Isomerizations

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[12]Annulynes from 1,5-Hexadiyne and Potassium *tert*-Butoxide? Franz Sondheimer's Hexadienynes!

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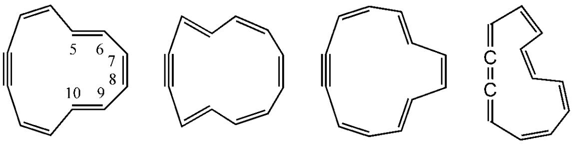
Recently, we were intrigued by the formulas of the [12]annulynes **1**–**3** and the cumulene **4** (Scheme 1) in a publication in this Journal.[1] The authors claimed to have prepared these compounds by the action of potassium *tert*-butoxide (KO*t*Bu) on 1,5-hexadiyne—**1** and **2** in [D$_8$]THF as the solvent[2] and **3** and **4** in C_6D_6.[1] We could not conceive a mechanism for these transformations, and the authors also did not present a satisfactory rationalization. An oxidation would have to occur; however, KO*t*Bu is anything but an oxidizing agent.



1 **2** **3** **4**

Scheme 1. Structures of the products claimed to be formed on treatment of 1,5-hexadiyne with KO*t*Bu.

We then looked for evidence in favor of the formation of **1**–**3** and were highly surprised about the proposal by the authors of a coupling constant in the ^{1}H NMR spectra of 10 or 11 Hz over four bonds in the 1,3-butadiene subunits.[1,2] We had not previously encountered such an unusual long-range coupling constant,[3] which is why we thought that the ^{1}H NMR spectra might have been inaccurately interpreted. After all, structures **1**–**3** display a twofold symmetry, and the coupling constants cannot be determined just by measuring the line distances in the spectra of such systems.[3] More specifically, H5–H10 of **1**–**3** form a spin system similar to that of 1,3,5-cycloheptatriene, which gives rise to a typical spectrum of higher order.[3] However, this idea had to be discarded on inspection of the H,H-COSY spectrum (Figure 1 of Ref. [2]), since the products indeed furnish first order spectra. Nevertheless, a careful look at the spectra in both publications (Figure 1 of Ref. [1] and Figure 2 of Ref. [2]) brought remarkable insights.

The multiplicities and the line distances within the multiplets of the alleged products **1** and **2** (Figure 2 of Ref. [2]) on the one hand and those of the alleged products **3** and **4** (Figure 1 of Ref. [1]) on the other are virtually the same. In addition, the signal positions of the first pair deviate only marginally (up to 0.407 ppm) from those of the second pair (Table 1). Such small differences are readily explained by a solvent effect. The ^{1}H NMR spectrum of a compound dissolved in $CDCl_3$ or [D$_8$]THF shows most signals at somewhat lower field and also sometimes several signals at a slightly higher field compared to the spectrum recorded in C_6D_6.[3] As the spectrum of the first pair was obtained from a solution in [D$_8$]THF and that of the second pair from a solution in C_6D_6, the alleged compound **1** is identical to the alleged compound **3**, and the alleged compound **2** is identical to the alleged compound **4**—only the ratio of the two products is different in the two spectra, namely about 1:1 in Ref. [2] and 5:1 in Ref. [1].

Table 1: ^{1}H NMR chemical shifts of the alleged compounds **1**–**4** as well as of *cis*- (**5**) and *trans*-1,3-hexadien-5-yne (**6**). For the signals of H6 of **5** and **6**, see Ref. [4].

Compound	Solvent	Chemical shifts [ppm] (assignment)				
alleged **1**	[D$_8$]THF	6.874	6.462	5.463	5.378	5.259
alleged **3**	C_6D_6	6.990	6.105	5.225	5.090	5.040
5	$CDCl_3$	6.89	6.47	5.46	5.41	5.31
		(H2)	(H3)	(H4)	(H1*Z*)	(H1*E*)
alleged **2**	[D$_8$]THF	6.628	6.397	5.642	5.308	5.167
alleged **4**	C_6D_6	6.520	5.990	5.365	4.935	4.850
6	$CDCl_3$	6.67	6.37	5.56	5.34	5.22
		(H3)	(H2)	(H4)	(H1*Z*)	(H1*E*)

Since the ^{1}H NMR spectra of the reaction products are of first order, it has to be concluded that the structures shown in Scheme 1 cannot be correct. Consequently, the compounds in question do not possess systems of ten spins, but contain only isolated systems of five protons, whose mutual interactions

