

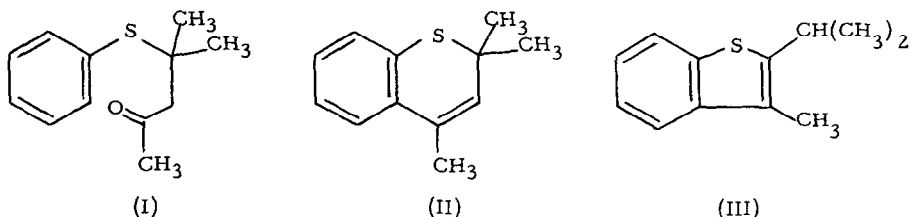
NOVEL RING CONTRACTION LEADING TO THE BENZO[B]THIOPHENE NUCLEUS

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Current interest in the chemistry of benzo[b]thiophenes¹ prompts us to report the discovery of an acid-catalysed rearrangement leading to the formation of this ring system. While attempting to bring about the cyclodehydration of the ketosulphide (I) to produce (II) employing polyphosphoric acid (PPA) as described in a literature method,^{2, 3} we have found in repeated experiments that the major volatile product (ca. 20%) is in fact an isomer formulated



as (III), although some (II), the only reported^{2, 3} product, is also formed (ratio (III):(II) ca. 6:1 for reaction bath temperature of 100°C). The structure of (III) was deduced spectroscopically: NMR (CDCl₃) τ , 8.68 (6H, doublet, J = 7Hz), 7.73 (3H, singlet), 6.63 (1H, heptuplet, J = 7Hz), ca. 2.2-3.1 (4H, ABCD spin system); and confirmed by unambiguous synthesis.

A variation in the product ratio (III):(II) with temperature is observed, (III) being favoured by temperatures higher than 100°C and (II) by lower temperatures, suggesting that (II) might be capable of rearranging to (III) under the reaction conditions. Accordingly, a sample of pure (II), isolated by gel permeation chromatography (200 x 2.5 cm column of Sephadex LH-20 modified⁴ with Nedox 1114, elution with methanol), was subjected to PPA at 100°C for 3 hr and indeed was found to undergo transformation into (III) in moderate yield, the remainder being mainly unrearranged (II).

