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Transformations of 1-alkyl-2,2-dibromo-1-ferrocenylcyclopropanes upon treatment with Bu^{t}OK in DMSO

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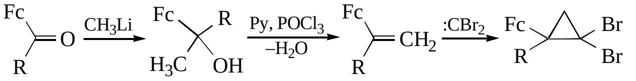
The interaction of 1-alkyl-2,2-dibromo-1-ferrocenylcyclopropanes with Bu^{t}OK in DMSO, depending on the reaction conditions, leads selectively to the corresponding *Z*-monobromocyclopropanes in high yield or to ferrocenyl-substituted cyclopropenes and other products.

Monohalogenocyclopropanes can be easily prepared by the reduction of the corresponding dihalogeno-cyclopropanes. However, this reaction is often accompanied by an undesirable process, namely, their total reduction to cyclopropanes.[1–4] Recently, we have shown that the interaction of 2,2-dibromo-1-ferrocenyl-1-methylcyclopropane with Zn in ethanol results in numerous by-products due to the specific influence of the ferrocenyl substituent. Thus, 2-bromo-1-ferrocenyl-1-methylcyclopropane could be obtained in satisfactory yield only in the presence of a base. As a rule, monohalogenocyclopropanes are isolated as a mixture of geometrical *Z*- and *E*-isomers.[5]

Aiming at the synthesis of ferrocenyl-substituted monohalogenocyclopropenes from the corresponding dibromocyclopropanes under the action of Bu^{t}OK in DMSO, we have studied this reaction with several representatives of ferrocenyldibromocyclopropanes. However, simply introducing the ferrocenyl group considerably changed the reactivity of the dibromocyclopropanes.

The initial dibromocyclopropanes **4a**–**c** were prepared from the acylferrocenes **1a**–**c**[5] *via* intermediate **2a**–**c** and **3a**–**c** according to Scheme 1.



1a–**c** **2a**–**c** **3a**–**c** **4a**–**c**

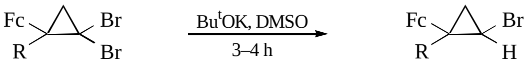
Fc = $C_5H_5FeC_5H_4$
a R = 1-Ad
b R = Bu^t
c R = Me (ref. 7)

Scheme 1

We found that Bu^{t}OK in DMSO, which is normally used as a dehydrohalogenation agent in the synthesis of cyclopropenes, appeared to be a good reducing agent for 1-alkyl-2,2-dibromo-1-ferrocenylcyclopropanes **4a**–**c**. The reduction proceeded smoothly, especially in the presence of bulky alkyl substituents (Bu^t or 1-Ad). The dibromides **4a**–**c** reduced completely to the monobromides **5a**–**c** in 3–4 h (Scheme 2).[†]

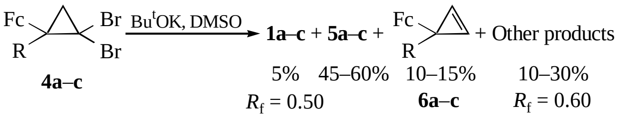
It is noteworthy that this kind of reduction of *gem*-dibromocyclopropanes with either aliphatic or aromatic substituents has never been reported. We believe that the probable rationale for the above reaction is the one-electron reduction of **4a**–**c** with Bu^{t}OK/DMSO followed by H atom transfer from the solvent. The high yield of monobromides **5a**–**c** demonstrates the sufficient stability of the suggested intermediate.

We found that the increase in the reaction time (up to 12 h or more) results in the formation of by-products: the corresponding cyclopropenes **6a**–**c**,[‡] the initial ketones **1a**–**c**, and several other products, some of which were identified (Scheme 3).



4a–**c** **5a**–**c**

Scheme 2

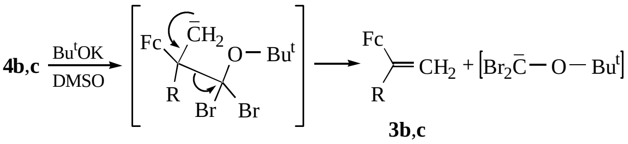


4a–**c** **6a**–**c**

Scheme 3

The formation of cyclopropenes under these conditions is easily explained by dehydrobromination of the monobromocyclopropanes **5a**–**c**. The ketones **1a**–**c** result in all cases from the reaction of the intermediate allylic cations (or radicals) with oxygen.

