Pergamon

Tetrahedron Vol. 51, No. 37, pp. 10209-10218, 1995
Elsevier Science Ltd
Printed in Great Britain
0040-4020/95 $9.50+0.00

0040-4020(95)00610-9

Polylithiumorganic Compounds - 21.[1]

On the Deprotonation of 1- and 3-Phenylpropyne as well as Phenylallene with Butyllithium. A Reinvestigation: Three Different Monoanions but one and the same Dianion.

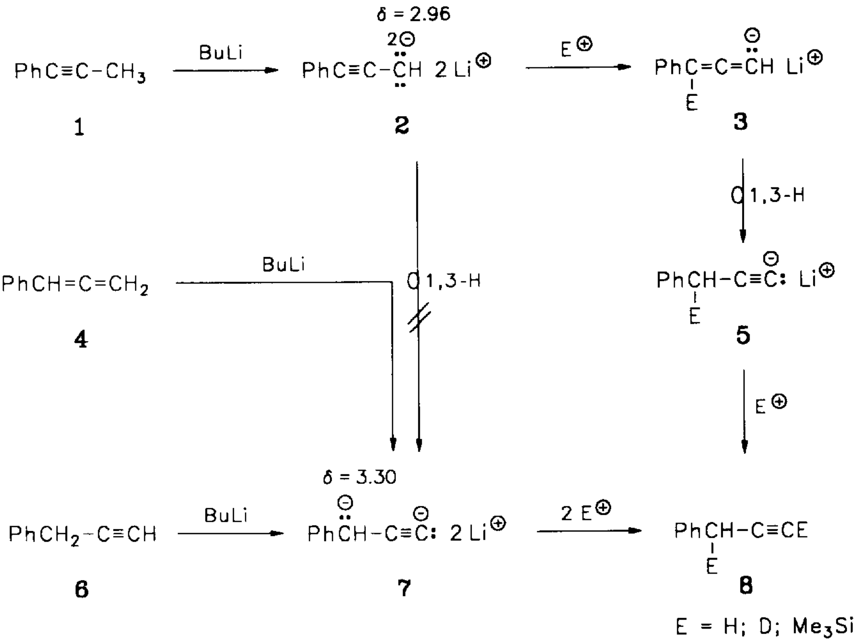
Adalbert Maercker* and Jakob Fischenich[2]

Institut für Organische Chemie der Universität Siegen
D-57068 Siegen (Germany)

Abstract: In contrast to the literature, with butyllithium only one and the same dianion - namely **7** - is formed starting with each of the three hydrocarbons **1**, **4**, and **6**. On the other hand, upon working at low temperature in tetrahydrofuran as the solvent we were able to detect the three corresponding monoanions **9**, **15**, and **16**, most interestingly **15** and **16** at temperatures higher than -40°C show rearrangement with 1,3-hydrogen shift.

Introduction

According to the literature[3] 1-phenylpropyne (**1**) on the one hand and 3-phenylpropyne (**6**) as well as phenylallene (**4**) on the other yield, upon deprotonation with butyllithium, two different dianions, **2** and **7**, which do not interconvert. In diethyl ether as the solvent **2** was reported to show a singlet in the ^1H NMR spectrum at $\delta = 2.96$, **7** a different one at $\delta = 3.30$ ppm. Remarkably, however, both dianions react with electrophiles (H_2O; D_2O; Me_3SiCl) to the same product **8** (E = H; D; Me_3Si), thus starting with **2** one has to assume first a completely regioselective attack of the electrophile at the benzylic carbon atom followed by a spontaneous 1,3-hydrogen shift **3** ——> **5**, the latter taking place even faster than e.g. deuterolysis.



