INTERACTION OF ETHOXYACETALDEHYDE WITH 1,3-DICARBONYL

COMPOUNDS

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It has been established that on interaction of ethoxyacetaldehyde with acetylacetone, acetoacetic ester, and benzoylacetone in the presence of piperidine acetate, β , γ -unsaturated compounds are formed,viz., 3-(2-ethoxy)vinyl substituted acetylacetone, acetoacetic ester, and benzoylacetone. Methods are proposed for the synthesis of 2,3,5-trisubstituted 4,5-dihydrofurans in the presence of trifluoroacetic or acetic acids by the cylization of the linear condensation products.

The interaction of ethoxyacetaldehyde (I) with the 1,3-dicarbonyl compounds acetylacetone (IIa), acetoacetic ester (IIb), and benzoylacetone (IIc) has been investigated. The general reaction scheme may be represented in the following manner.



 $II - VI a - c R^{1} = CH_{3}; a R^{2} = CH_{3}, b R^{2} = OC_{2}H_{5}, c R^{2} = Ph$

On interaction of ethoxyacetaldehyde with equimolar quantities of diketones IIa-c in the presence of piperidine acetate as catalyst β , γ -unsaturated compounds IVa-c were formed in place of the α , β -unsaturated products IIIa-c of a Knoevenagel condensation. The 3-(2ethoxy)vinylpenta-2,4-diene (IVa) obtained on reaction of ethoxyacetaldehyde with diketone IIa was practically completely in the enol form (Va) according to the data of PMR spectroscopy. On interaction of ethoxyacetaldehyde with diketone IIb not only was the appropriate linear condensation product IVb formed, enolized to 45%, but also the cyclic isomer 2methyl-5-ethoxy-3-carbethoxy-4,5-dihydrofuran (VIb), 9:1. The condensation product of ethoxyacetaldehyde with benzoylacetone was the β , γ -unsaturated diketone (IVc, Vc) enolized to 80 %. Analysis of the coupling constants of the protons of the AB system of the β , γ unsaturated adducts (J_{ABa} = 13.0; J_{ABb} = 12.5; J_{ABc} = 13.0 Hz) made it possible to assign the structure of the Z-isomer to this compound both in the keto and in the enol form.

On interacting ethoxyacetaldehyde with a fourfold excess of acetoacetic ester a Michael reaction occured following the Knoevenagel reaction and as a result a mixture of diastereomeric cyclohexanones VII 70:30 was formed the structure of which was confirmed by methods

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Compound	bp°C	1 D ²⁰	PMR spectrum,* ppm (CDC1 250 MHz)	М+	Foun %	d , '	Empirical formula	Calc	20- 20, %
	(mm)	<u> </u>	(с	н		с	н
VIa	78(2)	1,4810	5,46 (m,1H, X-H); 3,70 (m 2H, C-H, D-H); 2,80 (m, 2H, A-H, B-H); 2,17 (t $3H$, 2-CH ₃); 2,10 (s ,3H, CH ₃ C=O); 1,17 (t $3H$, OCH ₂ CH ₃)	170	63,5	8,4	$C_9H_{17}O_3$	63,5	8,2
VIÐ	81 (2)	1,4633	5,52 (d.d 1H, X-H); 3,80 , m 1H, C-H); 3,55 (m 1H, D-H); 3,49 (b 2H, CH ₂ O); 2,97 (m, 1H, A-H); 2,68 (m, 1H, B-H); 2,20 (q 3H, 2-CH ₃); 1,30 (t 3H, CH ₃ CH ₂ C=O); 1,0 (t 3H, CH ₃ CH ₂ O)	200	60,1	8,0	C ₁₀ H ₁₆ O ₄	60,0	8,1
VIc+VIc	133 (2)	1,5550	VI c 7.41 (m. 5H, Ph); 5.58 (d.d. 1H, X-H); 3.88 (q, 1H, C-H); 3.84 (q. 1H, D-H); 3.22 (m, 1H, A-H); 2.91 (m, 1H, B-H); 1.87 (t 3H, 2-CH ₃); 1.24 (t, 3H, CH ₃ CH ₂) VIc ₁ : 7.56 (m, 5H, Ph); 5.62 (d. d, 1H, X-H); 3.93 (q, 1H, C-H); 3.89 (q, 1H, D-H); 3.29 (d, 1H, A-H); 2.94 (d, 1H, B-H); 1.95 (s.3H, CH ₃ C=O); 1.27 (t 3H, CH-CH ₂ O)	232	72,4	6,8	C ₁₄ H ₁₆ O ₃	72,4	6,9

