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A SIMPLE ONE-STEP SYNTHESIS OF 5-ACETOXY-6-CHLORO-2-HEXANONE

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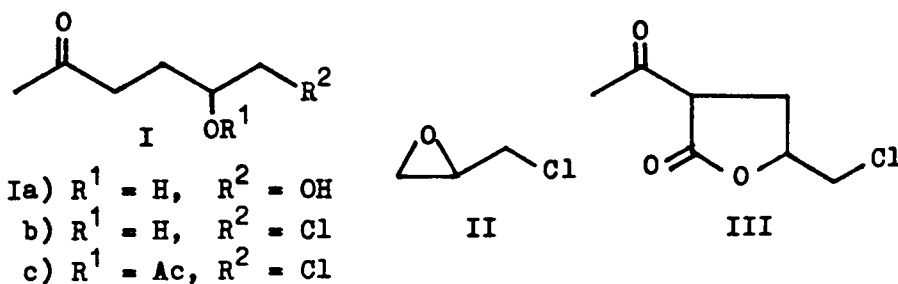
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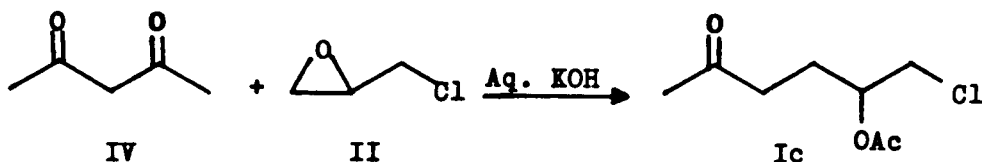
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The synthesis of 5,6-dihydroxy-2-hexanone (Ia) and its derivatives which serve as models of desoxy sugars,¹ has been studied extensively.^{2,3} The general synthetic strategy involved base-catalyzed condensation of ethyl acetoacetate and chloromethylloxirane (II) to give lactone III, which upon treatment with potassium carbonate yielded Ia.² As the corresponding 6-chloro derivative Ib could not be prepared by the anticipated ring opening of lactone III with mineral



acids, Pojarlieff developed a five-step procedure from ethyl acetoacetate and II and obtained Ib in poor overall yield (ca. 3%).³ Furthermore, because of its strong tendency to undergo internal condensation and polymerization, Ib was directly converted into its stable derivatives such as methylactolide or acetate Ic.³ This communication reports a convenient one-step synthetic method for preparation of Ic⁴ by treatment of 2,4-pentanedione (IV) with II in aqueous KOH in 40% yield. The compound was fully characterized by analytical and spectral data described in the Experimental Section. The identity of the product was further supported by preparation of its semicarbazone derivative with identical melting point reported in literature³ and by its spectral and analytical data. Though much remains to be done to establish the mech-



anism of its transformation, it seems reasonable to assume the intermediacy of 3-acetyl-6-chloro-5-hydroxy-2-hexanone formed by the attack of anion of IV on oxiranyl ring of II, followed by *in-situ* carbon to oxygen acetyl transfer reaction. However, we have not been able

to isolate this intermediate.

EXPERIMENTAL SECTION

The purity of the product was checked by TLC over silica gel-G. The proton and carbon-13 NMR spectra were recorded on a Bruker AM 400 instrument at field strengths of 400 and 100 MHz respectively in deuterated chloroform using TMS as an internal standard. Chemical shifts are described in δ ppm units.

5-Acetoxy-6-chloro-2-hexanone (Ic).- A solution of 2,4-pentanedione (5.0 g, 0.05 mol) in aqueous KOH (6.7%, 50 ml) was stirred under nitrogen atmosphere⁵ with chloromethyl-oxirane (5.55 g, 0.06 mol) for 48 hrs. The reaction mixture was extracted with ether, the ethereal extract was washed with water, dried over sodium sulphate and concentrated. The oily product thus obtained was subjected to distillation under vacuum to give 3.85 g (40%) of pure Ic, bp. 102°/2 mm, lit.³ 117°/5 mm. ¹H NMR: δ 1.88-2.04 (m, 2H, C₄H₂), 2.09 (s, 3H, C₅OCOCH₃), 2.16 (s, 3H, C₁H₃), 2.51 (t, 2H, C₃H₂, J = 7.3 Hz), 3.57 (dd, 1H, C₆H, J = 5.5 and 11.7 Hz), 3.64 (dd, 1H, C₆H, J = 4.6 and 11.7 Hz), 5.03 (m, 1H, C₅H).

¹³C NMR: δ 20.89 (C₅-OCOC), 25.71 (C₁), 29.87 (C₃), 38.97 (C₄), 45.58 (C₆), 72.16 (C₅), 170.43 (C₅-OC), 207.03 (C₂).

Anal. Calcd for C₈H₁₃ClO₃: C, 49.88, H, 6.80. Found: C, 50.10, H, 6.98

Semicarbazone of Ic.- Treatment of Ic with semicarbazide hydrochloride as usual gave instantaneously its semicarbazone derivative, mp. 131°, lit.³ 131°.

¹H NMR: δ 1.87 (s, 3H, C₁H₃), 1.97 (m, 2H, C₄H₂), 2.09 (s, 3H, C₅OCOCH₃), 2.30 (t, 2H, C₃H₂, J = 7.3 Hz), 3.61 (m, 2H, C₆H₂), 5.14 (m, 1H, C₅H).

¹³C NMR: δ 15.83 (C₁), 20.94 (C₅-OCOC), 27.57 (C₃), 34.00 (C₄), 45.39 (C₆), 72.14 (C₅), 148.66 (C₂), 158.22 (NH₂-CO), 170.40 (C₅-OC).

Anal. Calcd for C₉H₁₆ClN₃O₃: C, 43.29, H, 6.46, N, 16.82

Found: C, 43.42, H, 6.29, N, 17.03

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5. Without the nitrogen atmosphere, a complex mixture of intractable products was obtained.
