

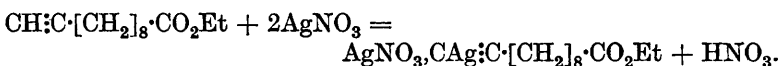
CCXLIX.—*The Action of the Metallic Derivatives of Ethyl Dehydroundecenoate upon Alkyl Halides.*

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AN attempt to synthesise Δ^{10} -stearolic acid by acting upon the silver derivative of ethyl dehydroundecenoate with heptyl bromide in alcoholic solution resulted in the formation of silver bromide, ethyl heptyl ether, and free ethyl dehydroundecenoate. With the silver derivative in absence of alcohol, an excess of heptyl bromide gave silver bromide, heptene, and ethyl dehydroundecenoate. In each case, the yields of silver bromide and ethyl ester were practically quantitative.

n-Propyl, isobutyl and ethyl bromides and ethyl iodide were used in succession, and in each case quantitative yields of silver halide and ethyl dehydroundecenoate were obtained. Other products in these reactions were not investigated. The silver derivative obviously reacts with halogen acid derived from the alkyl halide.

During the preparation of the silver derivative by the action of alcoholic silver nitrate upon the ester, we followed the reaction more closely than Krafft (*Ber.*, 1896, **29**, 2232) and found the yields of silver derivative and free nitric acid required for the equation:



We add to Krafft's observations that the silver derivative is soluble in hot alcohol and is stable in bright sunlight. The presence of a little free dehydroundecenoic acid in the ester results in the formation of a grey silver derivative which rapidly darkens in daylight.

Sodium derivatives of acetylenic compounds are not so readily prepared as the silver derivatives, but by the action of finely powdered sodamide upon ethyl dehydroundecenoate in toluene we obtained the sodium derivative of dehydroundecenoamide. The action of this compound upon alkyl halides was similar to that of the silver derivative.

EXPERIMENTAL.

Bromination of Undecenoic Acid.—Light petroleum (b. p. 60—80°) was treated with a slight excess of bromine, washed after some time with sodium bisulphite solution and with water, dried, and distilled. To a solution of 170 g. of undecenoic acid (m. p.

24.5°; b. p. 168.3°/15 mm.) in 500 c.c. of the solvent, cooled in a freezing mixture, 150 g. of bromine were added during 1½ hours with efficient stirring. After 1 hour the precipitate was filtered off, washed with 100 c.c. of cold solvent, and dried (250 g.; m. p. 38.5°). The remainder of the dibromo-acid was obtained as an oil after washing the filtrate with a solution of sodium bisulphite and then with water and drying and evaporating the solvent. The yield of oil was practically the same in a number of brominations (Found: Br, 46.2; equiv., by titration with alkali, 345.1. Calc. for $C_{11}H_{20}O_2Br_2$: Br, 46.5%; equiv., 344.0).

Preparation of Ethyl Dehydroundecenoate and its Silver Derivative.—Dehydroundecenoic acid was prepared from the dibromo-acid by Krafft's method (*loc. cit.*) and esterified with lime-dried alcohol and concentrated sulphuric acid. The ester had b. p. 145°/15 mm.

(a) A solution of 2 g. of the ethyl ester in 5 c.c. of absolute alcohol was added to 3.24 g. of silver nitrate in 105 c.c. of alcohol; 4.7 g. of the silver derivative were obtained. The filtrate and washings (10 c.c.) were shaken with solid potassium chloride and filtered. The filtrate required for neutralisation 9.0 c.c. of *N*-sodium hydroxide.

(b) 17.5 G. of the ester, 28.4 g. of silver nitrate, and 1 l. of alcohol gave 38.5 g. of the silver derivative, and the filtrate required 82.1 c.c. of *N*-alkali (Found: Ag, 44.5. Calc. for $C_{13}H_{21}O_2Ag, AgNO_3$: Ag, 44.3%).

Action of the Silver Derivative upon Heptyl Bromide in Alcohol.—The silver derivative precipitated from 17.5 g. of the ester was washed and dissolved in 300 c.c. of warm alcohol, 30 g. of heptyl bromide were added, and the solution was warmed under reflux on the water-bath; 30 g. of silver bromide separated during 3 hours. Alcohol was distilled from the filtered solution, and the residue fractionated.

Fraction (a), boiling below 140°/15 mm., was redistilled and collected up to 168°/760 mm. After it had been warmed with aqueous caustic potash to hydrolyse heptyl bromide and extracted with ether, an oil was obtained. Heptyl alcohol was removed from this by treatment with successive quantities of sodium. The remaining liquid was distilled and collected at 165—166°/760 mm. (3.5 g.) (Found: C, 74.65; H, 13.7. Calc. for $C_7H_{15}O \cdot C_2H_5$: C, 74.9; H, 14.0%).

Fraction (b) (16 g.), collected at 145°/15 mm., was ethyl dehydroundecenoate, since it gave after hydrolysis an acid of m. p. 43—44° (Found: C, 72.3; H, 10.2; equiv., by titration, 185.2. Calc. for $C_{11}H_{18}O_2$: C, 72.5; H, 10.0%; equiv., 182.1).

Action of the Silver Derivative upon Heptyl Bromide in Absence of Alcohol.—The silver derivative from 15 g. of the ester was dried in a

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vacuum desiccator during 2 days and then warmed with 50 g. of heptyl bromide on the water-bath, the flask being shaded. The cooled solution was filtered after dilution with ether. The filtrate gave a fraction, b. p. 95—100°/760 mm. On redistilling this, 4.5 g. were collected at 96—98°. Bromine in the cold converted this into an oil, b. p. 105—107°/15 mm. $\alpha\beta$ -Dibromoheptane has b. p. 105—107°/15 mm. (Found: Br, 61.5. Calc. for $C_7H_{14}Br_2$: Br, 62.0%).

Formation of the Sodium Derivative.—Ethyl dehydroundecenoate was heated under reflux for about 2 days with toluene in which a 5% excess of finely powdered sodamide was suspended; ammonia was slowly evolved. The flocculent precipitate of the sodium derivative of dehydroundecenoamide was treated with excess of heptyl bromide. Sodium bromide was slowly formed and the filtered solution gave practically the whole of the ethyl dehydroundecenoate.

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