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THE PREPARATION OF γ -THIOPYRAN

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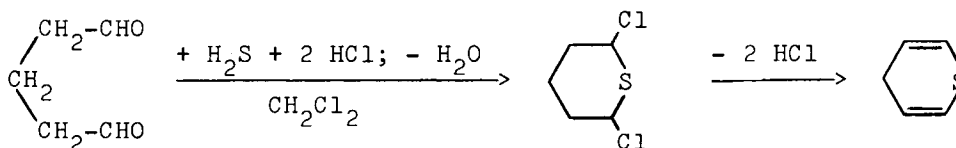
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THE PREPARATION OF γ -THIOPYRAN

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In a communication by Strating, Keijer, Molenaar and Brandsma¹ 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 given², the experimental details of the synthesis of 4 H-thiopyran (γ -thiopyran) are only reported in the thesis of E. Molenaar³.

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

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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 in a nitrogen atmosphere **. 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 $40-80^{\circ}/16$ 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 $30^{\circ}/12$ 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} ($-\text{CH}_2-$), 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).

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

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

Analysis: Found: C 61.5, 61.4; H 6.3, 6.3; S 32.8, 32.7.
 $\text{C}_5\text{H}_6\text{S}$ (98.16) Calc.: C 61.17 ; H 6.16 ; S 32.67.

REFERENCES

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* By distilling a commercially available 25-30% solution of glutaric dialdehyde in water, through a 30 cm Widmer column, water is removed at $25^\circ/15$ mm. After the removal of water, glutaric dialdehyde distills at $76^\circ/12$ 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.

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