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A NOVEL RING CONTRACTION OF 4-BROMO-2,3-DIHYDROBENZO-[b]THIEPIN-5(4H)-ONE

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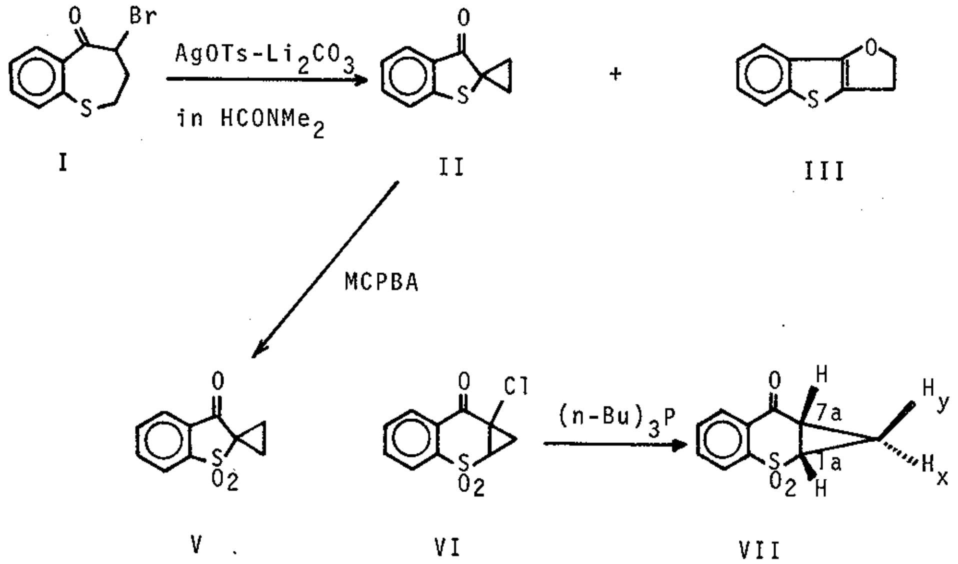
The unexpected ring contraction of 4-bromo-2,3-dihydrobenzo[b]thiepin-5(4H)-one (I) to 3-oxo-2,3-dihydro[1]benzothiophen-2-spirocyclopropane (II) besides 2,3-dihydro[1]benzothieno[3,2-b]furan (III) is reported.

Recently, much attention has been directed toward the chemistry of benzothiepins.[1] The first report on the ring contraction of 4-bromo-2,3,4,5-tetrahydrobenzo[b]thiepin-5-ol to 2-(2-bromoethyl)benzo[b]thiophen has been described by Chatterjee et al. in 1974.[2] We now wish to report an other but totally different example of ring contraction reaction of 4-bromo-2,3-dihydrobenzo-[b]thiepin-5(4H)-one (I) to 3-oxo-2,3-dihydro[1]benzothiophen-2-spirocyclopropane (II) and 2,3-dihydro[1]benzothieno[3,2-b]furan (III) which was found during our work on thiaazulenes.[3]

The reaction of I (0.5 g) with 2 molar equiv of AgOTs-Li_2CO_3 in refluxed dry $HCONMe_2$ for 12 hr gave two crystalline compounds, which were separated by preparative thin-layer chromatography on silica-gel (Wakogel B-10) using a mixed benzene- n-hexane (1 : 3) solvent, II as colorless prisms in 24 % yield, mp 70° from CH_2Cl_2- n-hexane, and III as colorless prisms in 6 % yield, mp 59-60° from n-hexane (lit.[4] mp 58-60°). The structure assignment of II is based on the following spectral data : nmr ($CDCl_3$) δ 1.25-1.98 (4H, m, A_2B_2, $C_{2'}$-H, $C_{3'}$-H), 7.02-7.62, and 7.68-7.92 (each 2H, m, ArH); ir ν max (KBr) 1690, 1590, 1450, 1320, 1080, 970, and 735 cm^{-1}. And II was also chemically confirmed by oxi-

