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Formation and rearrangement of *gem*-dilithiodiphenylethene[1]

Adalbert Maercker *, Benno Bös, Mohammad Taghi Hajgholipour

Institut für Organische Chemie der Universität Siegen, Adolf-Reichwein-Straße, D-57068 Siegen, Germany

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Abstract

1,1-Dilithio-2,2-diphenylethene (**14**) is accessible through double bromine lithium exchange reaction starting from 1,1-dibromo-2,2-diphenylethene (**5**) with lithium metal at −110°C. **14** undergoes rearrangement into (*E*)-1-lithio-2-(2-lithiophenyl)-2-phenylethene (**13**) at temperatures above −100°C. The (*Z*)-compound **15** was formed from the (*E*)-compound **13** at temperatures above −25°C.

Keywords: Rearrangement; Lithiumorganic compounds; *gem*-Dilithioalkenes; Lithiation; Quasi dianion complexes

1. Introduction

Mitchell and Amamria reported on the attempted preparation of 2,2-dilithiostyrene (**2**) by reaction of 2,2-bis(trimethylstannyl)styrene (*1*) with methyllithium [2]. Although the corresponding disubstituted derivatives were formed by quenching the reaction mixture with electrophiles, the precursor of these products (e.g. **4**) was not the dilithio alkene **2**, an *ate*-complex was formed instead. The *ate*-complex **3**, a Quasi Dianion Complex (QUADAC) [3], reacts stepwise with the electrophile forming disubstituted derivatives, thus only pretending the formation of dilithio compound **2** (Scheme 1).

Similar observations had been made in the reaction of 2,2-diiodo-1-isopropoxystyrene with *s*-butyllithium ([4]a) and 9-dibromomethylenefluorene with *n*-butyllithium [5]. We have developed several methods for the preparation of *gem*-dilithioalkenes and methods for their unequivocal detection [4]. The synthesis of certain geminal dilithioalkanes has been reported by G.W. Klumpp [6].

2. Experimental section

2.1. General conditions

All reactions with air and moisture-sensitive compounds were carried out under argon (99.996%). The argon was purified by passing through columns of molecular sieves of 10 Å and BTS-catalyst (Merck KG a. A., Darmstadt, Germany). Ethereal solvents were purified by adsorptive filtration over basic aluminium oxide (activity I from Fluka AG, Buchs, Switzerland) and distilled under argon from sodium-benzophenone ketyl. Other solvents were distilled under argon from sodium wire prior to use. Dimethyl sulphate was purified by distillation and stored over molecular sieves of 4 Å.

For analytical gas chromatography a Hewlett–Packard HP 5890 Series II instrument with FID and an HP 3396A integrator was employed. Quantitative amounts were determined in this case by using *n*-decane as an internal standard. Mass spectra were obtained on an Hewlett–Packard hp 5988 A quadrupol mass spectro-

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* Corresponding author. Fax: +49 271 7402330.

[1] B. Bös, Über Bildungstendenzen, Folgereaktionen und Simulationen von 1,1-Dilithio-1-alkenen, Shaker, Aachen, 1992. (b) M. T. Hajgholipour, Versuche zur Darstellung polylithiumorganischer Verbindungen durch Addition von Lithium an Vinyllithium-Verbindungen, Shaker, Aachen, 1994 [1].

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meter with an HP gas chromatograph (same model as described above) in the case of GC–MS-coupling.

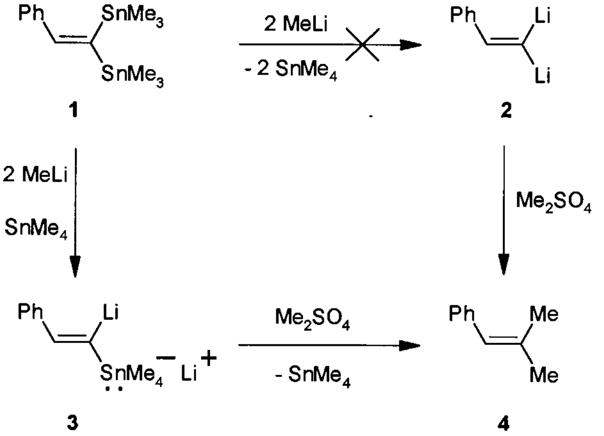
Nuclear Magnetic Resonance (^{1}H, ^{13}C) spectra were recorded on the Bruker instruments WP 80 or AC 200. Chemical shifts are reported in parts per million (δ) downfield from an internal TMS reference. Coupling constants (J) are reported in Hertz (Hz) and spin multiplicities are indicated by the following symbols s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet).

Glass-equipment used with moisture-sensitive compounds was stored for 48 h at 180°C and cooled-down under argon.

Lithium-di-*t*-butylbiphenyl (LDBB) in THF was prepared as described [7] using an excess of di-*t*-butylbiphenyl [8] to avoid contents of unreacted lithium metal in the radical-anion solution. If not stated otherwise, reactions were performed in a Schlenk tube, equipped with mercury valve, thermometer, dropping funnel, and a magnetic stirring bar.

