tion of monotypic polymers such as the extent of substitution of cellulose acetates, while these indices for inert probes are more sensitive to the supermolecular structure of polymer solutions than their rotational mobility coefficients.

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SYNTHESIS OF ESTERS OF 2-SUBSTITUTED 4-KETOPENTANOIC ACIDS BY

THE ALKYLATION OF CH-ACIDS USING CHLOROACETONE UNDER PHASE

TRANSFER CATALYSIS CONDITIONS

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An improved method was developed for the synthesis of ethyl esters of 2-substituted 4-ketopentanoic acids by the alkylation of  $CH_2(X)CO_2Et$  using chloroacetone in the liquid-solid KOH ( $K_2CO_3$  or  $Na_2CO_3$ )-DMF-PhCH<sub>2</sub>(Et)<sub>3</sub>NCl system.

Ketoesters with the general formula  $CH_3COCH_2CH(X)CO_2Et$  (Ia)-(Ic) have found common use in the synthesis of a series of physiologically active compounds, poly- and heterocycles, in particular, 2-formylpyrroles, tricyclic lactones, and fungicides [1-5]. The accepted approach to the preparation of these compounds involves the alkylation of the corresponding CH-acids by chloroacetone. However, the disadvantages of this approach, in particular, the use of alkali metals, their hydrides, and alcoholates and the relatively low yields (~60%) of the desired products, have led to the search for improved methods of their synthesis [6].

We have developed a convenient method for the synthesis of (Ia)-(Ic) under phase transfer catalysis (PTC) conditions in the liquid-solid system containing KOH ( $K_2CO_3$  or  $Na_2CO_3$ ), DMF, and benzyltriethylammonium chloride (BTEAC).

$$\begin{split} \mathrm{XCH}_2\mathrm{CO}_2\mathrm{Et} &+ \mathrm{ClCH}_2\mathrm{COCH}_3 \to \mathrm{CH}_3\mathrm{COCH}_2\mathrm{CH}(\mathrm{X})\mathrm{CO}_2\mathrm{Et} \\ & & (\mathrm{Ia}-\mathrm{c}) \\ \mathrm{X} &= \mathrm{CO}_2\mathrm{Et} \ (\mathrm{a}), \ \mathrm{COCH}_3 \ (\mathrm{b}), \ \mathrm{CN} \ (\mathrm{c}). \end{split}$$

The reaction proceeds with slight heat evolution also in the absence of the phase transfer catalysis but the yield of the desired products is 15-20% less with significantly longer reaction times. The yields of (Ia)-(Ic) depend on the nature of the deprotonating agent and increases in the series  $Na_2CO_3 < K_2CO_3 < KOH$  from 65 to 80%. The best yield was achieved using ground KOH. The use of granulated alkali reduces the yield by 15-20%. The reaction is carried out with the simultaneous addition of a mixture of the reagents to a dispersed suspension of the solid base in DMF.

The structure of (I) was supported by IR, PMR, and <sup>13</sup>C NMR spectroscopy and mass spectrometric molecular mass determination.

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Com- pound	Yield %	Bp, °C (p, mm Hg)	$n_{D}^{20}$	<sup>v,</sup> cm <sup>-1</sup>	PMR (ô, ppm)	<sup>13</sup> C NMR (ô, ppm) M+
(Ia)	75-80	85-88 (0.1)	1.4388	1720(CO). 1755(CO- ester)	1.27 t (6H, 2×CH <sub>3</sub> - ester), 2.15 s (3H, CH <sub>3</sub> CO). 2.84 d (2H, CH <sub>2</sub> ). 3.68 t (1H, CH), 4.15 q (4H, CH <sub>2</sub> -	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$
( <b>Jb</b> )	70-75	87-90 (0.1)	1,4398	1720(CO), 1755(CO - ester)	ester) 1.25 t (3H, $CH_3 - ester$ ), 2.12 s (3H, $CH_3CO$ ). 2,30 s (3H, $CH_3CO$ ). 2,30 s (3H, $CH_3CO$ ). 2,89 m (2H, $CH_2$ ), 3.97 t (1H, CH), 4.12 q (2H, $CH_2 - ester$ )	(CO) 13.8 $q$ (CH <sub>2</sub> - ester), 186 29.1 $q$ (CH <sub>3</sub> ). 41.3 t (CH <sub>2</sub> ). 53.5 d (CH), 61.4 d (OCH <sub>2</sub> ). 168.6 s (CO - ester), 201.7 s (CO), 205.1 s (CO)
(]c) *	65-75	92-95 (0.1)	1,4414	1723(CO), 1754(CO ester) 2257(CN)	1.32 t (3H, $CH_3 - ester$ ), 2.18 s (3H, $CH_3CO$ ). 3.05 m (2H, $CH_2$ ), 3.86 t (1H, $CH_2$ ), 3.86 t (1H, $CH_1$ ), 4.23 q (2H, $CH_2 - ester$ ),	$\begin{array}{c} 13.5 \ q \ (CH_2 - ester), \\ 29.0 \ q \ (CH_3CO), \\ 31.5 \ d \ (CH), \ 41.7 \ t \\ (CH_2), \ 62.7 \ t \ (OCH_2), \\ 116.0 \ s \ (CN), \ 165.1 \ s \\ (CO - ester), \ 202,5 \ s \\ (CO) \end{array}$

TABLE 1. Yields and Indices of Products (Ia)-(Ic)

\*Lit. data [4]: bp 116°C (0.5 mm),  $n_0^{20}$  1.4428.

## EXPERIMENTAL

The IR spectra were taken on a UR-20 spectrometer in  $CHCl_3$ . The PMR spectra were taken in  $CCl_4$  relative to TMS on a Tesla BS-467 spectrometer at 60 MHz. The <sup>13</sup>C NMR spectra were taken in  $CHCl_3$  relative to TMS on a Bruker WH-250 spectrometer. The mass spectra were taken on a Varian MAT CH-6 mass spectrometer. The boiling points were not corrected.

General Procedure for the Synthesis of (Ia)-(Ic). A mixture of 9.3 g (0.1 mole) freshly distilled chloroacetone and 0.1 mole  $XCH_2CO_2Et$  was added dropwise with strong stirring to 5.6 g (0.1 mole) ground KOH in 200 ml DMF in the presence of 0.001 mole BTEAC at a rate such that the temperature did not rise over 35°C. The mixture was then stirred for an additional 1.5 h at 45°C. The mixture was neutralized with very dilute hydrochloric acid and extracted with three 100-ml portions of ether. The combined extracts were washed with 100 ml water, dried over MgSO<sub>4</sub>, evaporated on a rotary evaporator, and distilled. The indices and yields of (Ia)-(Ic) are given in Table 1.

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