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SYNTHESIS OF β-ACYLOXY KETONES

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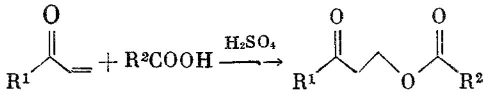
β-Acyloxy ketones, which are intermediates in the synthesis of boric acid extractants [1], are obtained by the addition of carboxylic acids to α,β-unsaturated ketones in the presence of $Hg(OAc)_2$ [2], KOAc, and K_2CO_3 [3].

We found that this reaction is also catalyzed by strong mineral acids, for example H_2SO_4.



(I), (II)

$R^1 = n\text{-}C_6H_{13}$ (I), $n\text{-}C_7H_{15}$ (II); $R^2 = H$ (a), CH_3 (b); C_2H_5 (c); $n\text{-}C_3H_7$ (d); $i\text{-}C_3H_7$ (e); $n\text{-}C_4H_9$ (f); $i\text{-}C_4H_9$ (g); $t\text{-}C_4H_9$ (h); $n\text{-}C_6H_{13}$ (i).

Under acid catalysis conditions this reaction is reversible. The rate of reaching equilibrium is independent of the H_2SO_4 concentration and is determined by the structure of the added acid. In the case of straight-chain acids the equilibrium is reached in 2-5 h at 20-40°C, and in 5-10 h for the branched acids. In all cases the conversion exceeds 90%. However, when distilled in vacuo the β-acyloxy ketones partially cleave the carboxylic acid, and as a result the yield drops to ∿80%.

The structure of the obtained compounds was confirmed via the IR and PMR spectra, and their composition via the elemental analysis data. The IR spectra of the β-acyloxy ketones have intense absorption bands of the carbonyl group in the 1720-1725 cm^{-1} region. For (Ib-i) and (IIb) the absorption band of the ester group is found at 1745-1755 cm^{-1}, and for (Ia) at 1735 cm^{-1}. The PMR spectra of all of the β-acyloxy ketones contain three triplets with centers at δ 4.15-4.25 ppm (2H, CH_2OCO), 2.55-2.65 ppm (2H, $CO\underline{CH_2}CH_2OCO$), 2.25-2.40 ppm (2H, $\underline{CH_2}COCH_2CH_2O$), J_{vic} ∿ 7 Hz. In the spectra of compounds (Ic-g, i) the last triplet has a complex structure due to the superimposition of the signals of the α protons of the acyl groups (2.10-2.45 ppm). For (Ia) the singlet of the proton of the formyloxy group is found at 7.88 ppm, while that of the protons of the acetoxy group of compounds (Ib) and (IIb) is found at 1.91 ppm. The signals of the other aliphatic protons have a complex structure and are located in the 0.6-1.6 ppm region. The conversion of the α,β-unsaturated ketones to β-acyloxy ketones was determined by GLC.

EXPERIMENTAL

The IR spectra were obtained on a UR-20 spectrometer in CCl_4 solution, and the PMR spectra were obtained on a Tesla BS-487 instrument (80 MHz) for 20-40% CCl_4 solutions relative to TMS. The GLC analysis was run on a Chrom-4 chromatograph using a 120 × 0.4 cm column packed with 0.5% PEGA deposited on glass (0.25-0.2 mm), a flame-ionization detector, nitrogen as the carrier gas (30 ml/min), 70-150°, and a rate of temperature rise of 20 deg/min.

The starting 1-nonen-3-one and 1-decen-3-one were obtained by acylating ethylene with the heptanoyl and octanoyl chlorides in the presence of $AlCl_3$ and subsequent dehydro-

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TABLE 1. Properties of β-Acyloxy Ketones

Acyloxy ketone	Reaction time, h	T., °C	Yield, %	bp, °C (p, mm Hg)	$n_D(t, °C)$	Found Calculated, %		Empirical formula
						C	H	
1-Formyloxy-3-nonanone (Ia)	2	20	83	109(3)	1,4352(26)	64,84 64,49	9,93 9,74	$C_{10}H_{18}O_3$
1-Acetoxy-3-nonanone (Ib)	5	20	80	112(2)	1,4350(20)	65,98 65,97	10,17 10,07	$C_{11}H_{20}O_3$
1-Propionyloxy-3-nonanone (Ic)	3	40	84	110–111(2)	1,4336(24)	67,24 67,25	10,20 10,35	$C_{12}H_{22}O_3$
1-Butyryloxy-3-nonanone (Id)	3	40	71	120(0,5)	1,4388(21)	68,60 68,38	10,41 10,59	$C_{13}H_{24}O_3$
1-Isobutyryloxy-3-nonanone (Ie)	5	40	83	84–86(0,2)	1,4367(20)	68,46 68,38	10,55 10,59	$C_{13}H_{24}O_3$
1-Valeryloxy-3-nonanone (If)	5	40	80	131–132(1)	1,4407(21)	69,50 69,38	10,72 10,81	$C_{14}H_{26}O_3$
1-Isovaleryloxy-3-nonanone (Ig)	5	40	78	98–100(0,2)	1,4391(20)	69,33 69,38	10,51 10,81	$C_{14}H_{26}O_3$
1-Pivaloyloxy-3-nonanone (Ih)	10	40	76	90–91(0,2)	1,4355(18)	69,51 69,38	10,60 10,81	$C_{14}H_{26}O_3$
1-Heptanoyloxy-3-nonanone (Ii)	5	40	85	mp,30°	–	71,06 71,07	11,00 11,18	$C_{16}H_{30}O_3$
1-Acetoxy-3-decanone (IIb)	5	20	80	92–93(0,1)	1,4393(20)	67,69 67,25	10,49 10,35	$C_{12}H_{22}O_3$

chlorination of the 1-chloro-3-nonanone and 1-chloro-3-decanone by aqueous NaOH solution [1].

Addition of Carboxylic Acid to α,β-Unsaturated Ketone. A mixture of 0.1 mole of either 1-nonen-3-one or 1-decen-3-one in 50 ml of the carboxylic acid and 1 mmole of H_2SO_4 was kept for 2-10 h at 20-40°. The reaction product was isolated by vacuum distillation. The yields and constants of the synthesized compounds are given in Table 1.

CONCLUSIONS

A convenient method was developed for the synthesis β-acyloxy ketones by adding carboxylic acids to α,β-unsaturated ketones in the presence of catalytic amounts of H_2SO_4.

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