

SYNTHESIS OF β -DIKETONES: SYMMETRICAL DIACYL METHANES
FROM ISOPROPENYL ESTERS, ENOL ESTERS X¹.

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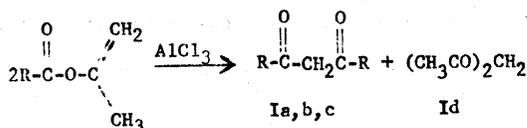
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In pursuing our studies of acylation by the agency of long chain enol esters under conditions

of aluminum chloride catalysis, we have discovered a simple one-step synthesis of symmetrical β -diketones. Treatment of a hexane solution of an isopropenyl ester with 0.25 to 1.0 mole of aluminum chloride forms diacylmethanes in typically 65-70% yields. The reaction mixture is a single homogeneous phase mixture, and at room temperature the reaction time is 0.25 hours. Thus from the stearate (1), laurate, octanoate (2) and acetate isopropenyl esters respectively were directly obtained following diacylmethanes: distearoylmethane (heptatriacontadione-18,20), Ia, R=C₁₇H₃₅, m.p. 77.3-77.8°; dilauroylmethane (pentacosadione-12,14), Ib, R=C₁₁H₂₃, m.p. 53°; dioctanoylmethane (heptadecadione-8,10), Ic, R=C₇H₁₅, m.p. 20-21°; and acetylacetone, Id, bp 142°.

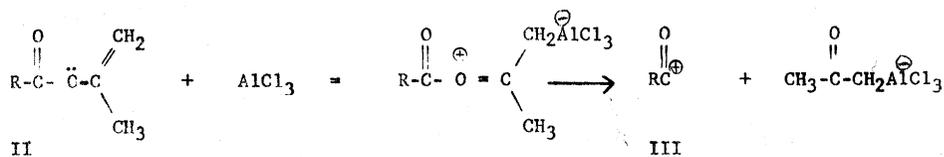


Such symmetrical diacylmethane products are different from the acetyl ketones obtained in photo-(3), or acid-catalysed (4) Fries Rearrangements. The mild conditions of reaction contrast with the 500° temperature requirement for thermal rearrangement reported by Young and coworkers(5). The products are also different from those reported by the last named authors who obtained benzoylacetone and not dibenzoylmethane from boron trifluoride-catalysed reaction of isopropenyl benzoate.

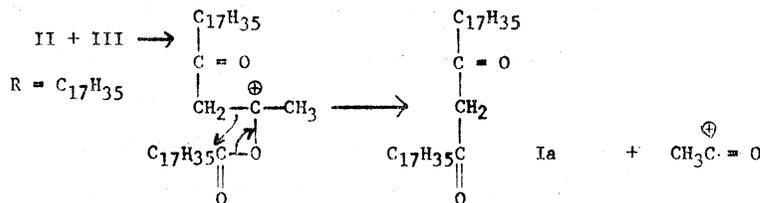
Saturated esters are not, in general, useful Friedel-Crafts acylating agents (6). We ascribe the exceptional behavior of enol esters, such as isopropenyl stearate, to the ease of acylium ion formation since most enol ester reactions, e.g. ester-acid interchange, seem to depend on available negative charge at the terminal methylene carbon atom rather than on carbonyl group polarization.

¹ For the previous paper in this series see E. S. Rothman, J. Am. Oil Chemists' Soc. 45, 189 (1968).

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In accord with this hypothesis we have found that isopropenyl stearate-aluminum chloride complex not only reacts with benzene to form stearophenone, but also with 9-octadecene and with methyl oleate to form α,β -unsaturated ketones. The products are consistent with the following mechanism:



It is convenient to isolate the β -diketones as copper chelate derivatives: I-a, m.p. 114°, lilac color; I-b, m.p. 110°, lilac color; I-c, m.p. 110.2-110.7°, blue color; I-d, m.p. 146°, blue color. The free beta diketones may be easily liberated from the copper chelate complexes by shaking their solutions in chloroform with N/10 aqueous hydrochloric acid. On evaporating the dried chloroform solution a residue of the free diketone remains.

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- (6) P. H. Gore, in "Friedel-Crafts and Related Reactions", G. A. Olah, ed. Interscience Publ., N. Y. (1964) Vol. III, part I, p.34.