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OXIDATIVE CYCLIZATION OF 1,6-DIPHENYL-1,3,4,6-HEXA-NETETRONE WITH A MIXTURE OF DIMETHYL SULPHOXIDE, IOD AND SULPHURIC ACID

In order to characterize the polyoxocompounds of the type RCOCH₂COCOCH₂COR, their behaviour with different oxidative reagents was examined. Balenović and al. have carried out the oxidation of hexanetetrones by means of lead (IV) acetate and have obtained corresponding 4-hydroxypones [1,2,3]. This oxidation was also investigated by Bird and Thorley [4]. Other oxidizing agents for the oxidation of this type of compounds are: selenium(IV)oxide, which gives 2,5-diacyl-3,4-dihydroxyselenophene as reaction product [5]; dinitrogen trioxide, which yields 1,6-diaryl-2,5-bis (diazo)-1,3,4,6-tetraoxohexane [6]; and phenyliodozodiacetate which gives 2-acyl-6-alkyl(aryl)-3-hydroxy-4H-pyran-4-ones [7].

As a part of an approach to synthesis of vicynal hexaketones we have investigated the oxidation of 1,6-diphenyl-1,3,4,6-tetraoxohexane with a mixture of dimethyl sulphoxide, iodine and sulphuric acid.

By an oxidation of 1,3-diketones with a mixture of dimethyl sulphoxide and iodine in the presence of concentrate sulphuric acid the active mothylen group converts into keto-group and vicinal triketones were obtained. The mechanism of this reaction is described by Furukawa and al. [9]. By analogy, we expected vicinal polyketone to be obtained as reaction product by oxidation of 1,6-diphenyl-1,3,4,6-hexaretetrone with the same oxidative mixture. The reaction was carried out by heating of the reaction mixture on a steam bath for 8 hrs. Contrary to our expectation this reaction produced not vicinal polyketone, but two different compounds, one with m.p. 178°C as yellow needles and other with m.p. 166° as yellow prisms. Based on the results of elemental analysis and determination of molecular mass we have determined, at the moment, only the empirical formula of the product with higher m.p. (178°): C₁₈H₁₂O₄ (Mr 292.28). For the determination of its structure NMR- and IR-spectra were recorded. NMR-spectrum shows broad signal at 10.93 of protons which belongs to OH-group. The presence of OH-group was also determined by preparation of its methoxy derivative with diazomethane. IR-spectrum shows several characteristic bands: at 3190 cm⁻¹ (m) O—H stretching vibration; in the region from 3000 to 31000 cm⁻¹ several bands due to C—H stretching vibrations were observed; strong bands at 1675 and 1620 due to C = O; and another band around 750 cm⁻¹ due to C—H out of plane bonding was found.

IR-spectrum of methoxy derivative shows an absence of O—H stretching vibration. At 2930 cm⁻¹ (w) stretching vibration of C—H from O—CH₃ and deformation vibration of CH₃ from O—CH₃ at 1400 cm⁻¹; stretching vibration of C—O from C—O—CH₃ at 1222 cm⁻¹ appear. The presence of C=O group was confirmed by preparation of its 2,4-dinitrophenylhidrazone.

These results indicate that reaction product (m.p. 178°C) can be regioisomer of dehydroacetic acid which has already been obtained by oxidation of 2,6-diphenyl-1,3,4,6-hexanetetrone with PhI(OAc)₂ [7]. That oxidation product of 1,6-diphenyl-1,3,4,6-hexanetetrone obtained by our method, is identical with 2-benzoyl-6-phenyl-3-hydroxy-4H-pyran-4-one [7], was confirmed by unchanged melting point of a mixture of these two compounds and by its identical IR-spectra.

Balenović suggested that formation of dehydroacetic acid by oxidation of 1,3,4,6-hexanetetrones with lead (IV) acetate proceeds through oxidative cleavage to benzoyl keten and its dimerization [3]. Bird and al. [4] examining this reaction by deuterio-1,3,4,6-hexanetetrones with mass spectroscopy, concluded that, opposite to the above suggestion, the oxidative cyclization is an intramolecular process and may be envisaged as proceeding through the carben and keten or equivalent species as by oxidation of β -diketones with lead tetraacetate [12]. Although phenyliodosodiacetate and lead (IV) acetate are oxidative reagents with similar properties, they oxidize 1,3,4,6-hexanetetrones in a different manner. Poje [7] remarked that oxidation of above tetraketones with PhI (OAc)₂ goes not to dehydroacetic acids but to regioisomers of these acids and suggests that it proceeds with intramolecular rearrangements as by aurones [11].

