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ONE STEP SYNTHESIS OF BETA KETO ALDEHYDES FROM VINYL ESTERS, ENOL ESTERS XI[1]

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We have previously reported[1] a simple synthesis of beta diketones involving treating isopropenyl esters with aluminum chloride. We have now found that the synthesis is also applicable to the conversion of vinyl esters to beta keto aldehydes. In view of the wide difference in the chemical reactions of the homologous isopropenyl and vinyl esters[3] (e.g. *only* the former functions as an acylation agent) one could not predict reaction parallels a *priori*. It is therefore surprising enough that the beta keto aldehyde forms at all, but even more peculiar that, by altering *only the time allotted for the reaction*, one can isolate exclusively *either* the ketoaldehyde *or* the same diacyl methane obtainable from the isopropenyl ester. Thus, by treating vinyl stearate with an equivalent of aluminum chloride in homogeneous hexane solution at reflux for 25 minutes one obtains only formylstearoylmethane (3-oxoeicosanal) in 60% yield (examination of an aliquot showed that after 0.5 hr. at 25° no significant amount of beta keto aldehyde had yet formed); whereas, after 2 hours' reflux, the sole product is distearoylmethane in 73% yield. The beta keto aldehydes are not damaged by their contact with aluminum chloride, but in the relatively pure condition they are rapidly decomposed by adsorption on silica gel chromatographic columns to intensely red-colored mixtures of aldol and *bis*aldol products. For this reason it is preferable to purify the ketoaldehydes of traces of diketones by chromatography of the copper chelate derivatives from which the ketoaldehyde is easily regenerated by treatment with mineral acid. Thus were obtained *3-oxoeicosanal*, m.p. 56-57°, uv (isooct.) 268 mμ, E = 6050, ir 1087, 1459, 1590, 1630 cm^{-1}, copper chelate m.p. 127-128.2°, uv 245 mμ, E = 7300 and 302 mμ, E = 8850, ir 1350, 1445, 1498, 1585 cm^{-1}; *3-oxooctadecanal*, m.p. 51.5-52.2°, lit.[4] 47°, copper chelate m.p. 125-126.5°; and *3-oxotetradecanal* (35% yield as copper chelate), m.p. 32.5-33.0°, copper chelate m.p. 126.8-127.4°, from vinyl stearate, vinyl palmitate and vinyl laurate respectively. Carboxylic acid starting materials used in this study were better than 99.5% pure by GLC analysis.

REFERENCES

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