BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49(3), 825—826 (1976)

Rearrangement of 4,5-Benzo-3-thiatricyclo[4.1.0.0^{2,7}]heptenes Promoted by Butyllithium: A New Synthetic Route to 3,4-Benzo-2-thiabicyclo[3.2.0]hepta-3,6-dienes

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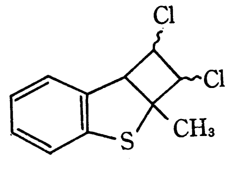
(Received August 18, 1975)

Synopsis. The reaction of 4,5-benzo-3-thiatricyclo[4.1.0.0^{2,7}]heptenes (**1a**—**d**) with butyllithium followed by quenching with water or methyl iodide at −60 °C gives the expected bridgehead substituted products, whereas the same reaction conducted at somewhat higher temperature gives the skeletal rearrangement products, 3,4-benzo-2-thiabicyclo[3.2.0]hepta-3,6-dienes (**2a**—**f**), almost quantitatively. A mechanism in line with the results is proposed.

The well-known bridgehead deuteration and alkylation of the bicyclo[1.1.0]butanes involve an anion intermediate and electrophilic attack of the corresponding reagents.$^{1)}$ During the course of our study on 4,5-benzo-3-thiatricyclo[4.1.0.0^{2,7}]heptene (**1a**)$^{2-6)}$ we found that the deuteration of **1a** with *n*-BuLi/D_2O at 0 °C gives the skeletal rearrangement product, 3,4-benzo-2-thiabicyclo[3.2.0]hepta-3,6-diene-6-*d* (**2a**), exclusively.$^{3)}$ We report on the generality of this type of rearrangement of **1**.

When 4,5-benzo-3-thiatricyclo[4.1.0.0^{2,7}]heptene (**1a**) was lithiated with *n*-BuLi in ether at −60 °C and then methylated with excess methyl iodide at −30 °C, the expected bridgehead methyl derivative (**1b**)$^{6)}$ was obtained quantitatively. However, when lithiation was performed at 0 °C in ether, the rearrangement product (**2b**) was obtained quantitatively after methyl iodide quenching at 0 °C. Definite proof of the structure of the product is obtained from its NMR spectrum and synthesis from 4-methyl-1-benzothiepin (**3a**)$^{6)}$ by photoisomerization. The rearrangement usually took place at 0 °C. However, a lower temperature, −20 °C, also sufficed in the case of methyl substituted substrates, **1b**$^{6)}$ and **1c**$^{6)}$ which afforded 1,6-dimethyl-3,4-benzo-2-thiabicyclo[3.2.0]hepta-3,6-diene (**2e**) and 5,6-dimethyl-3,4-benzo-2-thiabicyclo[3.2.0]hepta-3,6-diene (**2f**), respectively. Assignment of structures **2e** and **2f** was based on their spectral data. In addition, **2f** was available from photoisomerization of 4,5-dimethyl-1-benzothiepin (**3b**).$^{6)}$

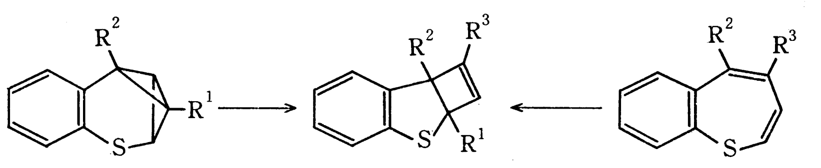
Other examples were also found in the case of water quenching experiments. On treatment with *n*-BuLi/H_2O, **1b** afforded 1-methyl-3,4-benzo-2-thiabicyclo[3.2.0]hepta-3,6-diene (**2c**). The structure assigned to **2c** follows from its spectral data coupled with an independent synthesis. Thus, dechlorination of the photoadduct (**4**),$^{7)}$ obtained from irradiation of a mixture of 2-methylbenzo[*b*]thiophene and *cis*-dichloroethylene in the presence of benzophenone as sensitizer, with sodium phenanthrene$^{8)}$ in THF at 0 °C afforded **2c** in 40% yield.