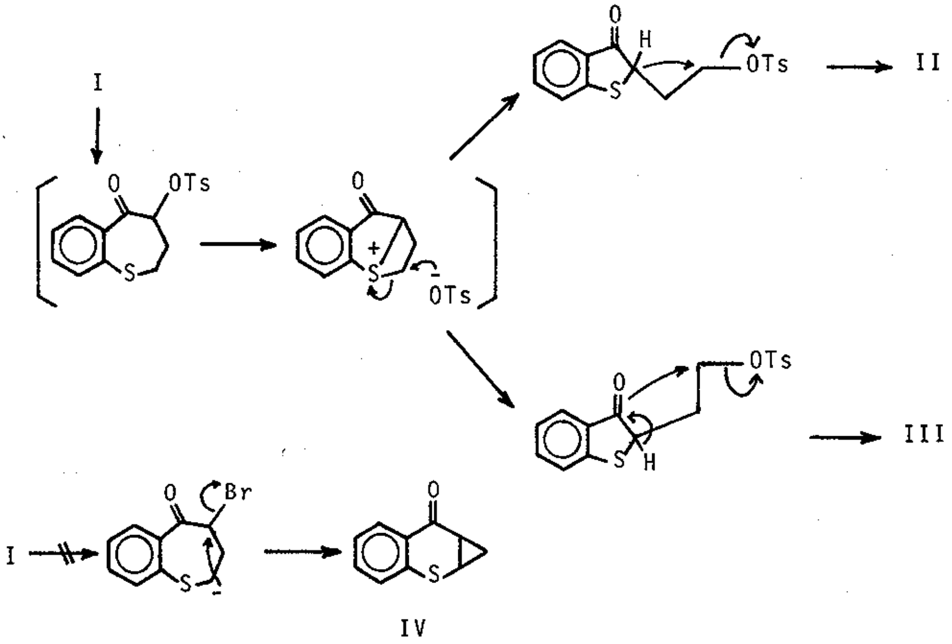


dation using m-chloroperbenzoic acid (MCPBA) to afford 3-oxo-2,3-dihydro[1]benzothiophen-2-spirocyclopropane 1,1-dioxide (V) as colorless prisms in 92 % yield, mp 202° from CH_2Cl_2- n-hexane : nmr ($CDCl_3$) δ 1.70-2.21 (4H, m, A_2B_2, $C_{2'}$-H, $C_{3'}$-H) and 7.60-8.19 (4H, m, ArH); ir ν max (KBr) 1720, 1590, 1460, 1350, 1150, and 990 cm^{-1}.

Quite recently, a similar reaction[4] between I and LiBr-Li_2CO_3 in the refluxing $HCONMe_2$ was reported to give III in 15 % yield and 1,1a,7,7a-tetrahydrobenzo[b]cyclopropa[e]thiopyran-7-one (IV) in 1 % yield. Interestingly, the data on II are in good accord with those of IV. However, our compound, V is apparently different in both their nmr and ir spectra from 1,1a,7,7a-tetrahydrobenzo[b]cyclopropa[e]thiopyran-7-one 2,2-dioxide (VII) which is colorless oil, bp_2 120° and was prepared in 48 % yield by reduction of 7a-chloro-1,1a,7-trihydrobenzo[b]cyclopropa[a]thiopyran-7-one 2,2-dioxide (VI)[5] with $(n\text{-}Bu)_3P$. VII : nmr ($CDCl_3$) δ 1.66 (1H, q, $J_{C_{1x}-C_{7a}} = J_{C_{1x}-C_{1a}} = 7$ Hz, C_1-H_x), 1.94 (1H, d.t, $J_{C_{1y}-C_{7a}} = 8$ Hz, $J_{C_{1y}-C_{1a}} = J_{C_{1y}-C_{1x}} = 7$ Hz, C_1-H_y), 2.82 (1H, d.t, $J_{C_{7a}-C_{1y}} = J_{C_{7a}-C_{1a}} = 8$ Hz, $J_{C_{7a}-C_{1x}} = 7$ Hz, C_{7a}-H), 3.42 (1H, d.q, $J_{C_{1a}-C_{7a}} = 8$ Hz, $J_{C_{1a}-C_{1x}} = J_{C_{1a}-C_{1y}} = 7$ Hz, C_{1a}-H), and 7.69-8.12 (4H, m, ArH); ir ν max (film) 1690, 1600, 1450, 1320, 1150, 970, and 870 cm^{-1}.[6]

Thus, we propose the following mechanism (Scheme I) for the transformation of I into II and III.[2]

Further related studies directed toward the applications to other ring systems are also in progress.



Scheme I

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6 All new compounds had satisfactory analytical data to support the assignment.

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