We isolated and identified by ^{1}H NMR spectroscopy[§] the following by-products: (*a*) the allylic ether **7** derived from dibromocyclopropane **4a**; (*b*) the linear dimer **8** derived from



3b,c

Scheme 4

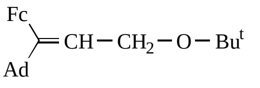
[†] *Typical procedure*: A mixture of dibromocyclopropanes **4a**–**c** (1 mmol) and Bu^{t}OK (1.5 mmol) in DMSO (25 ml) was stirred for 3–4 h at 25 °C. Benzene (50 ml) was then added. The organic layer was separated and concentrated. Monobromocyclopropanes **5a**–**c** were isolated from the residue by preparative TLC on neutral Al_2O_3 (Brockmann activity II) in a good yield (~ 60–75%), R_f ~ 0.72 (hexane). According to NMR spectral data,[5–7] compounds **5a**–**c** were obtained exclusively as *Z*-isomers ($\Delta\delta_Z = \delta_B - \delta_A \geq 0.30$ ppm; $\Delta\delta_E \leq 0.20$ ppm) (*cf.* refs. 1–5).

5a: yield 76%, yellow crystals, mp 106–107 °C. ^{1}H NMR ($CDCl_3$) δ: 1.38 (dd, 1H, *J* 8.5, 5.6 Hz), 1.69 (pseudo-t, 1H, *J* 5.6, 5.6 Hz), 2.0–1.20 (m, 15H, Ad), 3.40 (dd, 1H, *J* 8.5, 5.6 Hz), 4.10 (m, 1H, C_5H_4), 4.11 (m, 1H, C_5H_4), 4.22 (m, 2H, C_5H_4), 4.12 (s, 5H, C_5H_5). Found (%): C, 63.10; H, 6.04; Fe, 12.93; Br, 18.27. Calc. for $C_{23}H_{27}BrFe$ (%): C, 62.89; H, 6.20; Fe, 12.72; Br, 18.19.

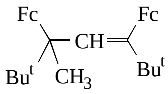
5b: yield 78%, yellow crystals, mp 54–55 °C. ^{1}H NMR ($CDCl_3$) δ: 0.76 (s, 9H), 1.39 (dd, 1H, *J* 8.5, 5.6 Hz), 1.71 (pseudo-t, 1H, *J* 5.6, 5.6 Hz), 3.35 (dd, 1H, *J* 8.5, 5.6 Hz), 4.10 (m, 2H, C_5H_4), 4.15 (m, 1H, C_5H_4), 4.19 (m, 1H, C_5H_4), 4.13 (s, 5H, C_5H_5). ^{13}C NMR ($CDCl_3$) δ: 20.36 (CH_2), 26.15 (CH), 27.88 (CH_3), 31.31 (C), 33.68 (C), 65.3, 66.14, 71.19 (C_5H_4), 69.57 (C_5H_5), 93.22 (C_{ipso}Fc). Found (%): C, 56.29; H, 6.03; Fe, 15.71; Br, 21.96. Calc. for $C_{17}H_{21}BrFe$ (%): C, 56.54; H, 5.86; Fe, 15.47; Br, 22.13.

5c: yield 78%, yellow crystals, mp 54–55 °C. ^{1}H NMR ($CDCl_3$) δ: 1.36 (dd, 1H, *J* 8.1, 5.6 Hz), 1.53 (s, 3H), 1.74 (pseudo-t, 1H, *J* 5.6, 5.6 Hz), 3.12 (dd, 1H, *J* 8.1, 5.6 Hz), 4.06 (s, 5H, C_5H_5), 3.85–4.25 (m, 4H, C_5H_4). ^{13}C NMR ($CDCl_3$) δ: 21.42 (CH_2), 26.28 (CH), 28.23 (CH_3), 29.70 (C), 33.68 (C), 69.70 (C_5H_5), 65.24, 67.30, 72.01 (C_5H_4), 92.09 (C_{ipso}Fc). Found (%): C, 56.29; H, 6.03; Fe, 15.71; Br, 21.96. Calc. for $C_{17}H_{21}BrFe$ (%): C, 56.54; H, 5.86; Fe, 15.47; Br, 22.13.

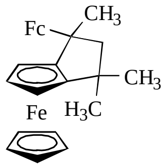
dibromocyclopropane **4b**; and (*c*) the homocyclodimer **9** derived from dibromocyclopropane **4c**.[6,7]



7



8 (*Z*,*E*)



9

The formation of the ether **7** is associated with the ring-opening of the monobromocyclopropane **5a** as the reaction time with Bu^{t}OK in DMSO increases. The dimers **8** and **9**[6] are formed most probably by homodimerisation of the ferrocenylalkenes **3b** and **3c**, for which this process is known to occur easily in the presence of traces of acids.[6,7] We admit that lengthy contact of Bu^{t}OK/DMSO with the dibromides **4b** and **4c** results in retrocyclisation and formation of the initial ferrocenylalkenes **3b**,**c**. The latter are not sufficiently stable in solutions and dimerise according to a radical mechanism.[6–8] The ferrocenyl substituent can favour the cleavage of the C–C bond in the intermediate product and lead to formation of the ferrocenylalkenes **3b**,**c** (Scheme 4).

To the authors' knowledge, this kind of retrocyclisation of small rings has not been reported so far, though numerous examples of nucleophilic ring-opening of electrophilic cyclopropanes are documented.