(**4**)

Furthermore, dimethyl derivative (**1d**) gave 1,5-dimethyl-3,4-benzo-2-thiabicyclo[3.2.0]hepta-3,6-diene (**2d**) on treatment with *n*-BuLi/H_2O at ambient temperature. The NMR spectrum of **2d** was in complete accord with the proposed structure.

In all the cases, we found that the newly introduced methyl or hydrogen is always bonded at C-6 position of **2**. The complete regiospecificity of this rearrangement was interpreted by assuming the intermediacy of a carbene type species (**B**), derived from an initially formed bridgehead anion (**A**), which is subsequently converted into the vinyl anion (**C**). Electrophilic attack of methyl iodide or water would give the observed products. Since **1a** is readily accessible,$^{1,2)}$ the present reactions provide a useful synthetic route to the substituted 3,4-benzo-2-thiabicyclo[3.2.0]hepta-3,6-dienes (**2**).



(**1**)

a: $R^1=R^2=H$
b: $R^1=CH_3$, $R^2=H$
c: $R^1=H$, $R^2=CH_3$
d: $R^1=R^2=CH_3$

(**2**)

a: $R^1=R^2=H$, $R^3=D$
b: $R^1=R^2=H$, $R^3=CH_3$
c: $R^1=CH_3$, $R^2=R^3=H$
d: $R^1=R^2=CH_3$, $R^3=H$
e: $R^1=R^3=CH_3$, $R^2=H$
f: $R^1=H$, $R^2=R^3=CH_3$

(**3**)

a: $R^2=H$, $R^3=CH_3$
b: $R_2=R_3=CH_3$

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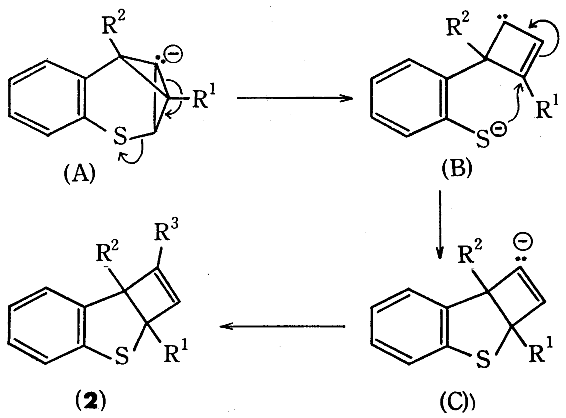

Experimental

Generals. The UV spectra were measured with a Hitachi Model 124 spectrophotometer. All the absorptions are given in nm with log ε in parentheses. The NMR spectra were recorded on a Varian XL-100-15 spectrometer with tetramethylsilane as an internal standard.

*General Procedure for Rearrangement of **1**.* To a stirred solution of **1** (0.25 mmol) in 2—5 ml of dry ether was added dropwise a solution of *n*-BuLi (0.25 mmol) in hexane at temperatures indicated in the text [**1a**→**2b**: 0 °C; **1b**→**2e**: –20 °C; **1c**→**2f**: –20 °C; **1d**→**2d**: room temp] under nitrogen atmosphere. The mixture was stirred for 15 min at the specified temperature and treated with 20 fold excess of methyl iodide or water. Excess water was added and the aqueous iayer was washed with water and dried over anhydrous magnesium sulfate. Removal of the solvent afforded **2** quantitatively. Analytically pure compounds were obtained by column chromatography on a deactivated (with 5% of water) alumina with light petroleum ether.

2b: Colorless liquid, Found: C, 75.58; H, 5.99%. Calcd for $C_{11}H_{10}S$: C, 75.82; H, 5.78%. NMR (CCl_4) δ 1.73 (3H, d, *J*=1.8 Hz, CH_3), 4.52 (2H, s, H-1,5), 5.73 (1H, q, *J*=1.8 Hz, H-7), 6.90—7.17 (4H, m, arom.); UV (cyclohexane) (λ_{max} (log ε)) 217 (4.26), 255 (sh, 3.89), 257 (3.92), 263 (sh, 3.83), 297 (3.29), 305 nm (3.22).

