Erratum

A Mild and Efficient Synthesis of Buta-1,3-dienes Substituted with a Terminal Pentafluoro-λ^6-sulfanyl Group

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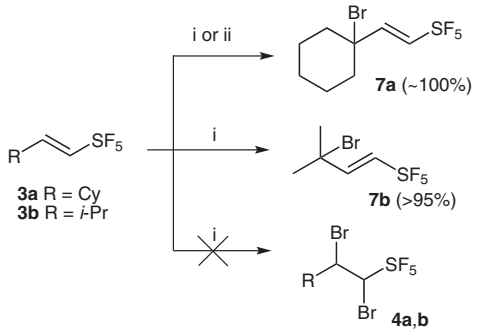
For the reaction of compounds **3a**,**b** with bromine according to Scheme 4, we had observed that the corresponding dibromides **4a**,**b** were obtained. However, we have since encountered difficulties in providing a suitable explanation for the mechanism of bisdehydrobromination of **4a**,**b** leading to the formation 1,3-dienes **5a**,**b** (Scheme 6). Moreover, it has been reported that tertiary hydrogens in benzylic and allylic systems are quite reactive toward molecular bromine or *N*-bromosuccinimide, but in all such cases, an initiator – either irradiation or high temperature – was used.[1] These points led us to continue the investigation of the bromination reactions of olefins **3a**,**b**.

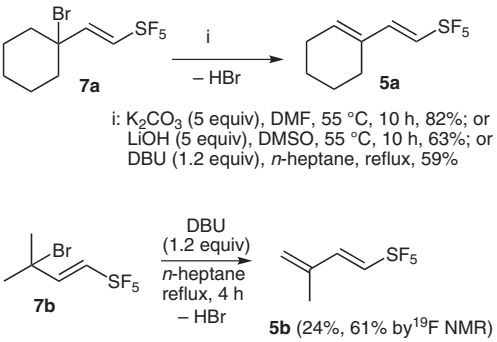
We have thus re-examined the bromination of **3a**,**b** with molecular bromine in pentane, according to the procedure described in our previous paper, and have studied the reaction of **3a** with *N*-bromosuccinimide in carbon tetrachloride using *m*-chloroperoxybenzoic acid as an initiator. The latter system was used to exclude the possible formation of **4a**. However, under both conditions, the same product was obtained (NMR analysis), which had been determined previously to be the dibromide **4a** according to elemental analysis and MS data. The peaks, namely *m*/*z* (%) = 393 (10) $[M - H]^+$, 395 (15) $[M - H + 2]^+$, 397 (10) $[M - H + 4]^+$, had been mistakenly interpreted by us as the molecular ion peaks of the dibromide **4a**. In contrast, in a mass spectrum of product (**7b**) that was obtained after bromination of **3b** (Scheme 8, i) we did not observe any characteristic molecular ions for structures **4b** and **7b**. Therefore, the MS data is insufficient for proving the structures of the products **4a**,**b**. The repetition of elemental analysis of the products, separated from the corresponding reaction mixtures after bromination of **3a**,**b** (Scheme 8, i, ii), confirmed beyond any doubt the structures of the allylic bromination products **7a**,**b**. More significantly, the ^{13}C and ^1H NMR are better correlated with the structures of **7a**,**b** than with those of **4a**,**b**. The substituent $CH{=}CHSF_5$ in **7a**,**b** forms groups of multiplets in the ^1H NMR spectra similar to SF_5-substituted olefins **4c**,**d**, namely a doublet at 6.7 ppm ($^{trans}J_{HH}$ = 14.7 Hz) and a doublet of quintets at 6.52 ppm with characteristic coupling constants J_{HF} = 6 Hz and $^{trans}J_{HH}$ = 14.7 Hz for the $CHSF_5$ proton. Quintets for the carbon atoms of **7a**,**b**, as well as **4c**,**d**, bound to the SF_5 group and the carbon atoms β to the SF_5 group were observed in the ^{13}C NMR spectra with characteristic coupling constants $^2J_{CF}$ = 20–21 Hz and $^3J_{CF}$ = 6.7–7.7 Hz in the 135–144 ppm region.



i: Br_2 (1.2 equiv), pentane, 12 h, r.t.
ii: for **3a**, NBS (1.1 equiv), CCl_4, MCPBA (cat.), reflux, 6 h

Scheme 8 Allylic bromination of **3a**,**b**

The subsequent HBr elimination of **7a**,**b** after treatment with base gave the corresponding 1,3-dienes **5a**,**b** in good yields (Scheme 9). Consequently, the formation of **5a**,**b** is the result of 1,2-elimination similar to the dehydrobromination of **4c**,**d** (Scheme 7).



i: K_2CO_3 (5 equiv), DMF, 55 °C, 10 h, 82%; or LiOH (5 equiv), DMSO, 55 °C, 10 h, 63%; or DBU (1.2 equiv), *n*-heptane, reflux, 59%

Scheme 9 Dehydrobromination of **7a**,**b**

1-Bromo-1-[(*E*)-2-(pentafluoro-λ^6-sulfanyl)vinyl]cyclohexane (7a)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.75 (d, *J* = 14.7 Hz, 1 H), 6.52 (dquin, J_{HH} = 14.7 Hz, J_{HF} = 6.0 Hz, 1 H), 2.00–2.30 (m, 2 H, Cy), 1.56–1.80 (m, 7 H, Cy), 1.29 (m, 1 H, Cy).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.9 (quin, *J* = 6.8 Hz), 139.5 (quind, *J* = 20.8, 1.5 Hz), 66.1 (CBr), 39.7 (Cy), 25.3 (Cy), 23.2 (Cy).

^{19}F NMR (376 MHz, $CDCl_3$): δ = 83.0 (9 lines, A-part), 64.0 (dd, *J* = 150.3, 6.0 Hz, B_4-part).

MS (EI): *m*/*z* (%) = 393 (10), 395 (15), 397 (10), 127 (100) [SF_5], 81 (42) [Br]$^+$, 79 (42) [Br]$^+$.

Anal. Calcd for $C_8H_{12}BrF_5S$: C, 30.49; H, 3.84; Br, 25.35; S, 10.18. Found: C, 30.47; H, 3.88; Br, 25.02; S, 10.51.

(1*E*)-3-Bromo-3-methyl-1-(pentafluoro-λ^6-sulfanyl)but-1-ene (7b)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.77 (d, *J* = 14.7 Hz, 1 H), 6.52 (dquin, J_{HH} = 14.7 Hz, J_{HF} = 6.0 Hz, 1 H), 1.90 (s, 6 H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.1 (quin, *J* = 6.7 Hz), 138.6 (quin, *J* = 21.1 Hz), 57.1 (CBr), 32.7 (CH_3).

^{19}F NMR (376 MHz, $CDCl_3$): δ = 82.7 (9 lines, A-part), 64.0 (dd, *J* = 150.3, 6.0 Hz, B_4-part).

MS (EI): *m*/*z* (%) = 195 (100) [M – Br]$^+$, 87 (45), 67 (25) [M – HBr – SF_5]$^+$.

Anal. Calcd for $C_5H_8BrF_5S$: C, 21.83; H, 2.93; Br, 29.05; S, 11.66. Found: C, 21.80; H, 3.03; Br, 28.85; S, 12.01.

References

Pfeiffer W. D. In *Science of Synthesis*, Vol. 35; Schaumann E., Ed.; Thieme: Stuttgart, **2007**, 423.