unripe baccate fruit
р	ropyl	typically apple-like
is	opropyl	fruit, type ranging between blackberry and
a	llyl	fruit, type ranging between pineapple and mango
b	utyl	milky to fat
is	obutyl	fat, resembling waxes and vegetable oils
a	myl	fat to cocoa, resembles hardened fat
is	oamyl	fragrance of fine fermented cheese, later becoming cocoa to chocolate

Physico-chemical constants and the organoleptic characteristics of prepared alkyl esters of 3-cyclohexylbutanoic acid are presented in Tables I and II.

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