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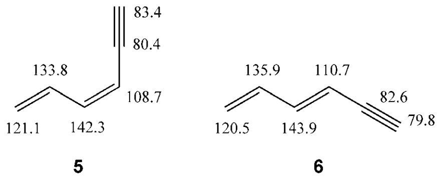
are revealed by the H,H-COSY spectrum (Figure 1 of Ref. [2]). From the coupling patterns, we suspected the products were 1-substituted 1,3-butadienes. Taking into account the constitution of the starting material, we finally arrived at *cis*- (**5**) and *trans*-1,3-hexadien-5-yne (**6**; Scheme 2).

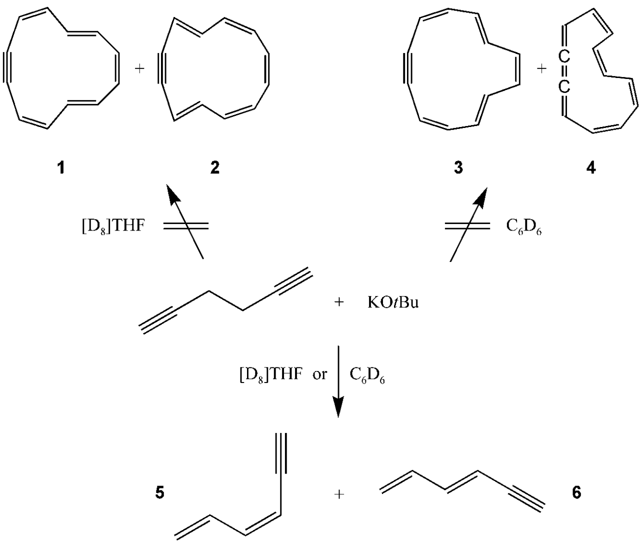


Scheme 2. Structures and ^{13}C NMR chemical shifts (δ [ppm]; solvent: $CDCl_3$) of *cis*- (**5**) and *trans*-1,3-hexadien-5-yne (**6**).[5]

Their ^1H NMR chemical shifts have been published,[4] and are compared in Table 1 to those of the products with the alleged structures **1**–**4**. In view of the different solvents ($CDCl_3$ and $[D_8]THF$), the agreement is excellent. The splitting in the spectra of **5** and **6** originating from the small coupling constants ($J_{1,1'}$ and the long-range coupling constants),[4] typical for 1,3-butadienes,[3] are hardly resolved in Figure 1 of Ref. [1] and Figure 2 of Ref. [2] because of the rather broad lines.

The ^{13}C NMR chemical shifts of **5** and **6** are not documented in the literature, but Ernst and Ibrom[5] provided these data and gave us permission to quote them. These data are included in Scheme 2, and are also in excellent agreement with the spectrum of the reaction products shown in Figure 4 of Ref. [2]. Only one signal ($\delta = 128.5$ ppm) remains unexplained and could originate from an impurity (probably benzene, which is known to be formed from **5** and **6** on thermolysis[6]), since the product was not purified. The authors considered a further signal to be necessary for the alleged structure **2**. Its absence in the spectrum was attributed to it being so broadened that it was not visible.[2]

The hexadienynes **5** and **6** are isomers of 1,5-hexadiyne, from which **1**–**4** were claimed to be formed on treatment with KO*t*Bu.[1,2] Although the authors[1,2] did not mention this simple isomerization of 1,5-hexadiyne, it had already been described in the literature a long time ago. Sondheimer et al.[7] prepared **5** and **6** for the first time by this transformation in 1961; only the solvent was different—*tert*-butyl alcohol was originally used[7] and replaced by $[D_8]THF$[2] and C_6D_6[1] in the recent studies. A detailed examination of the rearrangements of 1,5-hexadiyne to **5** and **6** was published in 1971.[8]



Scheme 3. The alleged and the actual reaction of 1,5-hexadiyne with KO*t*Bu.

In summary, there is no doubt that the action of KO*t*Bu on 1,5-hexadiyne brings about neither the [12]annulynes **1** and **2** in $[D_8]THF$ as the solvent nor the [12]annulyne **3** and the cumulene **4** in C_6D_6, but gives *cis*- (**5**) and *trans*-1,3-hexadien-5-yne (**6**) in both solvents (Scheme 3).

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