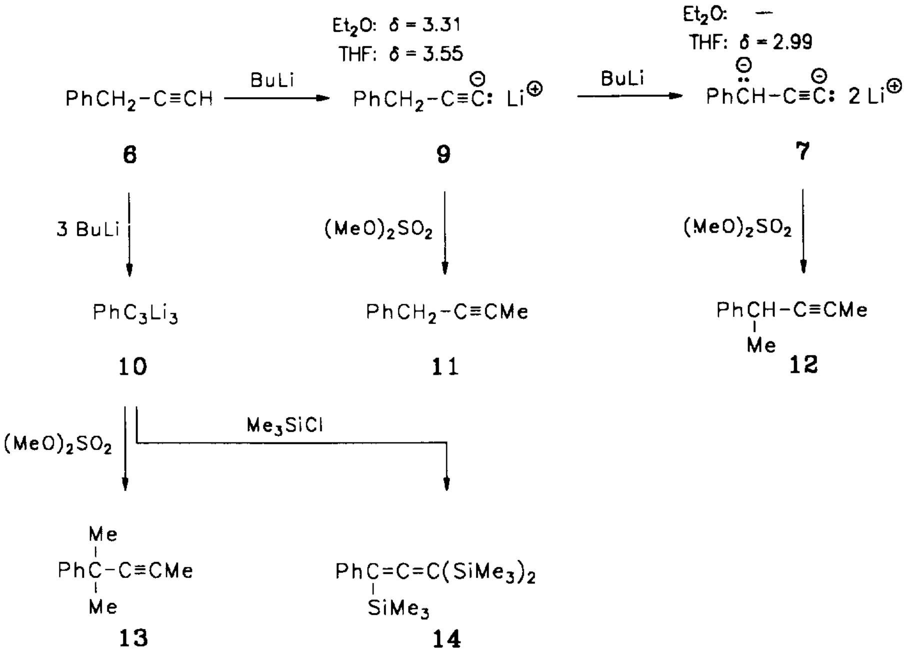
The first doubt came up when we, in another connection,[2] prepared the unsubstituted anion **3** (E = H) independently and could show that the 1,3-hydrogen shift indeed takes place, the rate of this rearrangement, however, cannot compete even with silylation. We therefore decided to reinvestigate the proposed reaction mechanism including the preparation of the corresponding monolithiumorganic compounds, which are intermediates in the dimetallation of **1**, **4**, and **6** without any doubt.

Deprotonation of 3-Phenylpropyne

3-Phenylpropyne (**6**) is readily deprotonated by one equivalent of butyllithium yielding the acetylide **9** which is only fairly soluble in diethyl ether but shows a sharp singlet in the ^{1}H NMR spectrum at δ = 3.31 ppm, i.e. a chemical shift identical with that reported by Klein and Brenner[3] for the dianion **7**. In our hands this dianion **7** is formed with excess butyllithium as a deep red oily substance, nearly insoluble in diethyl ether, showing no sharp signals in the ^{1}H NMR spectrum. On the other hand, both the lithiumorganic compounds are readily soluble in THF-d_8 showing sharp singlets at δ = 3.55 (for **9**) and δ = 2.99 (for **7**), respectively.

The acetylide **9** can be obtained in a pure form by working in pentane or hexane as the solvent and one equivalent of butyllithium yielding **9** as a *white* precipitate which can be filtered off. On the other hand, the dilithiumorganic compound **7** in hydrocarbons represents a *yellow insoluble* solid. With three and more equivalents of butyllithium even an third proton can be abstracted as was already shown by Klein and Brenner.[3] The formation of **10**, however, is slow: with nearly five equivalents of butyllithium in diethyl ether after four days at -80°C still 12% of 4-phenyl-2-pentyne (**12**) besides 88% of 4-methyl-4-phenyl-2-pentyne (**13**) are obtained upon work-up with dimethyl sulfate. Interestingly, silylation yields the allenic compound **14**.[3]

The solution of **9** in diethyl ether or - better - THF is yellow yielding with D_2O starting material **6** deuterated in the 1-position while 1-phenyl-2-butyne (**11**) is formed with dimethyl sulfate.