TABLE 1. Properties of 2,3,5-Trisubstituted 4,5-Dihydrofurans

*The spectrum of compound (VIa) was taken at 60 MHz.

of IR and ¹³C NMR spectroscopy. Similar conversion of Knoevenagel condensation products has been observed for a series of monosaccharides in [1].



The cyclization has been investigated by us of the products of interaction of ethoxyacetaldehyde with diketones IIa-cunder the action of acids. On heating a solution of the linear adduct IVa in CCl₄ (70°C, 7 h) in the presence of catalytic quantities of trifluoroacetic acid 2-methyl-5-ethoxy-3-acetyl-4,5-dihydrofuran (VIa) was isolated in 85% yield. From the mixture of condensation products (IVb-VIb) 2-methyl-5-ethoxy-3-carbethoxy-4,5-dihydrofuran (75%) was formed in the presence of acetic acid (70°C, 2 h). The condensation product of ethoxyacetaldehyde with diketone (IIc) cyclized in the presence of trifluoroacetic acid (70°C, 2 h) to the corresponding dihydrofuran in 95% yield. Analysis of the PMR spectra (250 MHz, CDCl₃) of the dihydrofuran showed that it was a mixture of the two isomers (VIc) and (VIc₁) 2:1.



The formation of these two compounds is explained by the possibility of attack at the carbon center of the vinyl ether both from the side of the benzoyl and from the side of the acetyl group. Since arylacetones are enolized to a greater extent at the benzoyl group than at the acetyl group more compound (VIc) is formed. The existence of two isomers was confirmed by the data of ¹³C NMR spectroscopy.

EXPERIMENTAL

The PMR spectra were obtained on Tesla BS-467 and Bruker WM-250 (60 and 25 MHz) instruments in 5-10% solutions in CCl₄, C_6D_6 , and CDCl₃, the internal standard was HMDS. The ¹³C NMR spectra were obtained on a Bruker WM-250 instrument in C_6D_6 . IR spectra were taken on UR-20 and Specord-75 instruments in thin film. Mass spectra were recorded on a Varian CH-6 instrument by direct insertion of samples into the ion source, ionizing voltage was 70 eV. Analysis by GLC was carried out on a Khrom-4 instrument with a flame ionization detector, column 1000 × 4 mm, stationary phase 15% Tween on Chromaton, carrier gas nitrogen, and analysis temperature 150°C.

The characteristics of compounds VIa-c are given in Table 1.

Interaction of Ethoxyacetaldehyde with 1,3-Dicarbonyl Compounds (General Procedure). The 1,3-dicarbonyl compound (0.5 mole) and a few drops of piperidine acetate catalyst were added to a solution of ethoxyacetaldehyde (0.5 mole) in an organic solvent. The mixture was left for 4 h in the dark. After removal of water the organic portion was dried over sodium sulfate, the solvent distilled off, and the residue distilled in vacuum.

 $\frac{3-(2-\text{Ethoxy})\text{vinylpentane-2,4-dione (Va)}_{\text{D}} \text{ Dione Va was obtained from compounds I and IIa.}$ Yield was 28%, bp 74°C (2 mm), $n_{D}^{2°}$ 1.4828. PMR spectrum (60 MHz, CCl₄): 16.2 (s, 1 H, OH). 6.0 (d, A-H, J_{AB} = 13.0 Hz), 5.15 (d, 1 H, B-H, J_{AB} = 13.0 Hz), 3.74 (q, 2 H, OCH₂, J = 7.0 Hz), 2.0 (s. 6 H, CH₃C=0), 1.23 ppm (t, 3 H, CH₃CH₂O, J = 7.0 Hz). IR spectrum: 2980, 1640, 1330, 1260 cm⁻¹. Mass spectrum: M⁺ 170.

