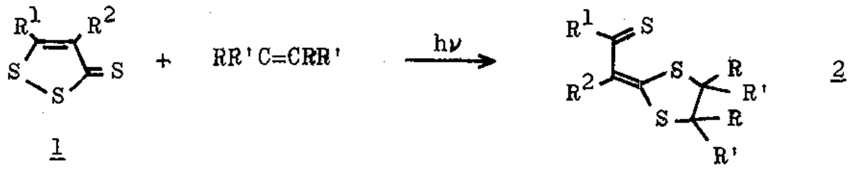
HETEROCYCLES. Vol. 6, No. 3. 1977

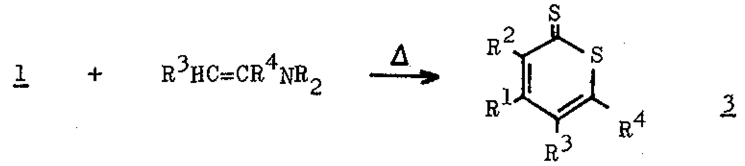
REACTION OF 1,3-DITHIOLE-2-THIONES WITH ENAMINES. FORMATION OF 1,3-DITHIONIN-2-THIONE, A NOVEL HETEROCYCLE

Fumio Ishii, Renji Okazaki, and Naoki Inamoto*
Department of Chemistry, Faculty of Science,
The University of Tokyo, Hongo, Tokyo 113, Japan

Reaction of 4-phenyl- (4a) and 4,5-diphenyl-1,3-dithiole-2-thione (4b) with 1-pyrrolidinocyclopentene gave 1,3-dithionin-2-thiones (5a,b), novel heterocycles, while reaction of 4a with 1-pyrrolidinocyclohexene afforded thiophene (7).

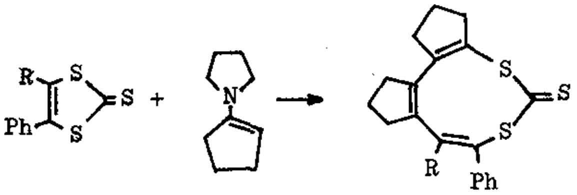
We have previously reported the photochemical reaction of 1,2-dithiole-3-thiones (1) with olefins giving thioacylketene thioacetal (2)[1] and one of us (F.I.) has disclosed the reaction of 1 with enamines leading to thiopyran-2-thiones (3).[2]





In connection with these studies, we became interested in the reaction of enamines with 1,3-dithiole-2-thione (4), the isomer of 1.[3] We wish to report here its preliminary results.

The reactions of 4-phenyl- (4a) and 4,5-diphenyl-1,3-dithiole-2-thione (4b) with excess 1-pyrrolidinocyclopentene (in refluxing acetonitrile, 2 hr, under nitrogen) led to the formation of 1,3-dithionin-2-thiones (5a) and (5b) in 17 and 27% yields, respectively. The structure of 5 was determined by spectral[4] and analytical data and Raney nickel desulfurization of 5a giving compound 6. Similar UV spectra of 5a and 5b[4] suggest that both have the same conjugated system.