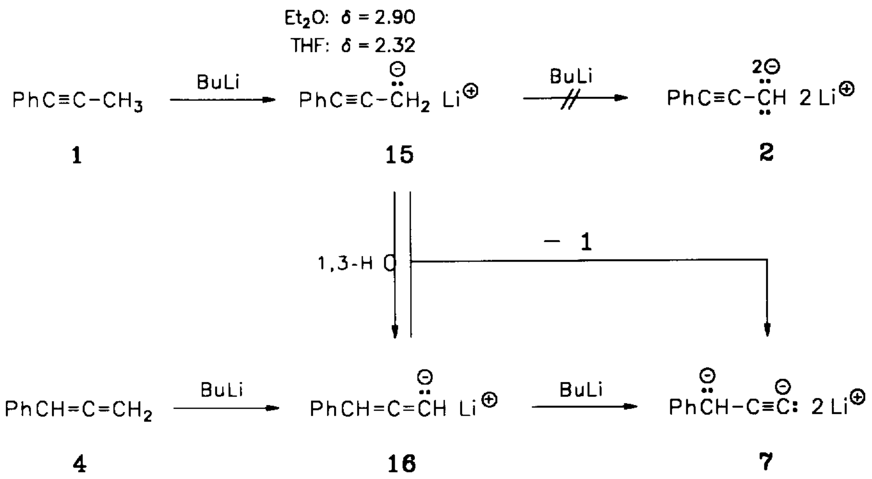


The precipitated dilithiumorganic compound **7** prepared with two equivalents of butyllithium in pentane as the solvent was also filtered off and dried in oil pump vacuum. In contrast to **9** the yellow powder **7** is highly pyrophoric and nearly insoluble in diethyl ether and even THF after having been dried. The deep-red suspension yields pure 4-phenyl-2-pentyne (**12**) upon reaction with dimethyl sulfate. With 3-phenylpropyne (**6**) comproportionation takes place with the formation of two equivalents of the most stable monoanion **9**.

Deprotonation of 1-Phenylpropyne

Of the three hydrocarbons under investigation deprotonation of **1** proves to take place in the most complicated manner. The monoanion **15** in Et_2O-d_{10} shows a singlet in the ^1H NMR spectrum at $\delta = 2.90$ ppm, i.e. a chemical shift similar to that reported by Klein and Brenner[3] for the dianion **2**. The reported signal at $\delta = 2.02$[3] could not be detected. On the other hand, disproportionation of the monoanion **15** to starting material **1** and a dianion can be confirmed. The dianion, however, is *not* **2** but again the oily, in diethyl ether insoluble **7** showing no sharp ^1H NMR signals.

On working in THF-d_8 instead of diethyl ether we succeeded to deprotonate 1-phenylpropyne (**1**) already at -70°C, a temperature where the monolithiumorganic compound **15** is stable (even in the presence of excess butyllithium) showing the ^1H NMR singlet at $\delta = 2.32$ ppm. Most interestingly, at temperatures higher than -40°C rearrangement **15** ——> **16** with 1,3-hydrogen shift can be observed. The rearranged monoanion **16** in THF-d_8 shows two doublets ($^4J = 5.0$ Hz) in the ^1H NMR spectrum at $\delta = 3.94$ and 5.02 ppm and is independently prepared by deprotonation of phenylallene (**4**). It is reasonable to assume that in diethyl ether as the solvent where deprotonation of 1-phenylpropyne (**1**) takes place only at temperatures above -30°C disproportionation of **15** or further deprotonation, respectively, is also preceded by the rearrangement **15** ——> **16**. The formation of the reported[3] dianion **2** - even in trace amounts - never could be detected, and

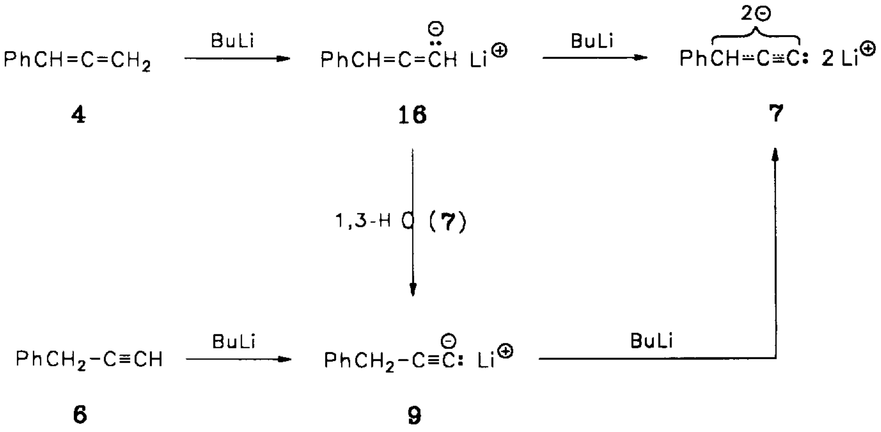


the proposed spontaneous 1,3-hydrogen shift **3** ——> **5** during work-up[3] therefore no longer has to be taken into account. For **15** ——> **16** we suggest an intramolecular 1,3-hydride shift favoured by the negative charge in the carbanion inasmuch as a 1,3-proton shift would contradict the Woodward-Hoffmann rules.[4]

In hydrocarbons as the solvent deprotonation of 1-phenylpropyne (**1**) is slow and does not take place at room temperature. However, in refluxing hexane with a large excess of butyllithium replacement of even three,[5] four[5] and finally of all eight protons[6] has been reported.