<u>3-(2-Ethoxyvinylbenzoylacetone (Vc).</u> A mixture of compounds IVc + Vc was obtained from substances I and IIc. Yield was 53%, bp 136-137°C (2 mm, n^{20} 1.5582. PMR spectrum (250 MHz, C₆D₆): (IVc), 7.85 (m, 5 H, Ph), 6.71 (d, 1 H, A-H, J_{AB}^{D} = 13.0 Hz), 5.5 and 5.45 (d.d, 1 H, B-H, J_{AB} = 13.0, J_{BX} = 13.5 Hz), 4.1 (d, 1 H, X-H, J_{BX} = 13.5 Hz), 3.33 (q, 2 H, CH₂O, J = 7.0 Hz) 2.0 (d, 3 H, CH₃C=O, J = 1 Hz), 0.96 ppm (t, 3 H, CH₃CH₂O, J = 7.0 Hz); (Vc) 17.6 (s, 1 H, OH), 7.50 (m, 5 H, Ph), 6.67 (d, 1 H, A-H, J_{AB} = 13.0 Hz), 5.83 (d, 1 H, B-H, J_{AB} 13.0 Hz), 3.32 (], 2 H, CH₂O, J = 7.0 Hz), 1.96 [d, 3 H, CH₃C(OH)=C, J = 1.0 Hz], 0.91 ppm (t, 3 H, CH₃CH₂O, J = 70 Hz). The ratio of IVc to Vc was 20:80. IR spectrum: 2980, 1635, 1600, 1350, 1240 cm⁻¹. Mass spectrum: M⁺ 232.

Interaction of Aldehyde (I) with Acetoacetic Ester. A mixture of isomers IVb + Vb + VIb was obtained from compounds I and IIb. The yield of the mixture of isomers was 55%, bp 98-100°C (2 mm), n_D^{21} 1.4621. PMR spectrum (250 MHz, CDCl₃): (IVb) 6.25 (d, 1 H, A-H, J_{AB} = 12.5 Hz), 5.02 and 4.07 (d.d, 1 H, B-H, J_{AB} = 12.5 Hz, J_{BX} = 12.5 Hz), 3.99 (q, 2 H, CH₂OC=0, J = 7.0 Hz), 3.74 (d, i H, X-H, J_{BX} = 12.5 Hz), 3.49 (q, 2 H, CH₂O, J = 7.0 Hz), 1.0 ppm (t, 3 H, CH₃CH₂O, J = 7.0 Hz); (Vb) I3.42 (s, 1 H, OH), 6.22 (d, 1 H, A-H, J_{AB} = 12.5 Hz), 5.3 (d, 1 H, B-H, J_{AB} = 12.5 Hz, 3.97 (q, 2 H, CH₂OC=0, J = 7.0 Hz), 3.35 (q, 2 H, CH₂O, J = 7.0 Hz), 1.89 (s, 3 H, CH₃C=C), 1.15 (t, 3 H, CH₃OC=O, J = 7.0 Hz), 0.85 ppm (t, 3 H, CH₃CH₂O, J = 7.0 Hz). The PMR spectrum of isomer VIb is given in Table 1.

<u>3-Methyl-5-ethoxymethyl-4-carbethoxycyclohex-2-enone (VII)</u>. Diketone IIb (130 g: 1 mole) and piperidine (6 drops) were added to compound I (22 g: 0.25 mole) in benzene (100 ml). Compound VII (19.5 g: 0.08 mole) was obtained, yield was 32%, bp 130-131°C (2 mm), $n_D^{2^3}$ 1.4788. ¹³C NMR spectrum (250 MHz, C₆D₆): (VII) 196.6 (s, C-1), 127.6 (d, C-2), 154.99 (m, C-3), 48.84 (d, C-4), 35.7 (d, C-5), 37.51 (t, C-6), 22.33 (q, C-7), 171.21 (s, C-8), 71.45 (t, C-9), 14.5 (q, C-10), 60.71 (t, C-11), 66.07 (t, C-12), 13.74 ppm (q, C-13);

(VII₁) 197.5 (s, C-1), 128.01 (d, C-2), 155.97 (m, C-3), 48.10 (d, C-4) 35.6 (d, C-5), 37.41 (t, C-6), 22.7 (q, C-7), 169.53 (s, C-8), 71.22 (t, C-9), 14.5 (q, C-10), 60-59 (t, C-11), 66.07 (t, C-12) 13.74 ppm (q, C-13). IR spectrum: 1770, 1680, 1640 cm⁻¹, M⁺ 242.