2c: Colorless liquid, Found: C, 75.94; H, 5.75%. Calcd for $C_{11}H_{10}S$: C, 75.82; H, 5.78%. NMR (CCl_4) δ 1.68 (3H, s, CH_3), 4.10 (1H, bs, H-5), 5.96 (1H, dd, *J*=2.8, 0.7 Hz, H-7), 6.13 (1H, dd, *J*=2.8, 0.5 Hz, H-6), 6.85—7.17 (4H, m, arom.); UV (cyclohexane) (λ_{max} (log ε)) 218 (4.24), 223 (sh, 4.06), 254 (3.95), 258 (3.96), 296 (3.29), 298 (3.27), 305 (3.23).

2d: Colorless liquid, Found: C, 76.55; H, 6.45%. Calcd for $C_{12}H_{12}S$: C, 76.55; H, 6.42%. NMR (CCl_4) δ 1.43 (3H, s, 5-CH_3), 1.53 (3H, s, 1-CH_3), 5.93 (1H, d, *J*=2.6 Hz, H-7), 6.00 (1H, d, *J*=2.6 Hz, H-6), 6.90—7.15 (4H, m, arom.); UV (cyclohexane) (λ_{max} (log ε)) 216 (4.21), 236 (3.70), 255 (3.96), 293 (3.30), 302 (3.25).

2e: Colorless liquid, Found: C, 76.29; H, 6.36%. Calcd for $C_{12}H_{12}S$: C, 76.55; H, 6.42%. NMR (CCl_4) δ 1.67 (6H, m, 1- and 6-CH_3), 3.95 (1H, m, H-5), 5.84 (1H, dq, *J*=1.7, 0.5 Hz, H-7), 6.88—7.14 (4H, m, arom.); UV (cyclohexane) (λ_{max} (log ε)) 218 (4.23), 255 (sh, 3.91), 258 (3.92), 297 (3.32), 305 (3.27).

2f: Colorless liquid, Found: C, 76.72; H, 6.48%. Calcd for $C_{12}H_{12}S$: C, 76.55; H, 6.42%. NMR (CCl_4) δ 1.56 (3H, s, 5-CH_3), 1.65 (3H, dd, *J*=1.7, 1.6 Hz, 6-CH_3), 4.11 (1H, q, *J*=1.6 Hz, H-1), 5.61 (1H, q, *J*=1.7 Hz, H-7), 6.93—7.10 (4H, m, arom.); UV (cyclohexane) (λ_{max} (log ε)) 214 (4.31), 235 (sh, 3.79), 256 (3.95), 263 (sh, 3.89), 294 (3.30), 303 (3.25).

*Photoisomerization of **3a**, and **3b** to **2b** and **2f**.* A solution of **3** (0.25 mmol) in 0.5 ml of dry THF was irradiated through a pyrex filter with a 450w high-pressure mercury arc lamp at 0 °C for 4—5 hr. Removal of the solvent afforded **2** (*ca.* 90%) along with a small amount of the corresponding naphthalene (sulfur extrusion product).

*Independent Synthesis of **2c**.* A solution of sodium phenanthrene (4 ml) prepared from 310 mg of sodium metal and 2.67 g phenanthrene in 30 ml of dry THF, was added to 245 mg of 6,7-dichloro-1-methyl-3,4-benzo-2-thiabicyclo[3.2.0]heptene-3 (**4**) in 5 ml of dry THF. The color of the reagent solution rapidly vanished at the beginning but returned at the end of the addition. After 10 min, one drop of water was added to quench the excess of the reagent. The solvent was evaporated and the residue was chromatographed on a silver nitrate impregnated silica gel column with hexane. Removal of the solvent gave 70 mg (40%) of 1-methyl-3,4-benzo-2-thiabicyclo[3.2.0]hepta-3,6-diene which was identical in all respects with **2c**.

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