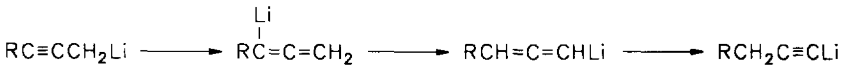
Deprotonation of Phenylallene

As already reported by Klein and Brenner[3] deprotonation of phenylallene (**4**) with butyllithium in diethyl ether yields the dianion **7** immediately. Only upon working at -70°C in THF-d_8 as the solvent we succeeded in preparing the monoanion **16** showing two doublets (^4J = 5.0 Hz) at δ = 3.94 and 5.02 ppm in the ^{1}H NMR spectrum, a product identical with that of the rearranged 3-lithio-1-phenylpropyne (**15**).



Interestingly enough **16** at temperatures above -45°C again undergoes a 1,3-hydrogen shift - possibly catalyzed by **7** - to the acetylide **9**, a reaction corresponding to the postulated[3] rearrangment **3** ——> **5** (E = H); the rate, however, cannot compete with deuterolysis or silylation. However, in hexane at room temperature, one mole of phenylallene (**4**) and one mole of butyllithium yield half a mole of **7** leaving half a mole of **4** unreacted. In this case, of course, the acetylide **9** need not be an intermediate. On the other hand, 1-phenylpropyne (**1**) does not react at all under these conditions.

As discussed by Klein and Becker[7] certain monolithio derivatives of ***aliphatic*** 2-alkynes - in contrast to that of 1-phenylpropyne (**1**) - indeed do rearrange by two consecutive sigmatropic 1,3-hydrogen shifts:[8]



$$RC{\equiv}CCH_2Li \longrightarrow R\overset{Li}{\overset{|}{C}}{=}C{=}CH_2 \longrightarrow RCH{=}C{=}CHLi \longrightarrow RCH_2C{\equiv}CLi$$

The present results show that this is also true for 1-phenylpropyne (**1**), and a second special mechanism has not to be assumed.

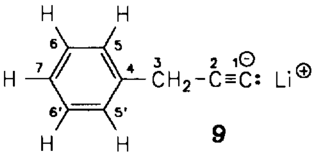
NMR Investigations

1-Lithio-3-phenyl-1-propyne (9)

The acetylide **9** is prepared from 3-phenylpropyne (**6**) and one equivalent of butyllithium in hexane as the solvent, the white precipitate being filtered off under argon and dried at 0.001 Torr. The solution in THF-d_8 (ca. 4 M) is yellow and shows the following ^1H (200 MHz) and ^{13}C (50 MHz) NMR data (Table 1).

Table 1: NMR Data of **9** in THF-d_8 at 25°C

Position	^1H	$^3J_{HH}$	^{13}C	$^1J_{CH}$	$^2J_{CH}$	$^3J_{CH}$
1			123.4			2.3
2			110.8		9.1	
3	3.55(s)		28.1	126.6		4.6
4			140.9		6.8	7.6
5,5'	7.53(AA')	7.1	128.9	157.7		7.6/3.0
6,6'	7.20(BB')	7.1	128.5	158.4		7.6
7	7.09(C)	7.1	126.2	157.7		7.6



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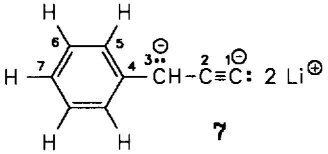
The solubility of **9** in Et_2O-d_{10} is much worse and the ^1H NMR signals of a saturated solution are much broader. The spectrum, however, is nearly identical besides the benzylic protons being shifted upfield to $\delta = 3.31$ ppm

1,3-Dilithio-3-phenyl-1-propyne (7)

3-Phenylpropyne (**6**) in THF-d_8 yields with two equivalents of butyllithium at -70°C first a yellow, later a deep red solution, which after about two minutes solidifies to a yellow material. At 0°C again a red solution (ca. 1 M) is obtained showing the following ^{1}H (200 MHz) and ^{13}C (50 MHz) NMR data (Table 2).