<u>2-Methyl-5-ethoxy-3-acetyl-4,5-dihydrofuran (VIa) (Table 1).</u> Trifluoroacetic acid (0.5 ml) was added to compound Va (8.5 g: 0.05 mole) in dry CCl₄ (40 ml) and the mixture stirred at 70°C for 7 h. The course of the reaction was checked by TLC (Silufol, hexane-ether, 1:2). The reaction mixture was treated with saturated NaHCO₃ solution, the solution dried with sodium sulfate, and after distilling off the solvent the residue was distilled in vacuum in a stream of nitrogen. Dihydrofuran (VIa) (7.2 g: 0.042 mole) was obtained in 85% yield.

<u>2-Methyl-5-ethoxy-3-carbethoxy-4,5-dihydrofuran (VIb).</u> Acetic acid (4 ml) was added to the mixture (10 g: 0.05 mole) of compounds IVb-VIb in CCl₄ (40 ml). The mixture was stirred at 70°C for 2 h. After distillation dihydrofuran VIb (7.5 g: 0.038 mole) was obtained, yield was 75%.

<u>2-Methyl-5-ethoxy-3-benzoyl-4,5-dihydrofuran (VIc) and 2-Phenyl-5-ethoxy-3-acetyl-4,5-dihydrofuran (VIc_1).</u> Trifluoroacetic acid (0.5 ml) was added to a mixture (4.2 g: 0.018 mole) of compounds IVc and Vc in CCl₄ (20 ml), the reaction mixture was stirred at 70°C for 2 h, and compounds (VIc + VIc_1) (4 g: 0.017 mole) were obtained. Yield was 95%. ¹³C NMR spectrum (250 MHz, C₆D₆): (VIc) 113.88 (C-2); 166.5 (C-3); 28.86 (C-4); 105.26 (C-5); 37.83 (C-6); 127.7-130.83 (C-7); 64.33 (C-8); 15.01 (C-9); 201.2 (C-10); (VIc_1) 116.53 (C-2); 172.5 (C-3); 29.4 (C-4); 104.8 (C-5); 38.21 (C-6); 127.7-130.83 (C-7); 64.33 (C-8); 15.23 (C-9); 196.7 (C-10). IR spectrum: 3065, 1705, 1655, 1080 cm⁻¹.

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ACID-BASE PROPERTIES AND STABILITY OF PYRYLIUM POLYMETHINE

DYES IN CHLOROHYDROCARBON SOLUTIONS .

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The reactions of pyrylocyanine dyes with aqueous alcoholic alkali and with acetic acid have been studied. It has been shown that decoloration of such dyes in chlorohydrocarbon solutions only occurred under the action of alkali and was linked with the formation of an intermediate acyclic form of the dye which was the addition product of hydroxyl ion at the α position of the pyrylium ring.

It is known from [1] that cyanine dyes are inclined to decoloration in solution both under the action of acid and of alkali. The ease of carrying out the reaction leading to decoloration may serve as a practical measure of the stability of cyanine dye molecules in solution in organic solvents. Reactions of such type have not been adequately studied for pyrylium polymethine dyes in spite of the urgency connected with the wise practical application of these dyes for example as materials for quantum electronics in [2, 3].

In the present work the special features of the development of acid-base properties of pyrylocyanine dyes in chlorohydrocarbon solutions has been considered. For this purpose the behavior of pyrylium polymethine dyes has been investigated in aqueous alcoholic alkali and acetic acid using the example of 2-[7-(4,6-diphenyl-2H-pyran-2-ylidene)-4-chloro-3,5-tri-methylene-1,3,5-heptatrienyl]-4,6-diphenylpyrylium perchlorate (dye PK-15) of [4] and several of its derivatives. Methylene chloride and 1,2-dichloroethane served as solvents.

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