Photochemical Reactions of Cyclic Sulphides

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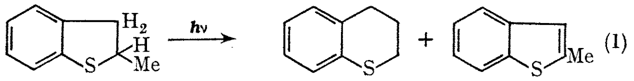
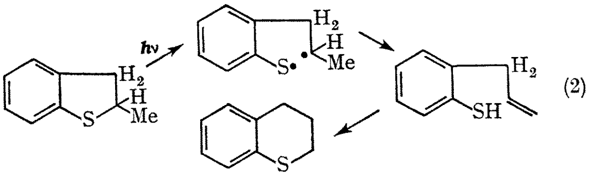
Summary Photochemical rearrangement and disproportiontion reactions of dihydrobenzo[*b*]thiophens and their derivatives are reported.

REPORTS on the photochemistry of cyclic keto-sulphides and their derivatives have included demonstrations that ring-contracted and ring-expanded products are observed.[1] In view of our interest in the chemistry of benzo[*b*]thiophens[2] as well as current interest in thermal rearrangements in these systems,[3] we have investigated the photochemistry of certain benzo[*b*]thiophen and dihydrobenzo[*b*]thiophen derivatives.[4]

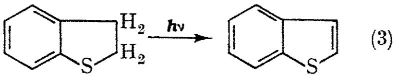
Irradiation (450 w mercury lamp, Pyrex test tubes, 0·01 M solution in benzene or heptane) of 2-methyldihydrobenzo[*b*]thiophen gave thiochroman as the major reaction product (Equation 1). The extent of conversion depended only slightly on degassing the sample, a far more crucial variable being the initial concentration of the dihydrobenzo[*b*]thiophen.[5] † The thiochroman product could be isolated using preparative g.l.c. A second product from the reaction, 2-methylbenzo[*b*]thiophen, appeared in minor amounts in hydrocarbon solvents, but could be an important product in chlorinated solvents. This product doubtless arises from disproportionation of the radical at the 2-position.



The most reasonable explanation for the formation of thiochroman from 2-methyldihydrobenzo[*b*]thiophen involves ring opening at the sulphur–C-2 bond, followed by abstraction from the methyl group and reclosure on the olefin double bond of the thiophenol, (Equation 2).



The generality of photochemical reactions of dihydrobenzo[*b*]thiophen systems is illustrated by the conversion of dihydrobenzo[*b*]thiophen itself to benzo[*b*]thiophen even in hydrocarbon solvents (Equation 3). As in the case of the 2-methyl derivative, conversion was facilitated by conducting the reaction in solvents which themselves could produce radicals ($CHCl_3$, CCl_4)(Table).



Solvent effects on the yield of benzo[b]*thiophen from* 2,3-*dihydrobenzo*[b]*thiophen*

Solvent	Yield of Benzo[*b*]thiophen
CCl_4	50—55%
$CHCl_3$	40—45%
Cumene	40—45%
Benzene	20—25%
Heptane	20%

We thank the Eli Lilly Corporation, the American Cancer Society, and the National Science Foundation (URP) for support, and the Holland Suco Chemical Company, a division of Chemetron Corporation, for a gift which allowed the purchase of the n.m.r. spectrometer used in these studies.

(*Received, May* 14*th,* 1969; *Com.* 679.)

† Conversion stopped with 15% 2-methyldihydrobenzo[*b*]thiophen remaining, because of the formation of coloured side-products.

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[2] G. Van Zyl, C. J. Bredeweg, R. R. Rynbrandt, and D. C. Neckers, *Canad. J. Chem.*, 1966, **44**, 2283.

[3] C. Y. Meyers, C. Rinaldi, and L. Bonoli, *J. Org. Chem.*, **1963, 28**, 2440; H. Kwart and C. M. Hackett, *J. Amer. Chem. Soc.*, 1962, **84**, 1754.

[4] For earlier studies on the photochemistry of benzo[*b*]thiophen, see W. E. Haines, R. V. Helm, G. L. Cook, and J. S. Ball, *J. Phys. Chem.*, 1956, **60**, 549; W. E. Haines, G. L. Cook, and J. S. Ball, *J. Amer. Chem. Soc.*, 1956, **78**, 5213.

[5] 2-Methyldihydrobenzo[*b*]thiophen was prepared by methods reported earlier; see E. N. Karavlova, D. Sh. Meilanova and G. D. Gal'pern, *Doklady Akad. Nauk. S.S.S.R.*, 1958, **123**, 99.