Table 2: NMR Data of **7** in THF-d_8 at 25°C

Position	^{1}H	^{13}C	$^1J_{CH}$
1 + 2		117.8 137.0	
3	2.99(s)	43.7	151.8
4		152.9	
5	6.52(s)	117.6	154.9
6		128.0	151.1
7	5.72(s)	109.0	157.3



The same procedure in Et_2O-d_{10} yields a deep-red nearly insoluble oily substance showing only very broad signals in the ^{1}H NMR spectrum - besides those of n-butane and the residual protons of the solvent.

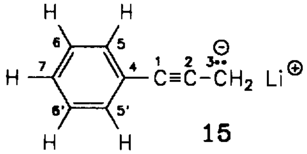
3-Lithio-1-phenyl-1-propyne (15)

In THF-d_8 1-phenylpropyne (**1**) can be deprotonated already at -70°C, a temperature where the corresponding monoanion **15** is stable. The yellow solution (ca. 2 M) shows the following ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR data (Table 3).

Table 3: NMR Data of **15** in THF-d_8 at 214 K

Position	^{1}H	^{13}C	$^1J_{CH}$
1		105.6$^{*)}$	
2		169.4$^{*)}$	
3	2,32(s)	37.7	159.1
4		146.4$^{*)}$	
5,5'	6.71(A,A')	124.9	156.8
6,6'	6.91(B,B')	127.7	156.4
7	6.53(C)	118.2	157.2

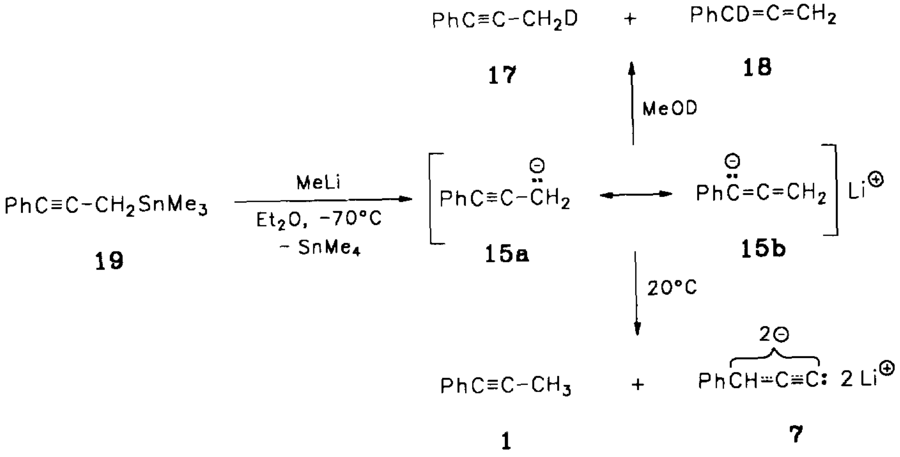
$^{*)}$ may be interchanged



Upon warming up the solution to 234 K (-39°C) signals of the rearranged anion **16** can be observed which, however, disappears again at 280 K (7°C) leaving only signals of the disproportionation products 1-phenylpropyne (**1**) and the dianion **7** (1:1) as well as those of the final product of rearrangement, the most stable monoanion **9**.

In $Et_2O\text{-}d_{10}$ as the solvent, where deprotonation takes place only at temperatures higher than -30°C, no rearranged intermediates can be detected - even with low butyllithium concentrations - and the final deep red oily product **7** shows only very broad signals at δ = 3.0, 6.2, and 6.8 ppm due to poor solubility.

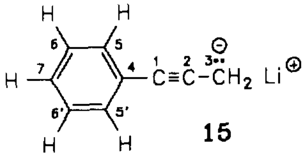
By tin-lithium exchange from **19** independently prepared **15** shows the same disproportionation to **1** and **7** while deuterolysis at low temperature yields **17** and **18** (2:3).



In $Et_2O\text{-}d_{10}$ **15** shows somewhat different NMR data compared with $THF\text{-}d_8$ (Table 4).

Table 4: NMR Data of **15** in $Et_2O\text{-}d_{10}$ at 273 K

Position	^1H	$^3J_{HH}$	^{13}C*)
1			104.5
2			175.5
3	2.90(s)		42.7
4			142.8
5,5'	7.13(A,A')	7.3	128.3
6,6'	7.07(B,B')	7.7	128.7
7	6.84(C)	7.2	122.9



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*) Correlation according to Table 3

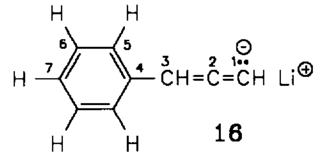
The lower up-field shift in the aromatic ring especially in the ortho positions compared with $THF\text{-}d_8$ as the solvent speaks for less delocalization of the negative charge as expected for the less polar solvent.

