Ring Contraction of a Benzo[*b*]thiepin Derivative to a Benzo[*b*]thiophen

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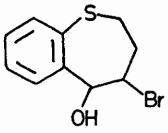
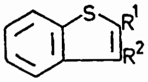
Summary The transformation of the benzo(*b*]thiepin *cis*-bromohydrin (I) into the benzo[*b*]thiophen derivative (IIb) through ring contraction is reported.

IN view of the recent interest[1] in benzo[*b*]thiophens and the related acid-catalysed ring contraction[2] of 2,2,4-trimethyl-2*H*-thiochromen to compound (IIa), we report our results on the ring contraction of the *cis*-bromohydrin (I) to the benzo[*b*]thiophen (IIb).



(I)

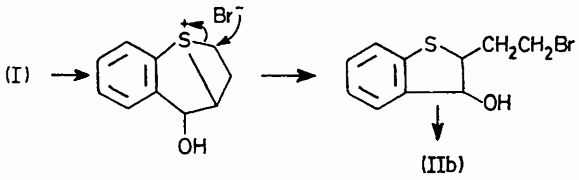


(II)

a; $R^1 = Pr^i, R^2 = Me$
b; $R^1 = CH_2CH_2Br, R^2 = H$
c; $R^1 = CH_2CH_2CN, R^2 = H$
d; $R^1 = CH_2CH_2CO_2H, R^2 = H$

$NaBH_4$ reduction by the literature method[3] of 4-bromo-2,3,4,5-tetrahydrobenzo[*b*]thiepin-5-one[4] in refluxing EtOH gave a mixture of products, but compound (I), m.p. 88—91°, could be isolated in 60% yield if the above reduction was carried out under controlled conditions. Refluxing a solution of the bromohydrin (I) in dioxan for 15 h afforded the thiophen† (IIb), m.p. 45—47° in nearly quantitative yield. Attempted dehydration of (I) with $KHSO_4$ *in vacuo* also provided (IIb) in comparable yield. Compound (IIb) on heating with KCN in wet dimethylformamide gave the nitrile (IIc), m.p. 58—59°, and this on saponification furnished in excellent yield the known[5] acid (IId), m.p. 134—135°.

A similar ring contraction of thiochroman derivatives has been reported[6] to give benzo[*b*]thiophens. We suggest the mechanism in the Scheme for the smooth transformation of (I) into (IIb).



SCHEME

As far as we know, this is the first report of ring contraction of a benzo[*b*]thiepin derivative.

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† All compounds described herein provided expected elemental analysis and spectral data.

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