

SHORT COMMUNICATIONS

KRATKA SAOPĆENJA

A Synthesis of 1,6-Bis-(2-thienyl)-1,3,4,6-hexanetetrone. Polyoxo Compounds. VI*

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In the course of investigations of polyoxo compounds carried out at our Institute it was found necessary to prepare a sulfur-containing 1,3,4,6-tetraketone. 1,6-bis-(2-thienyl)-1,3,4,6-hexanetetrone [I] was, therefore, prepared as a representative of this series, following the procedure described by Claisen and coworkers^{1, 2} for the preparation of 1,3,4,6-tetraketones.



I.

2-Acethiothione, prepared according to Kosak and Hartough³, was condensed with diethyl oxalate giving 1,6-bis-(2-thienyl)-1,3,4,6-hexanetetrone in a 82% yield. Its quinoxaline derivative was prepared for identification purposes.

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EXPERIMENTAL***

1,6-Bis-(2-thienyl)-1,3,4,6-hexanetetrone [I]

In a round-bottomed flask containing anhydrous ether (100 ml.), and fitted with reflux condenser and calcium chloride tube, metallic sodium (4.4 g., 0.2 mole) and absolute ethanol (9.2 ml., 0.2 mole) were added. The mixture was left for twelve hours at room temperature and then cooled with ice; a solution of 2-acethiothione³ (28 g., 0.2 mole) and diethyl oxalate (14.6 g., 0.1 mole) in ether (50 ml.) was gradually added through the condenser during five minutes, with occasional shaking. After standing for two days at room temperature, the sodium salt which had separated was filtered off and triturated with a mixture of ice and 10% hydrochloric acid. The crude 1,6-bis-(2-thienyl)-1,3,4,6-hexanetetrone (25.1 g., 82%) was recrystallized from ethyl acetate. Pale yellow leaflets, m. p. 200–201° were obtained.

Anal. 8.210 mg. subst.: 16.45 mg. CO₂, 2.55 mg. H₂O
 C₁₄H₁₀O₄S₂ (306.20) calc'd: C 54.87; H 3.29%
 found: C 54.68; H 3.48%

The quinoxaline derivative was prepared by heating a solution of equimolar quantities of 1,6-bis-(2-thienyl)-1,3,4,6-hexanetetrone and o-phenylene diamine in

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*** The melting points are uncorrected.

glacial acetic acid on a water bath for three hours. Recrystallization from acetic anhydride gave red needles, m. p. 247°.

Anal. 9.390 mg. subst.: 21.92 mg. CO₂, 3.25 mg. H₂O
C₂₀H₁₄N₂O₂S₂ (378.25) calc'd: C 63.45; H 3.73%
found: C 63.70; H 3.87%

REFERENCES

1. E. Brömme and L. Claisen, *Ber.* **21** (1888) 1134.
2. L. Claisen and N. Stylos, *Ber.* **21** (1888) 1141.
3. A. I. Kosak and H. D. Hartough, *Org. Syntheses* **28** (1948) 1.

IZVOD

Sinteza 1,6-di-(2-tienil)-1,3,4,6-heksantetrona.**Prilog poznavanju polioksa spojeva. VI***

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Kondenzacijom 2-acetotienona s dietiloksalatom priređen je u 82% iskorištenju 1,6 bis-(2-tienil)-1,3,4,6-heksantetron, t. t. 200—201°, i karakteriziran je kao kinoksalinski derivat.

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