1-Lithio-3-phenyl-1,2-propadiene (16)

Phenylallene (**4**) can be deprotonated by butyllithium easily already at -90°C in $THF\text{-}d_8$ as the solvent whereby even at that low temperature excess butyllithium has to be avoided because the second deprotonation to the dianion **7** is also very fast. The violet solution (ca. 2 M) shows the following ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR data (Table 5).

Table 5: NMR Data (tentative) of **16** in THF-d_8 at 220 K

Position	^{1}H	$^4J_{HH}$	^{13}C
1	5.02(d)	5.0	63.8
2			171.8
3	3.94(d)	5.0	91.3
4			149.0
5	6.5-7.4		116.8
6			127.9
7	6.38(m)		121.4



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Upon warming up the solution to about -45°C the ^{1}H NMR singlet of the acetylide **9** at δ = 3.55 ppm can be observed due to 1,3-hydrogen shift. With excess butyllithium, however, always the dianion **7** is formed at once. It is remarkable that even then the benzylic proton of **4** is not removed.

Experimental

General Methods. All reactions with air sensitive compounds were carried out under an atmosphere of dried argon (99.996%). The solvents were freshly distilled from sodium prior to use. Et_2O-d_{10} and THF-d_8 were dried over lithium aluminium hydride and freshly distilled under argon. Dimethyl sulfate was distilled and stored over molecular sieve (3Å). Mass spectra (MS) were obtained on a Hewlett-Packard GC-Mass Spec 5988a (5% phenylmethylsilicon quartz capillary); m/z values are reported followed by the relative intensity in parantheses. Nuclear Magnetic Resonance (^{1}H and ^{13}C) spectra were recorded on the Bruker instruments WP-80, AC-200, and AMX-400. Chemical shifts are reported in parts per million (δ) downfield from an internal TMS reference or the high-field signal of the corresponding solvent referred to TMS. Coupling constants (J) are reported in Hertz (Hz), and spin multiplicities are indicated by the following symbols: s(singlet), d(doublet), t(triplet), q(quartet), m(multiplet).

Preparation of the Starting Materials

1-Phenylpropyne (**1**) was prepared in 93% yield according to the literature[10] from phenylacetylene, butyllithium, and dimethyl sulfate: b.p. 66-68°C (10 Torr) [Lit.[11] 90°C (20 Torr)]. **MS** (70 eV): m/z 116 (M^+, 80), 115(100), 89(12), 65(5), 63(15), 57(6), 51(7), 39(8). **^{1}H NMR** (200 MHz, $CDCl_3$) δ 2.01 (s, 3H, methyl), 7.2-7.5 (m, 5H, phenyl). **^{13}C NMR** (50 MHz, $CDCl_3$) δ 4.4, 79.9, 85.9, 124.2, 127.6, 128.3, 131.6.

3-Phenylpropyne (**6**) was prepared in 83% yield according to the literature[12] from phenylmagnesium bromide and methoxyallene[13] using copper(I) bromide as a catalyst: b.p. 59-60°C (10 Torr) [Lit.[12] 60-61°C (12 Torr)]. **MS** (70 eV): m/z 116 (M^+, 73), 115(100), 89(11), 65(5), 63(10), 57(6), 51(8), 39(9). **^{1}H NMR** (200 MHz, $CDCl_3$) δ 2.18 (t, ^4J = 2.7 Hz, 1H methine), 3.59 (d, ^4J = 2.7 Hz, 2H, methylene), 7.2-7.4 (m, 5H, phenyl). **^{13}C NMR** (50 MHz, $CDCl_3$), δ 24.9, 70.6, 82.1, 126.8, 128.0, 128.7, 136.2.

Phenylallene (**4**) was prepared in 67% yield according to the literature[14,15] from phenylmagnesium bromide and 3-methoxypropyne[16] using copper(I) bromide as a catalyst: b.p. 60-62°C (10 Torr) [Lit.[14] 70°C (14 Torr)]. **MS** (70 eV):

m/z 116 (M^+, 74), 115(100), 89(14), 65(6), 63(16), 58(6), 51(11), 39(10). **^{1}H NMR** (200 MHz, $CDCl_3$) δ 5.12 (d, ^4J = 6.7 Hz, 2H, methylene), 6.14 (t, ^4J = 6.7 Hz, 2H, methylene), 6.14 (t, ^4J = 6.7 Hz, 1H, methine), 7.1-7.4 (m, 5H, phenyl). **^{13}C NMR** (50 MHz, $CDCl_3$), δ 78.9, 94.1, 126.8, 127.0, 128.7, 134.0, 209.9.

