Angewandte Corrigendum

Up the Hill: Selective Double-Bond Isomerization of Terminal 1,3-Dienes towards Z-1,3-Dienes or 2Z,4E-Dienes

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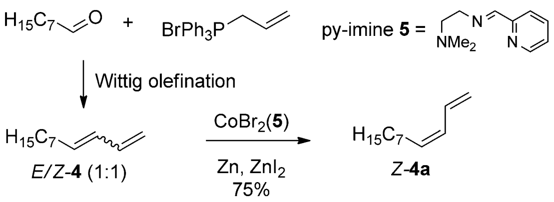
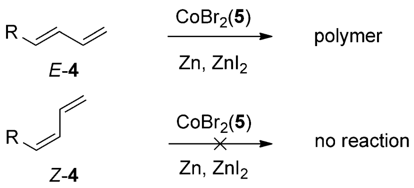
Several years ago the authors reported an isomerisation of E-1,3-dienes by a cobalt catalyst into Z-1,3-dienes in this Communication (Scheme 1—original scheme).



Scheme 1. Double bond isomerisation for the stereoselective generation of Z-**4a**.

The result was of high interest, as the reaction led to the thermodynamically less stable isomer Z–**4a**. Some time later, Prof. T. V. RajanBabu reported similar results with a somewhat different ligand system consisting of $CoCl_2$·(bidentate phosphine ligands) and $AlMe_3$.[1] The group of RajanBabu realised in a detailed investigation that the cobalt-catalysed reaction is not an isomerisation process but rather a kinetic resolution of the E/Z-isomers.[2] Subsequently, Dr. Felicia Weber tried to reproduce the original isomerisation reaction and observed essentially the same behaviour of a kinetic resolution of the E/Z-isomers by the catalyst system (Scheme 2). Also, when pure E-isomer was submitted to the reaction only traces of the Z-isomer could be detected by GCMS analysis. The formation of the Z-isomer was attributed to a thermodynamic equilibration of the pure E-isomer by a process other than the proposed cobalt isomerisation.

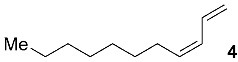
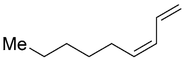
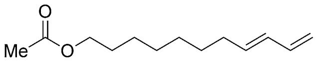
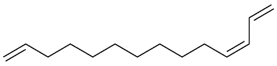
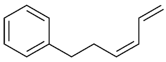
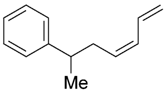
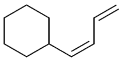
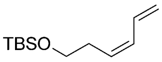
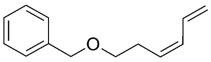
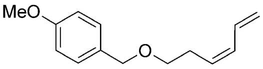


Scheme 2. Reaction of double bond isomers with the cobalt catalyst.

Whereas the E-isomers are converted mostly into a polymer of unknown constitution, the Z-isomer is relatively unreactive and in NMR spectra and GC analysis it could be shown that the signals for the E-isomer disappeared for many substrates while the signals for the Z-isomer remained unchanged. In fact, the previously mistakenly reported isomerisation towards the Z-isomer could not be observed. Accordingly, the results presented in Table 1 of the original Communication have to be corrected. The results of the kinetic resolution of E- and Z-1,3-dienes according to Scheme 2 are now presented in Table 1. Interestingly, for substrate **4c** the E-isomer remained while the Z-isomer disappeared over time, while **4g** remained essentially unchanged. The other Z-1,3-dienes could be isolated in moderate yields, and with E/Z ratios $<5:>95$ in most cases.

The kinetic resolution of the E/Z mixture is surely an interesting process on its own, but the authors regret the misinterpretation of the results reported and apologise for all inconvenience caused by the original Communication.

Table 1: Results of the cobalt-catalysed transformation of *E*/*Z*-1,3-dienes.[a]

Entry	SM[b] Ratio *E*:*Z*	Product	Yield (*Z*-**4**) (Ratio *E*:*Z*)
1	49:51	 **4a**	24 % (2:98)
2	49:51	 **4b**	~10 %[c] (3:97)
3	50:50	 **4c**	41 % (91:9)
4	48:52	 **4d**	27 % (8:92)
5	50:50	 **4e**	38 % (13:87)
6	40:60	 **4f**	40 %[d] (< 1:99)
7	67:33	 **4g**	51 % (69:31)
8	56:44	 **4h**	14 % (20:80)
9	58:42	 **4i**	41 % (< 1:99)
10	57:43	 **4j**	25 % (< 1:99)

[a] $CoBr_2$(py-imine **5**) (5–15 mol %), zinc powder (10–30 mol %), zinc iodide (10–30 mol %), 5–120 h, CH_2Cl_2, ambient temperature. [b] SM = starting material. [c] Due to its high volatility, product with acceptable purity was obtained in low yield. [d] The ^{1}H NMR spectrum shows another isomerisation product with chemical shifts that do not match those of the *E*-isomer.

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[1] Y. N. Timsina, S. Biswas, T. V. RajanBabu, *J. Am. Chem. Soc.* **2014**, *136*, 6215.
[2] Y. N. Timsina, S. Biswas, T. V. RajanBabu, *J. Am. Chem. Soc.* **2018**, *140*, 2700.