Erratum

A Mild and Efficient Synthesis of Buta-1,3-dienes Substituted with a Terminal Pentafluoro-1,6-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 mlz (%) = 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 13C and 1H NMR are better correlated with the structures of 7a,b than with those of 4a,b. The substituent CH=CHSF5 in 7a,b forms groups of multiplets in the 1H NMR spectra similar to SF5-substituted olefins 4c,d, namely a doublet at 6.7 ppm (transJHH = 14.7 Hz) and a doublet of quintets at 6.52 ppm with characteristic coupling constants JHF = 6 Hz and intransJHH = 14.7 Hz for the CHSF5 proton. Quintets for the carbon atoms of 7a,b, as well as 4c,d, bound to the SF5 group and the carbon atoms β to the SF5 group were observed in the 13C NMR spectra with characteristic coupling constants 2JCF = 20–21 Hz and 1JCF = 6.7–7.7 Hz in the 135–144 ppm region.

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).

Scheme 8  Allylic bromination of 3a,b

Scheme 9  Dehydrobromination of 7a,b
1-Bromo-1-[(E)-2-(pentafluoro-1H-sulfanyl)vinyl]cyclohexane (7a)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 6.75$ (d, $J = 14.7$ Hz, 1 H), 6.52 (d, $J_{HH} = 14.7$ 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$_3$): $\delta = 143.9$ (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$_3$): $\delta = 83.0$ (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$_2$], 79 (42) [Br$^+$.]

Anal. Calcd for C$_8$H$_{12}$BrF$_5$S: 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.

(1E)-3-Bromo-3-methyl-1-(pentafluoro-1H-sulfanyl)but-1-ene (7b)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 6.77$ (d, $J = 14.7$ Hz, 1 H), 6.52 (d, $J_{HH} = 14.7$ Hz, $J_{HF} = 6.0$ Hz, 1 H), 1.90 (s, 6 H, CH$_3$).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 144.1$ (quin, $J = 6.7$ Hz), 138.6 (quind, $J = 21.1$ Hz), 57.1 (CBr), 32.7 (CH$_3$).

$^{19}$F NMR (376 MHz, CDCl$_3$): $\delta = 82.7$ (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$_5$H$_8$BrF$_5$S: 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