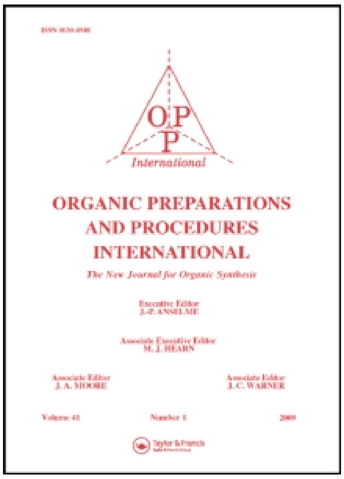


Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

THE PREPARATION OF γ-THIOPYRAN

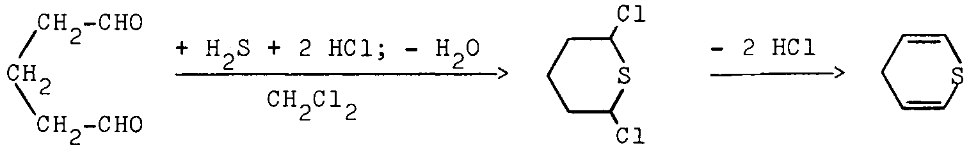
J. Strating[a]; E. Molenaar[a]
[a] Department of Organic Chemistry, The University, Groningen, The Netherlands

To cite this Article Strating, J. and Molenaar, E.(1969) 'THE PREPARATION OF γ-THIOPYRAN', Organic Preparations and Procedures International, 1: 1, 21 — 23
To link to this Article: DOI: 10.1080/00304946909458341
URL: http://dx.doi.org/10.1080/00304946909458341

ORGANIC PREPARATIONS AND PROCEDURES 1(1), 21-23 (1969)

THE PREPARATION OF γ-THIOPYRAN

J. Strating and E. Molenaar
Department of Organic Chemistry, The University
Bloemsingel 10, Groningen, The Netherlands



In a communication by Strating, Keijer, Molenaar and Brandsma[1] the preparation of γ-pyran and γ-thiopyran was announced briefly. Whereas the detailed procedure for the synthesis of 4 H-pyran (γ-pyran) has been given[2], the experimental details of the synthesis of 4 H-thiopyran (γ-thiopyran) are only reported in the thesis of E. Molenaar[3].

EXPERIMENTAL

To 500 ml of dichloromethane, cooled to -70°, 100 g (1.0 mole) of glutaric dialdehyde, obtained by heating the polymer[*] to about 110°[**], was added. A mixture of gaseous HCl and H_2S in the ratio of about 2:1[***] was passed in the above stirred solution. The temperature of the reaction mixture was kept between -30 and -25° by means of a dry ice acetone bath. After about 3 hours, the introduction of gas was stopped and the temperature of the reaction mixture raised to -15° by removing the bath after which, without stirring, the mixture was cooled slowly to -70°. The crystals of ice were removed by filtration and washed with cold dichloromethane (-70°). The filtrate was stirred with powdered calcium chloride until room temperature was reached and then filtered through a fluted filter paper. The solution was evaporated under reduced pressure (the receiver was cooled to -80°). The residue (which may contain some solvent) was gradually heated to 135° together with 300 g (2.0 mole) of N,N-diethylaniline. The entire operation was carried out with stirring <u>in a nitrogen atmosphere</u>[**]. After the mixture had been cooled to 100°, the crude reaction product was removed by distillation under reduced pressure (receiver cooled to -80°). The liquid boiling from 40-80°/16 mm was collected. Redistillation through a Widmer column gave γ-thiopyran with a purity of 98% (determined by GLC, Reoplex on Chromosorb W.A.W., temp. 100°, He flow 50 ml/min.). The boiling point of this product was 30°/12 mm, the melting point -28°, n_D^{20} 1.5623. The yield varied from 20-45%. γ-Thiopyran is a colorless, clear liquid with a penetrating odor; at room temperature and in contact with air it decomposes rapidly. In the solid state it can be stored for a long time.

IR spectrum (liquid film; Leitz spectrophotometer): 3100 cm^{-1} (= CH), 2940 and 2880 cm^{-1} (- CH_2-), 1640 cm^{-1} (C=C), 1600 cm^{-1} (C=C-S ?), 1450 and 1360 cm^{-1} (CH_2 def.) and 750 cm^{-1} (C-S ?). Unidentified peaks: 1320 cm^{-1} (s), 1040 cm^{-1} (m), 1000 cm^{-1} (m), 980 cm^{-1} (s), 930 cm^{-1} (m) and 850 cm^{-1} (broad, s).

UV spectrum (petroleum ether solution; Beckmann DK 2 spectrophotometer): maximum at 278 mμ (ε = 2430, log ε = 3.34) and a shoulder at 236 - 238 mμ (ε = 5270, log ε = 3.72).

PMR spectrum (in CCl_4 at -40°): S-C$\underline{H}$=C (τ 4.1 , very complex), S-C=C$\underline{H}$ (τ 4.5, very complex) and - C$\underline{H}_2$- (triplet with J = 4 cps; each peak consists of a triplet with J = 1 cps, τ = 7.15); integration ratio 1:1:1.

Analysis:	Found:	C 61.5, 61.4;	H 6.3, 6.3;	S 32.8, 32.7.
C_5H_6S (98.16)	Calc.:	C 61.17 ;	H 6.16 ;	S 32.67.

REFERENCES

1) J. Strating, J. H. Keijer, E. Molenaar and L. Brandsma, Angew. Chem., Intern. Ed. I, 399 (1962).

2) Houben Weyl, "Methoden der Organischen Chemie", VI/4, p. 108, 1966.

3) E. Molenaar, Thesis Groningen, 1967.

* By distilling a commercially available 25-30% solution of glutaric dialdehyde in water, through a 30 cm Widmer column, water is removed at 25°/15 mm. After the removal of water, glutaric dialdehyde distills at 76°/12 mm. At room temperature even when kept under nitrogen, it polymerises rapidly to a syrupy mass.
Depolymerisation of the glutaric dialdehyde polymer is effected by heating it. When the temperature reaches approximately 85°, depolymerisation appears to be complete and the temperature which previously increased slowly, now rises rapidly. Heating is discontinued at about 110°. The liquid may then be used without distillation.

** The underlined parts are particularly important for obtaining the yields mentioned.

*** The approximate ratio of 2:1 was obtained by comparing the velocity of bubbling through two washing flasks each filled with the same quantity of paraffin oil.

(Received June 21, 1968)