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OXIDATIVE CYCLIZATION OF 1,6-DIPHENYL-1,3,4,6-HEXANETETRONE WITH A MIXTURE OF DIMETHYL SULPHOXIDE, IODINE AND SULPHURIC ACID

In order to characterize the polyoxocompounds of the type  $\text{RCOCH}_2\text{COCOCH}_2\text{COR}$ , their behaviour with different oxidative reagents was examined. Balenović and al. have carried out the oxidation of hexanetetrone by means of lead (IV) acetate and have obtained corresponding 4-hydroxyones [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 vicinal 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 methylene 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-hexanetetrone 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°):  $\text{C}_{18}\text{H}_{12}\text{O}_4$  (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



## 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  $\delta$ -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 cm<sup>3</sup> dimethyl sulphoxide, 0.8 g iodine and 1 cm<sup>3</sup> 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 MgSO<sub>4</sub>, filtered off and after evaporation of the solvent the dry residue was fractionally recrystallized from acetone. 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 recrystallizations of the first product from ethanol, the light yellow needles with m.p. 178°C were obtained.

Analysis: C<sub>18</sub>H<sub>12</sub>O<sub>4</sub> (292.28) calc.: C 73.96% H 4.13%  
found: C 73.50% H 3.90%

MS: m/e 292 (M<sup>+</sup>)

<sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  : 6.93—8.09 (11H); 10.93 (1H of OH)

IR-spectrum (KBr)  $\nu$  cm<sup>-1</sup>: 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 recrystallized from ethanol. A small quantity of methoxy derivative with m.p. 144°C was obtained.

IR-spectrum  $\nu$ , cm<sup>-1</sup>: 2930 (w); 1222 (m) and  $\delta$  : 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, 2cm<sup>3</sup> of concentrate sulphuric acid and 15cm<sup>3</sup> of ethanol, a hot solution of 0.5g 2-benzoyl-6-phenyl-3-hydroxy-4H-pyran-4-one in 20cm<sup>3</sup> ethanol was added. The reaction mixture was allowed to stay overnight. The separated precipitate was filtered off, washed with ethanol and after five recrystallizations from acetic acid-water, dark-red needles with m.p. 248°C were obtained.

Analyses: C<sub>14</sub>H<sub>16</sub>N<sub>4</sub>O<sub>7</sub> (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

( Р е з и м е )

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-4Н-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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