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A two-step method is described for the synthesis of levulinic acid from ethyl acetoacetate and ethyl chloroacetate in 70% yield.

Despite the large variety of methods for the preparation of levulinic acid (I) [1-3] such as the hydrolysis of hexoses [4], cellulose [5], and furfural [6], the oxidative cleavage of alkyldihydrofurans [7], and the ozonolysis of rubber [8], none of these approaches is convenient for industrial use and, thus, the intensive search for new methods of the synthesis of this is continuing [9].

In the present work, a two-step synthesis of (I) is described based on the alkylation of ethyl acetoacetate by ethyl chloroacetate in a heterophase system continuing DMF and solid KOH, K_2CO_3 , or Na_2CO_3 in the presence of benzyltriethylammonium chloride (BTEAC) with subsequent hydrolysis of the diethyl ester of α -acetylbutanedioic acid (II)

 $CO_{2}Et$ $CH_{2}(COCH_{3})CO_{2}Et + CICH_{2}CO_{2}Et \rightarrow CH_{3}COCHCH_{2}CO_{2}Et \rightarrow \underbrace{(H^{+}) \text{ or } (OH^{-})}_{(11)}$ (11) $CH_{3}COCH_{2}CH_{2}COOH$ I

The yield of levulinic acid (I) relative to starting ethyl acetoacetate upon acid hydrolysis is 70%. This yield does not exceed 50% in the case of alkaline hydrolysis.

EXPERIMENTAL

The IR spectra were taken neat on a Perkin-Elmer spectrometer using NaCl plates. The PMR spectra were taken on a Tesla BS-467 spectrometer at 60 MHz.

Diethyl Ester of 2-Acetyl-1,4-butanedioic Acid (II). a. A sample of 12.3 g (0.1 mole) ethyl chloroacetate was added dropwise with rapid stirring to a mixture of 5.6 g (0.1 mole) ground KOH, 13 g (0.1 mole) ethyl acetoacetate, and 0.186 g (0.001 mole) BTEAC at 25-35°C. The mixture was stirred for an additional 1.5-2 h at 45-50°C, cooled to about 20°C, acidified by the addition of highly dilute hydrochloric acid until slightly acidic, and extracted with three 100-ml portions of ether. The combined extracts were washed with 50 ml water, dried over MgSO₄, evaporated on a rotary evaporator, and distilled in vacuum to give 16.2 g of a fraction with bp 145-155°C (10-12 mm). The yield was 75%, n_p^{20} 1.4364 (lit. bp 120-124°C (4 mm), n_p^{20} 1.4360). PMR spectrum in CCl₄ (δ , ppm, rel. to TMS): 1.23 t (3H, ester CH₃), 2.25 s (3H, CH₃), 2.76 m (2H, CH₂), 3.88 t (1H, CH), 4.15 q (2H, ester CH₂).

b. A sample of 12.3 (0.1 mole) ethyl chloroacetate was added dropwise with rapid stirring to a mixture of 16 g (0.12 mole) calcined K_2CO_3 or 10.6 g (0.12 mole) Na_2CO_3 , 15.6 g (0.12 mole) ethyl acetoacetate, and 0.23 g (0.0012 mole) BTEAC at 25-35°C. The mixture was stirred for 2 h at 50°C. The treatment and isolation of the product were carried out as described above to give 10.04 g (65%) (II).

Preparation of Levulinic Acid (I). a. A mixture of 4.32 g (0.02 mole) (II) and 20 ml 15% hydrochloric acid was heated at reflux for 2.5 h. After removal of HCl, the residue was distilled in vacuum, collecting the fraction with bp 145-150°C (15 mm) [10]. The product yield was 2.15 g (93%).

b. A mixture of 4.32 g (II) and 25 ml 10% aqueous KOH was heated for 2.5-3 h at 100-110°C. After cooling to about 20°C, the mixture was acidified to pH 3 and extracted with three 50-ml portions of ether. The ethereal solution was washed with 15 ml water, dried over

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 2, pp. 474-475, February, 1990. Original article submitted March 27, 1989. $MgSO_4$, and evaporated on a rotary evaporator. The residue (2.9 g) was heated for 0.5 h at 150-160°C (100-120 mm) and distilled, collecting the fraction with bp 148-150°C (13 mm). The product yield was 1.33 g (65%).

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REACTION OF *α*-CHLORONITROSOALKANES WITH THE TRIMETHYLSILYL

ESTER OF DIPHENYLPHOSPHONOUS ACID

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The reaction of α -chloronitrosoalkanes with the trimethylsilyl ester of diphenylphosphonous acid leads to the formation of products of the Allen reaction, namely, phosphorylated oximes.

The reactions of α -halonitroso compounds with the esters of P(III) acids (Allen reaction) have been studied rather extensively [1, 2]. On the other hand, the question of the use of silyl esters of P(III) acids as the phosphorus-containing reagent in these reactions has remained open. In the case of the trimethylsilyl ester of diphenylphosphonous acid (I), we have demonstrated the use of silyl esters of P(III) acids in the Allen reaction. Ester (I) reacts exothermally with α -chloronitrosoalkanes (II) at 10-15°C to give the corresponding phosphorylated oximes (IIIa)-(IIIe) in 37-44% yield.

> $(C_{6}H_{5})_{2}POSi(CH_{3})_{3} + R - | -N = 0 \xrightarrow[-CISi(CH_{3})_{3}]{} (C_{6}H_{5})_{2}PON = C \xrightarrow[R']{} R'$ (IIIa—e) $R = CH_3, \ R' = Cl (a), \ R = R' = CH_3 (b), \ R = C_2H_5, \ R' = Cl (c), \ R = C_3H_7, \ R' = Cl (d),$ $R = i - C_3 H_7$, R' = Cl(e).

Phosphorylated oximes (IIIa)-(IIIe) are white crystalline compounds whose composition and structure were demonstrated by elemental analysis and IR and NMR spectroscopy.

EXPERIMENTAL

The PMR and ³¹P NMR spectra were taken on a Bruker CXP-200 spectrometer in CDCl₃ relative to TMS (¹H NMR) and 85% H_3PO_4 (external standard for the ³¹P NMR spectra). 0-Methylchloroformiminodiphenylphosphonate (IIIa). A sample of 1.3 g (0.01 mole) 1,1dichloro-1-nitrosoethane was added with stirring in an argon stream to a solution of the

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