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A NOVEL REARRANGEMENT OF CYCLOPENTA[b]THIOPYRANS TO 2-FORMYLCYCLOPENTA[b]THIOPHEN-4-ONES

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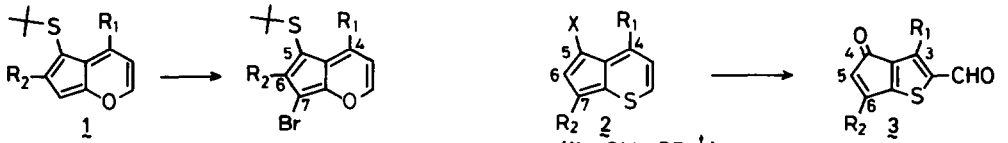
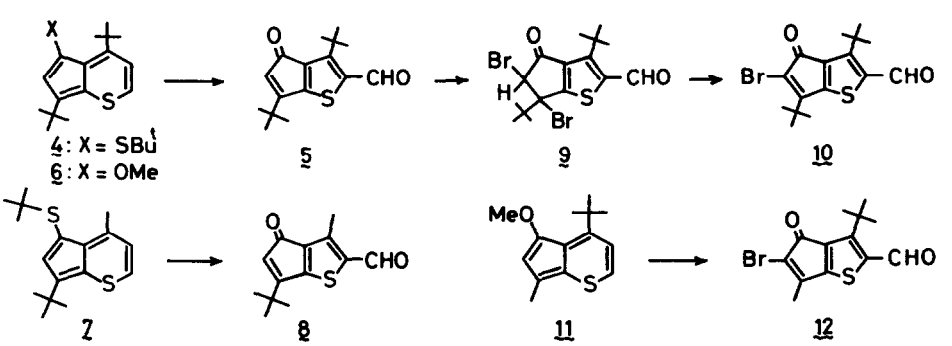
Summary: Substituted cyclopenta[b]thiopyrans afford 2-formylcyclopenta[b]thiophen-4-ones by the action of bromine. The mechanism of this novel rearrangement was discussed.

Recently we have reported the acid-catalyzed transformation of octadienyne-dial derivatives to cyclopenta[b]pyrans (1) and cyclopenta[b]thiopyrans (2).[1)-3)] Bromination of 4,6-dimethyl-5-*t*-butylthiocyclopenta[b]pyran (1, R_1=R_2=Me) gave 7-bromo derivative as a sole product in similar manner as reported by Boyd and Clark.[4)] However, bromination of 2, in which the reactive 5- and 7-positions are substituted, caused rearrangement of 2 to 2-formylcyclopenta[b]thiophen-4-one (3).[5)]



4,7-Di-*t*-butylthiocyclopenta[b]thiopyran (4) was allowed to react with 2eq. Br_2[6)] in CH_2Cl_2 and the reaction mixture was treated with an aqueous sodium hydrogencarbonate solution. After chromatography on silica gel 3,6-di-*t*-butyl-2-formylcyclopenta[b]thiophen-4-one (5) was obtained as orange prisms (58%). The reaction of 6 with Br_2 gave also 5 (31%) and similar treatment of 7 afforded 8 (20%). Bromination of 5 gave dibromide (9) in 75% yield, which was dehydrobrominated on chromatography on alumina. 5-Bromo-3,6-di-*t*-butyl-2-formylcyclopenta[b]thiophen-4-one (10) was obtained as red prisms (79%). The reaction of 11 with Br_2 gave directly the 5-bromocyclopenta[b]thiophen-4-one (12) in 32% yield.

When the reaction mixture of 4 and Br_2 in CH_2Cl_2 was treated with an aqueuos sodium thiosulfate solution, 4 was recovered quantitatively (99%). ^{1}H NMR[7)] and UV spectra of the solution obtained from 4 and Br_2 showed clearly the formation of the cyclopenta[b]thiopyrylium ion [13], ^{1}H NMR (CD_2Cl_2, 0°C): δ 10.04 d, J=9.0 (H_2), 8.98 d, J=9.0 (H_3), 7.50 s (H_6), 1.79 s, 1.36 s,



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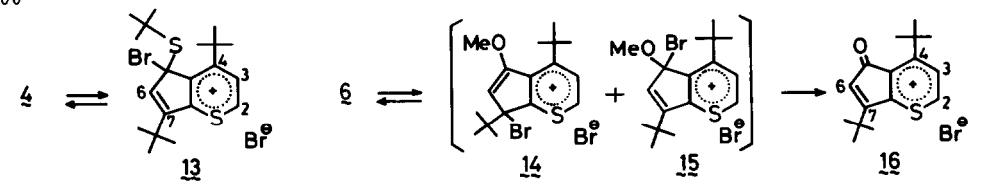
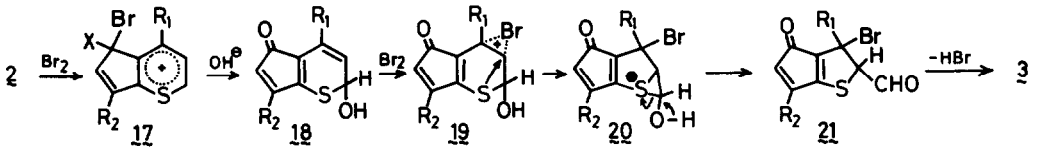
1.31 s (*t*-Bu); UV: $\lambda_{max}^{CH_2Cl_2}$ (ε)[8] 272.5 (48,700), 370sh (5,030) nm]. ^{1}H NMR spectrum of the solution obtained from 6 and Br_2 showed the mixture of the isomers (14 and 15), which gradually formed 16 as reddish orange needles (42%).