We suggest that the oxidative cyclization of 1,6-diphenyl-1,3,4,6-hexanetetrone to 2-benzoyl-6-phenyl-3-hydroxy-4H-pyran-4-one by our method proceeds according to Kornblum reaction [8] through an oxidative-reduction cycle of $I_2 \div 2e^- \Rightarrow 2I^-$ in acid media in the presence of $(CH_3)_2SO$ and formation of an iodointermediate as follows:

EXPERIMENTAL

The melting points are uncorrected. IR-spectra were made on Perkin Elmer 580 spectrophotometer, NMR-spectra on Varian T-60 spectrometer, chemical shifts are given in δ-units. Mass spectra were recorded on Varian CH-7-spectrometer at 70eV, 100mA.

1,6-diphenyl-1,3,4,6-hexanetetrone was prepared according to Bröme and Claisen [10].

OXIDATION OF 1,6-DIPHENYL-1,3,4,6-HEXANETETRONE

To a solution of 4.8 g 1,6-diphenyl-1,3,4,6-hexanetetrone in 48 cm³ dimethyl sulphoxide, 0.8 g iodine and 1 cm³ concentrate sulphuric acid were added. The reaction mixture was heated on a steam bath for 8 hrs. After cooling the reaction mixture was introduced to ice water. The separated crude product was filtered off, washed with water and dissolved in methylen chloride. This solution was dried with anhydrous MgSO₄, filtered off and after evaporation of the solvent the dry residue was fractionally recrystalized from aceton. Two different kinds of crystals were obtained: yellow needles with m.p. 172°C (15% yield) and yellow prisms with m.p. 160°C (15% yield). After five recrystalizations of the first product from ethanol, the light yellow needles with m.p. 178°C were obtained.

Analysis: C₁₈H₁₂O₄ (292.28) calc.: C 73.96% H 4.13% found: C 73.50% H 3.90%

MS: m/e 292 (M+)

¹H NMR (CDl₃) δ : 6.93—8.09 (11H); 10.93 (1H of OH)

IR-spectrum (KBr) ν cm⁻¹: 3190 (m); 1675 (vs) and 1620 (vs); several

bands from 3000 to 3100 (w) and 750 (ms)

PREPARATION OF 3-METHOXYDERIVATIVE OF 2-BENZOYL-6-PHENYL-3-HYDROXY-4H-PYRAN-4-ONE

To a cold suspension of 2-benzoyl-6-phenyl-3-hydroxy-4H-pyran-4-one in methanol, the ethereal solution of diazomethane was added. The next day, the solvent was evaporated and the residue was recrystalized from ethanol. A small quantity of methoxy derivative with m.p. 144°C was obtained.

IR-spectrum ν , cm⁻¹: 2930 (w); 1222 (m) and δ : 1400 (m)

PREPARATION OF 2,4-DINITROPHENYLHYDRAZONE OF 2-BENZOYL-6-PHENYL-4H-PYRAN-4-ONE

To a hot solution of 0.5g 1,2—dinitrophenylhydrazine, 2cm³ of concentrate sulphuric acid and 15cm³ of ethanol, a hot solution of 0.5g 2-bənzoyl-6-phenyl-3-hydroxy-4H-pyran-4-one in 20cm³ ethanol was added. The reaction mixture was allowed to stay overnight. The separated precipitate was filtered off, washed with ethanol and after five recrystalizations from acetic acid-water, dark-red needles with m.p. 248°C were obtained.

Analyses: C₁₄H₁₆N₄O₇ (472.41) calc.: C 61.01% H 3.41% N 11.86% found: C 61.56% H 3,46% N 11.96%

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ОКСИДАТИВНА ЦИКЛИЗАЦИЈА НА 1,6-ДИФЕНИЛ-1,3,4,6-ХЕКСАНТЕТРОН СО СМЕСА ОД ДИМЕТИЛ СУЛФОКСИД, ЈОД И СУЛФУРНА КИСЕЛИНА

(Резиме)

Со оксидација на 1,6-дифенил-1,3,4,6-хексантетрон со смеса од диметил сулфоксид, јод и концентрирана сулфурна киселина, се добива 2-бензоил-6-фенил-3-хидрокси-4H-пиран-4-он. За идентификација на добиеното соединение се синтетизирани: 1,2-динитрофенилхидразон и метокси дериват. Предложен е и механизам на оксидативната циклизација.

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