The reasons for this phenomenon could possibly be related to the specific role of the ferrocenyl group as a donor that weakens one of the C–C bonds in cyclopropanes with electron-acceptor substituents.

We have demonstrated that the homocyclodimer **9** is also formed in a yield of up to 76% upon treatment of 2-ferrocenylpropene **3c** with Bu^{t}OK in DMSO. This corroborates the suggested mechanism of the retrocyclisation of the dibromoferrocenylcyclopropanes **4b**,**c** and the radical character of the dimerisation of the alkenes **3b**,**c**.

It is evident from these results that the synthesis of 3-alkyl-3-ferrocenylcyclopropenes **6a**–**c** from the dibromides **4a**–**c** can be best performed by a two-stage reaction with Bu^{t}OK in DMSO, thus avoiding lengthy contact of the reactants in the first stage. First, it is advisable to reduce the dibromides **4a**–**c** to the monobromides **5a**–**c**. Then, the resulting monobromides should be isolated and treated repeatedly with Bu^{t}OK in DMSO. The yields of the main products in each stage are as high as 60–75%. 3-(1-Adamantyl)- and 3-*tert*-butyl-3-ferrocenylcyclopropenes (**6a** and **6b**, respectively) were isolated as yellow crystals stable in air. 3-Ferrocenyl-3-methylcyclopropene **6c** was a yellow oil, which rapidly darkened on storage.

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[‡] **6a**: mp 109–110 °C. ^{1}H NMR (CDCl$_3$) δ: 1.20–1.96 (m, 15H, Ad), 4.02 (s, 5H, C_5H_5), 3.97–4.01 (m, 4H, C_5H_4), 7.42 (s, 2H, CH=CH). ^{13}C NMR (CDCl$_3$) δ: 27.80, 29.98 (CH$_2$), 33.80, 35.60 (CH), 32.40, 30.01 (C), 68.06 (C_5H_5), 68.63, 65.79 (C_5H_4), 98.12 (C_{ipso}Fc), 118.20 (CH=CH). Found (%): C, 77.10; H, 7.37; Fe, 15.59. Calc. for $C_{23}H_{26}Fe$ (%): C, 77.10; H, 7.37; Fe, 15.59.

6b: mp 39–40 °C. ^{1}H NMR (CDCl$_3$) δ: 0.70 (s, 9H), 4.08 (m, 2H, C_5H_4), 4.10 (m, 2H, C_5H_4), 4.12 (s, 5H, C_5H_5), 7.35 (s, 2H, CH=CH). ^{13}C NMR (CDCl$_3$) δ: 29.73 (CH$_3$), 31.92, 34.53 (C), 68.12 (C_5H_5), 68.60, 66.05 (C_5H_4), 99.53 (C_{ipso}Fc), 116.19 (CH=CH). Found (%): C, 72.62; H, 6.94; Fe, 20.23. Calc. for $C_{17}H_{20}Fe$ (%): C, 72.87; H, 7.19; Fe, 19.94.

6c: orange oil. ^{1}H NMR (CDCl$_3$) δ: 1.49 (s, 3H), 4.01 (m, 4H, C_5H_4), 4.15 (s, 5H, C_5H_5), 7.15 (s, 2H, CH=CH). ^{13}C NMR (CDCl$_3$) δ: 19.21 (C), 25.38 (CH$_3$), 66.89, 67.12 (C_5H_4), 68.05 (C_5H_5), 98.76 (C_{ipso}Fc), 116.61 (CH=CH). Found (%): C, 70.85; H, 6.24; Fe, 23.17. Calc. for $C_{14}H_{14}Fe$ (%): C, 70.62; H, 5.93; Fe, 23.44.

[§] **7**: yellow crystals, mp 144–145 °C. ^{1}H NMR (CDCl$_3$) δ: 1.28 (s, 9H), 1.50–2.10 (m, 15H, Ad), 4.15 (s, 5H, C_5H_5), 4.22 (s, 4H, C_5H_4), 4.36 (d, 2H, *J* 5.8 Hz), 5.56 (t, 1H, *J* 5.8 Hz). Found (%): C, 75.21; H, 8.15; Fe, 13.04. Calc. for $C_{27}H_{36}FeO$ (%): C, 74.99; H, 8.39; Fe, 12.91.

8: orange oil. (Z:E ~ 1:1): ^{1}H NMR (CDCl$_3$) δ: 1.22 (s, Bu^t), 1.24 (s, Bu^t), 1.26 (s, CH$_3$), 1.38 (s, CH$_3$), 4.10 (s, C_5H_5), 4.12 (s, C_5H_5), 4.13 (s, C_5H_5), 4.15 (s, C_5H_5), 4.0–4.30 (m, C_5H_4), 5.6 (s, 1H, CH=), 6.0 (s, 1H, CH=). Found (%): C, 71.38; H, 7.73; Fe, 21.06. Calc. for $C_{32}H_{40}Fe_2$ (%): C, 71.65; H, 7.52; Fe, 20.83.