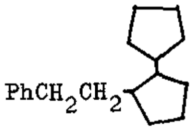


4a: R=H

4b: R=Ph

5a: R=H

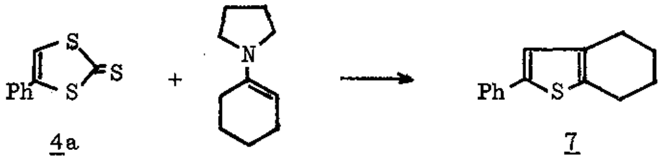
5b: R=Ph



6

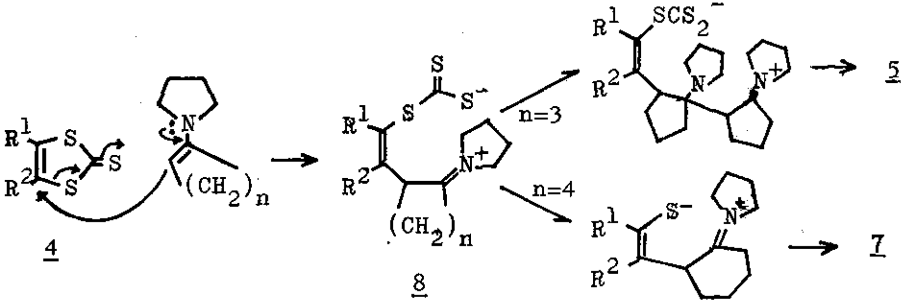
The 1,3-dithionin-2-thione here obtained is a novel heterocycle with 10π electrons in the ring and its chemistry would be an intriguing subject in view of the recent interest in 1,3-dithiole-2-thione associated with highly conductive organic charge transfer complex (TTF-TCNQ).[5]

In contrast with the reaction with 1-pyrrolidinocyclopentene, the reaction of 4a with 1-pyrrolidinocyclohexene afforded thiophene (7) in 20% yield.



The structure of 7 was established by comparison of the spectral data and melting point with reported values.[6]

The formation of 5 and 7 is considered to be explained by nucleophilic attack of an enamine at the position 4 (or 5) of 4 as depicted below.



A second enamine attacks a zwitterion (8) in the case of more reactive pyrrolidinocyclopentene, while 8 loses carbon disulfide in the case of less reactive pyrrolidinocyclohexene. These reactions are, to the best of our knowledge, the first example of nucleophilic attack at the position 4 (or 5) of 1,3-dithiole-2-thiones.

References and Notes

1) R. Okazaki, K. Okawa, and N. Inamoto, Chem. Comm., 1971, 843;

R. Okazaki, F. Ishii, K. Ozawa, and N. Inamoto, Chem. Lett., 1972, 9; R. Okazaki, F. Ishii, K. Okawa, K. Ozawa, and N. Inamoto, J. Chem. Soc. Perkin I, 1975, 270.

2) F. Ishii, M. Stavaux, and N. Lozac'h, Tetrahedron Lett., 1975, 1473.

3) 1,3-Dithiole-2-thione, unlike 1, does not undergo photoaddition to olefins.[1] The reaction of enamines with 2, the photoproduct from 1 and an olefin, has recently been reported. F. Ishii, R. Okazaki, and N. Inamoto, Tetrahedron Lett., 1976, 4283.

4) 5a: m.p. 152-153°C; NMR ($CDCl_3$) δ 1.52-1.97(m, 4H), 2.08-2.48 (m, 2H), 2.70-3.30(m, 6H), 6.98(d, J=3Hz, 1H), and 7.22-7.76 (m,5H); UV (n-hexane) λ_{max}(nm) (ε) 242(15800), 273(10700), 365(9400), 382(8600), 475(16300), and 499(29100); MS m/e(%) 342(M^+, 100). 5b: m.p. 180-181°C; NMR ($CDCl_3$) δ 1.50-1.97 (m, 4H), 2.13-2.52(m, 2H), 2.83-3.35(m, 6H), and 7.35(s, 10H); UV (n-hexane) λ_{max}(nm) (ε) 228(27900), 281(14900), 365(14600), 380(13700), 480(21100), and 505(37400); MS m/e(%) 418(M^+, 44).

5) J.P. Ferraris, D.O. Cowan, V. Walatka, Jr., and J.H. Perlstein, J. Am. Chem. Soc., 95, 948 (1973); L.B. Coleman, M.J. Cohen, D.J. Sandman, F.G. Yamagishi, A.F. Garito, and A.J. Heeger, Solid State Commun., 12, 1125 (1973); A.F. Garito and A.J. Heeger, Acc. Chem. Res., 7, 232 (1974).

6) W.D. Trieu and S. Hauptmann, Z. Chem., 13, 57 (1973).

Received, 10th January, 1977