

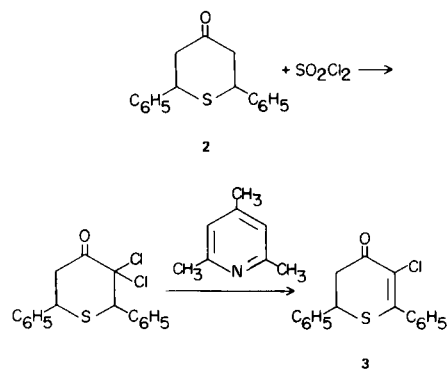
3-Chloro-2,6-diphenyl-5,6-dihydro-4*H*-thiopyran-4-one

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Although the yield is poor (15-20%), probably the best synthesis of 2,6-diphenyl-4*H*-thiopyran-4-one (**1**) is by reaction of the corresponding tetrahydro derivative (**2**) with phosphorus pentachloride followed by treatment with base to give **1** along with an approximately equal amount of 3-chloro-2,6-diphenyl-4*H*-thiopyran-4-one (**1**). In an attempt to improve this synthesis, we have investigated the reaction of **2** with sulfuryl chloride followed by treatment with 2,4,6-trimethylpyridine. The only product that was isolated differed from **2** in empirical formula by the addition of a chlorine atom and loss of hydrogen. On the basis of the mass spectral cracking pattern and the nmr spectra, which are described in the experimental section, the product was assigned structure **3** and was probably formed by the following reaction sequence:



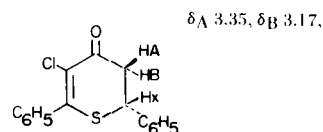
EXPERIMENTAL

To a solution of 27 g. (0.1 mole) of **2** (**1**) in 75 ml. of carbon tetrachloride was added 30 g. of sulfuryl chloride over a 0.5-hour period. There was an immediate reaction with copious evolution of gases. When the reaction had subsided, the mixture was heated on a steam bath causing more hydrogen chloride to be evolved.

During the heating, the solvent was allowed to evaporate. To the residue was added 100 g. of 2,4,6-trimethylpyridine, and the solution was refluxed for 3 hours. The cooled solution was poured into a large excess of dilute hydrochloric acid and the liquid was decanted from the gum. The gum was dissolved in ether, the solution dried (magnesium sulfate), and the solvent removed. The residue was dissolved in hot ethyl acetate, the solution was diluted with hexane, and the turbid solution was chilled giving 17 g. (57% yield) of solid **3**, m.p. 100-103°. The ir spectrum shows a strong absorption at 6 μ .

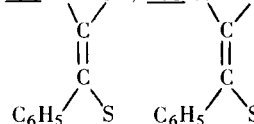
Anal. Calcd. for $C_{17}H_{13}ClOS$: C, 67.9; H, 4.4; S, 10.7. Found: C, 68.0; H, 4.3; S, 10.8.

The following data were obtained from the nmr (deuteriochloroform) by a computer program:



δ_x 4.77 ppm: $|J_{AB}|$ 16.4, $|J_{AX}|$ 14.2, and $|J_{BX}|$ 3.2 Hz.

The mass spectral cracking pattern (principal peaks underlined) showed: m/e 300 M^+ ; 283 M-OH; 265 M-Cl; 237 m/e 265-CO; 223 M-C₆H₅; 196 Cl CO; 168 Cl C; 134; 133.



Acknowledgments.

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REFERENCES

(1) F. Arndt, P. Nachtwey, and J. Pusch, *Chem. Ber.*, **58**, 1633 (1925).