Taking into account the formation of 13, 14, 15 and 16, the formation of the 2-formylcyclopenta[b]thiophen-4-one (3) can be rationalized by the reaction sequence shown in Scheme. The thiopyrylium ion (17) is converted into 18 on treatment with an aqueous sodium hydrogencarbonate, and then 18 is again brominated with excess Br_2 to give 19, which suffers ring contraction to give 3. Spectral data and physical properties of new compounds obtained are listed in Table.



Scheme

Table. Spectral Data and Physical Properties of New Compounds

5: mp 124.5 ∿ 125.9°C, IR (KBr-disk) 1705 s, 1639 s cm^{-1}; Mass(m/e) 276 (M^+); ^{1}H NMR ($CDCl_3$) δ 10.31 s (1H, CHO), 5.48 s (1H, H_5), 1.54 s (9H, C_3-*t*-Bu), 1.32 s (9H, C_6-*t*-Bu); ^{13}C NMR (acetone-d_6) δ 191.7 (C_4), 185.0 (CHO), 165.0, 164.1, 155.6, 146.0, 138.9 (sp^2-carbons), 122.0 (C_5), 38.1, 34.1, 31.8, 29.0 (*t*-Bu); UV $\lambda_{max}^{cyclohexane}$($\varepsilon$) 248 (5,470), 289.5 (23,900), 297 (27,400), 329.5 (2,140), 342 sh (1,770), 358 sh (909), 429 (1,090) nm.

8: viscous oil, IR(film) 1714 s, 1660 s cm^{-1}; Mass(m/e) 234 (M^+); ^{1}H NMR ($CDCl_3$) δ 9.95 s (1H, CHO), 5.56 s (1H, H_5), 2.61 s (3H, Me), 1.33 s (9H, *t*-Bu).

9: colorless prisms, mp 164 ∿ 167°C (dec.), IR (KBr-disk) 1725 s, 1651 s cm^{-1}; Mass(m/e) 438, 436, 434 (M^+); ^{1}H NMR ($CDCl_3$) δ 10.49 s (1H, CHO), 5.30 s, 5.18 s (1H, H_5 of *cis*- and *trans*-isomers), 1.58 s (9H, C_3-*t*-Bu), 1.55 s, 1.32 s (9H, C_6-*t*-Bu of *cis*- and *trans*-isomers); UV $\lambda_{max}^{CH_2Cl_2}$ (ε) 258.5 (25,000), 297 (9,890) nm.

10: mp 210 ∿ 212°C, IR (KBr-disk) 1726 m, 1713 m, 1635 s cm^{-1}; Mass(m/e) 356, 354 (M^+); ^{1}H NMR ($CDCl_3$) δ 10.32 s (1H, CHO), 1.53 s (9H, C_3-*t*-Bu), 1.50 s (9H, C_6-*t*-Bu); UV $\lambda_{max}^{CH_2Cl_2}$ (ε) 253 (5,980), 299 sh (27,100), 307.5 (29,900), 340.5 (2,710), 471 (1,490) nm.

12: reddish orange prisms, mp 151.5 ∿ 155.0°C, IR (KBr-disk) 1730 m, 1711 m, 1629 s cm^{-1}; Mass(m/e) 314, 312 (M^+); ^{1}H NMR ($CDCl_3$) δ 10.30 s (1H, CHO), 2.15 s (3H, Me), 1.54 s (9H, *t*-Bu).

18: mp 166.0 ∿ 169.5°C (dec.), IR (KBr-disk) 1732 s cm^{-1}; Mass(m/e) 261 (M^+); ^{1}H NMR (CD_3CN) δ 9.45 d, J=9.5 (1H, H_2), 8.74 d, J=9.5 (1H, H_3), 6.46 s (1H, H_6), 1.55 s (9H, *t*-Bu), 1.48 s (9H, *t*-Bu).

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References and Notes

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6) Treatment of 4 with 1eq. Br_2 gave 5 (42%) along with the recovered 4 (15%).
7) The solution obtained from 4 and Br_2 (1.8eq.) in CD_2Cl_2 was directly subjected to the measurement of ^{1}H NMR spectrum.
8) The ε-values were calculated assuming quantitative conversion of 4 into 13.

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