3-Phenyl-2-propynyltrimethylstannane (**19**) was prepared in 79% yield according to the literature[17] from 3-phenyl-2-propynylmagnesium bromide and chlorotrimethylstannane at -20°C: b.p. 77-80°C (0.04 Torr) [Lit.[17] 82°C (15 Torr)]. **^{1}H NMR** (200 MHz, $CDCl_3$) δ 0.32 (s, 9H, methyl), 1.87 (s, 2H, methylene), 7.2-7.5 (m, 5H, phenyl).

Metalation Reactions

1-Lithio-3-phenyl-1-propyne (**9**): To a solution of 11.6 g (0.10 mol) 3-phenylpropyne (**6**) in 400 ml of dry pentane was added under argon 60 ml (0.10 mol) 1.6 M butyllithium in hexane (Chemetall, Frankfurt) at room temperature. The white precipitate was filtered off under argon using a G3 filter frit (porosity 16-40 μm) and washed twice with 20 ml of pentane. A 2 h drying at 0.001 Torr yielded 11.6 g (0.10 mol, 100%) **9** as a white solid.

The yellow solution of 3.54 g (29 mmol) **9** in 100 ml of diethyl ether was treated at -50°C with 10 ml of dimethyl sulfate, whereby decoloration took place. The excess dimethyl sulfate was destroyed with 25% aqueous ammonia, the organic phase washed twice with saturated sodium bicarbonate solution and dried over magnesium sulfate. Distillation yielded 3.19 g (25 mmol, 85%) 1-phenyl-2-butyne (**11**) of b.p. 75-85°C (10 Torr). **MS** (70 eV): m/z 130 (M^+, 83), 129(63), 128(64), 127(28), 115(100), 63(18), 51(39), 50(20). **^{1}H NMR** (80 MHz, $CDCl_3$) δ 1.83 (t, ^5J = 2.6 Hz, 3H, methyl), 3.53 (q, ^5J = 2.6 Hz, 2H, methylene), 7.1-7.4 (m, 5H, phenyl).

The yellow solution of 3.91 g (32 mmol) **9** in 100 ml of THF was treated at 0°C with 5 ml of deuterium oxide. Distillation of the organic phase yielded 3.52 g (30 mmol, 94%) 3-phenyl-1-propyne-1-d_1 of b.p. 58-62°C (10 Torr). **MS** (70 eV): m/z 117 (M^+, 62), 116(100), 115(11), 90(8), 63(12), 51(29), 50(21), 39(18). **^{1}H NMR** (80 MHz, $CDCl_3$) δ 3.59 (s, 2H, methylene), 7.1-7.4 (m, 5H, phenyl).

1,3-Dilithio-3-phenyl-1-propyne (**7**): To a suspension of 1.70 g (14 mmol) 1-lithio-3-phenyl-1-propyne (**9**) in 50 ml of dry pentane was added under argon within 5 min 8.7 ml (14 mmol) 1.6 M butyllithium in hexane at room temperature, whereby the originally white precipitate turned yellow. After stirring the yellow precipitate for 48 h it was filtered off under argon, washed with 20 ml of pentane, and dried under vacuum. The extremely pyrophoric powder was suspended in 30 ml of pentane and treated at -40°C with a solution of 10 ml of dimethyl sulfate in 15 ml of THF. After work-up as described above distillation of the organic phase yielded 1.38 g (10 mmol, 69%) 4-phenyl-2-pentyne (**12**) of b.p. 74-78°C (10 Torr). **MS** (70 eV): m/z 144 (M^+, 49), 130(10), 129(100), 128(85), 127(32), 115(9), 77(13), 51(12). **^{1}H NMR** (200 MHz, $CDCl_3$) δ 1.44 (d, ^3J = 7.1 Hz, 3H, methyl-C_5), 1.84 (d, ^5J = 2.5 Hz, 3H, methyl-C_1), 3.70 (qq, ^3J = 7.1 Hz, ^5J = 2.5 Hz, 1H, methine), 7.1-7.5 (m, 5H, phenyl).

