A Novel Rearrangement of a Benzo[*b*]thiepin Derivative[1]

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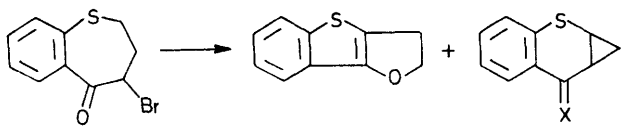
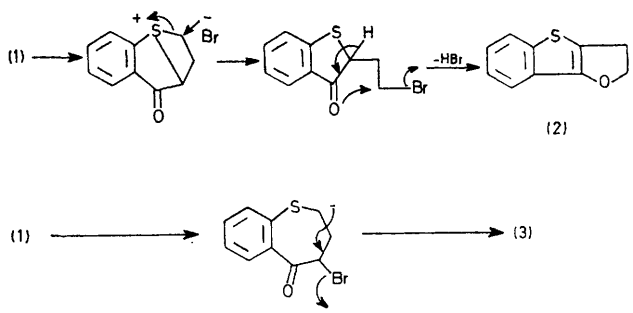
Summary The unexpected transformation of 4-bromo-2,3-dihydrobenzo[*b*]thiepin-5(4*H*)-one (**1**) into 2,3-dihydro-[1]benzothieno[3,2-*b*]furan (**2**) and 1,1a,7,7a-tetrahydrobenzo[*b*]cyclopropa[*e*]thiopyran-7-one (**3**) is reported.

THE recent report[2] on the ring contraction of 4-bromo-2,3,4,5-tetrahydrobenzo[*b*]thiepin-5-ol to 2-(2-bromoethyl)-benzo[*b*]thiophen prompts us to report our preliminary work



(1) (2) (3) X = O (4) X = H,OH

on a novel rearrangement of the thiepinone (**1**). It was recently reported that identifiable products could not be isolated from the reaction of (**1**) with a wide variety of bases.[3] In our hands, reactions of (**1**) with LiBr–Li_2CO_3 in refluxing $HCONMe_2$ gave two crystalline compounds which we have identified as (**2**) (m.p. 58—60 °C; 15% yield) and (**3**) (m.p. 70—71 °C; 1%) on the basis of their elemental and spectral analyses.† Compound (**2**) was recovered unchanged from attempted reduction with $LiAlH_4$, whereas compound (**3**) gave the alcohol (**4**), m.p. 93—94 °C, with $LiAlH_4$.



SCHEME

We rationalize the formation of (**2**) as shown in the Scheme. A similar mechanism was proposed in ref. 2. We postulate that (**3**) is formed by anion formation α to the sulphur with subsequent intramolecular displacement of Br^-.

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† All new compounds gave analytical figures for C, H, and S to within ±0·20% of theory; spectral data, compound (**2**): δ ($CDCl_3$) 3·27 and 5·00 (each 2H, t, *J* 8·5 Hz, 2- and 3-H, respectively), and 7·13—7·83 (4H, ArH); ν_{max} (KBr) 1590, 1450, 755, and 730 cm^{-1}; λ_{max} (EtOH) 210, 251, 304, and 313 nm; *m/e* 176 (M^+, 100%), 147 (74%), and 115 (30%); the peak at *m/e* 144 (M^+ − S) was of <5% intensity; compound (**3**): δ($CDCl_3$) 1·25—1·62 (2H, m, 1-H), 1·68—1·98 (2H, m, 1a- and 7a-H), and 7·02—7·62 and 7·68—7·92 (each 2H, m, ArH); ν_{max} (KBr) 1695, 1000, 1455, 1310, 910, and 655 cm^{-1}; *m/e* 176 (M^+, 100%), 147 (82%), 136 (17%), 115 (30%), and 108 (21%).

[1] For previous paper in the series: Heterocycles, see P. M. Weintraub, *J. Medicin. Chem.*, 1972, **15**, 419.
[2] A. Chatterjee and B. K. Sen, *J.C.S. Chem. Comm.*, 1974, 626.
[3] V. S. Traynelis, J. C. Sih, and D. M. Borgnaes, *J. Org. Chem.*, 1973, **38**, 2629.