Deprotonation of 3-phenylpropyne (6) with excess butyllithium: 5 ml (8.0 mmol) 1.6 M butyllithium in hexane was placed in a Schlenk tube and the solvent removed under oil pump vacuum. The residue was dissolved in 1 ml of Et_2O-d_{10}, cooled to -80°C, and treated via syringe with 0.2 g (1.7 mmmol) 3-phenylpropyne (**6**) in 1 ml of Et_2O-d_{10}. The ^{1}H NMR spectrum showed only signals of butyllithium and butane as well as the residual protons of the solvent. Working up with dimethyl sulfate after four days yielded a mixture (0.2 g) of 12% 4-phenyl-2-pentyne (**12**) and 88% 4-methyl-4-phenyl-2-pentyne (**13**). **MS** (70 eV): m/z 158 (**13** M^+, 10), 144(12), 143(100), 128(54), 115(19), 77(14), 65(13), 51(15). **^{1}H NMR** (200 MHz, $CDCl_3$) δ 1.55 (s, 6H, 2 x methyl), 1.86 (s, 3H, methyl), 7.1-7.6 (m, 5H, phenyl).

3-Lithio-1-phenyl-1-propyne (**15**): Into a solution of 2.78 g (10 mmol) 3-phenyl-2-propynyltrimethylstannane (**19**) in 50 ml of diethyl ether, cooled to -70°C, 6.3 ml (10 mmol) of a 1.6 M solution of methyllithium in pentane was added dropwise. After 3 h 10 ml of methanol-d_1 was added and the work-up performed as usual. Distillation of the crude product yielded 0.98 g (8 mmol, 84%) of a mixture containing 61% 1-phenylallene-1-d_1 (**18**) and 39% 1-phenylpropyne-3-d_1 (**17**). **^{1}H NMR** (80 MHz, $CDCl_3$) δ 2.00 (t, $^2J_{(HD)}$ = 2.5 Hz, **17** methyl), 5.11 (s, **18** methylene), 7.1-7.4 (m, phenyl).

NMR samples

1-Lithio-3-phenyl-1-propyne (**9**): The white powder prepared as described above from 2.00 g (17 mmol) 3-phenylpropyne (**6**) and 10 ml (16 mmol) 1.6 M butyllithium was dissolved at -40°C in 4 ml of THF-d_8. About 0.6 ml of this solution was filled under argon into an NMR tube. The NMR spectra in Et_2O-d_{10} were run with a saturated solution, the concentration being much smaller than in THF-d_8.

1,3-Dilithio-3-phenyl-1-propyne (**7**): 5 ml (8.0 mmol) 1.6 M butyllithium in hexane was placed in a Schlenk tube and the solvent removed under oil pump vacuum. The residue was dissolved in 2 ml of THF-d_8, cooled to -70°C, and treated via syringe with a solution of 464 mg (4.0 mmol) 3-phenylpropyne (**6**) in 2 ml of THF-d_8. The solution at first turned yellow then red yielding finally a yellow precipitate, which, however, at higher temperatures redissolved to a red solution, 0.7 ml of which at -10°C was filled with a syringe into an NMR tube.

3-Lithio-1-phenyl-1-propyne (**15**): Into a solution of 8.0 mmol butyllithium in 2 ml of THF-d_8 prepared as described above a solution of 927 mg (8 mmol) 1-phenylpropyne (**1**) in 2 ml of THF-d_8 was added dropwise via syringe at -70°C within three minutes. Part of the yellow clear solution was cooled to -100°C and filled into an NMR tube precooled also to -100°C.

1-Lithio-3-phenyl-1,2-propadiene (**16**): Here one has to work in an inverse manner introducing the solution of 8.0 mmol butyllithium in 2 ml of THF-d_8 via syringe into a solution of 997 mg (9.0 mmol) phenylallene (**4**) in 2 ml of THF-d_8 at -90°C. Part of the violet solution was filled with a syringe into an NMR tube precooled also to -90°C.

Acknowledgements

We thank the *Volkswagen-Stiftung* and the *Fonds der Chemischen Industrie* for their generous support.

References and Notes

Dedicated to Professor Harald Günther on the occasion of his 60th birthday.

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(*Received in Germany* 26 *May* 1995; *revised* 21 *July* 1995; *accepted* 24 *July* 1995)