2.2. Reaction of 1,1-dibromo-2,2-diphenylethene (**5**) [9] with LDBB

A solution of 3.38 g (10 mmol) of **5** in 30 ml of THF was dropped slowly at −70°C to a solution of LDBB, prepared from 0.32 g (46 mmol) lithium dust [10] and 14.0 g (53 mmol) of di-*t*-butylbiphenyl, in 100 ml THF. After 1 h at −70°C, a solution of 10 ml (105 mmol) of dimethyl sulphate in 20 ml of THF was added at −70°C. The reaction mixture was allowed to warm to 0°C. At this temperature the excess of dimethyl sulphate was destroyed by adding 50 ml of concentrated ammonia (25%) and stirring overnight at r.t. The aqueous layer was extracted three times with pentane. The combined organic layers were washed with a saturated ammonium chloride solution and brine and then stored over magnesium sulphate for one night. The solvent was removed and the residue was recondensed in a cooled trap. The gas chromatographic analysis showed 0.03 g (0.2 mmol) of 1,1-diphenyl-1-propene (**7**), 0.74 g (3.6 mmol) of 2-methyl-1,1-diphenyl-1-propene (**8**), 1.06 g (5.1 mmol) of (*E*)-1-(2-methylphenyl)-1-phenyl-1-propene (**9**), and about 13 g of di-*t*-butylbiphenyl. Before NMR examination the large excess of di-*t*-butylbiphenyl was removed by fractional distillation.



Scheme 1.

1,1-Diphenyl-1-propene (**7**) [11]: MS (70 eV): *m*/*z* 194 (M$^+$, 100), 193 (63), 179 (36), 178 (41), 165 (25), 130 (20), 129 (37), 115 (91), 91 (17), 89 (19).

2-Methyl-1,1-diphenyl-1-propene (**8**) [12]: MS (70 eV): *m*/*z* 208 (M$^+$, 100), 193 (45), 179 (26), 178 (36), 165 (31), 130 (13), 129 (43), 115 (82), 91 (38), 89 (19). ^{1}H-NMR (80 MHz, $CDCl_3$): δ 1.78 (s, 6 H, methyl), 7.20 (m, 10 H, aromatic H).

(*E*)-1-(2-Methylphenyl)-1-phenyl-1-propene (**9**) [13]: MS (70 eV): *m*/*z* 208 (M$^+$, 32), 191 (6), 179 (100), 178 (40), 165 (10), 115 (25), 91 (10), 89 (8), 51 (7), 39 (6). ^{1}H-NMR (80 MHz, $CDCl_3$): 1.88 (d, $^3J = 7$ Hz, 3 H, allyl), 1.98 (s, 3 H, benzyl), 5.73 (q, $^3J = 7$ Hz, 1 H, vinyl), 7.20 (m, 9 H, aromatic H).

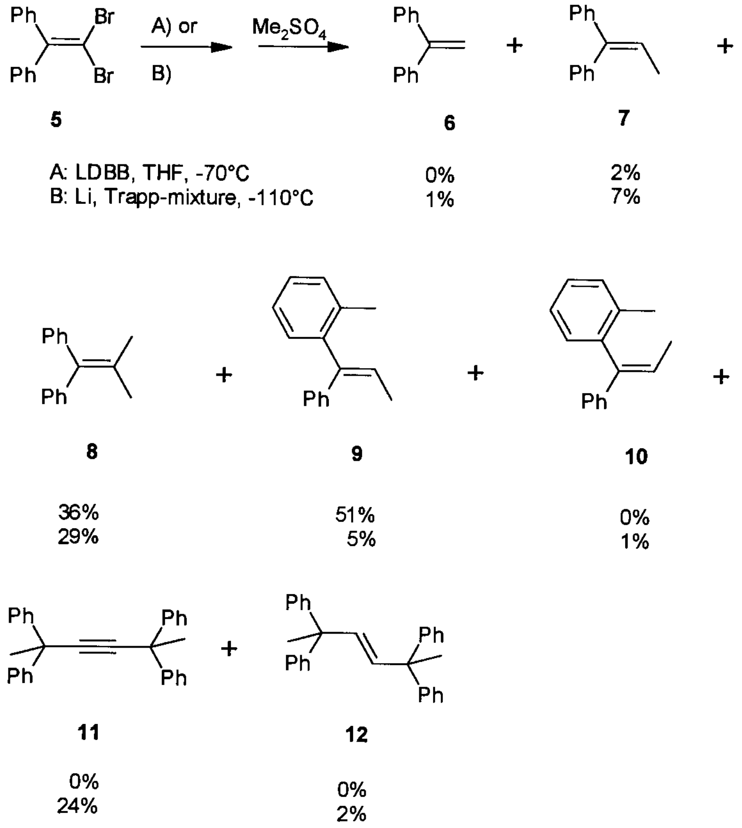
2.3. Reaction of 1,1-dibromo-2,2-diphenylethene (**5**) with lithium dust

In the same equipment as described above, a solution of 3.4 g (10.0 mmol) of 1,1-dibromo-2,2-diphenylethene (**5**) in a mixture of 48 ml of THF, 12 ml of diethylether, and 12 ml of pentane was treated with 0.7 g (100 mmol) lithium dust [10] at −110°C. After 3 h stirring at the same temperature, the dark-red coloured mixture was filtered under argon through a G 3 glass sinter frit and then quenched with dimethyl sulphate at −80°C. After work-up as described above, the slurry was recondensed in a cooled trap and the resulting residue recrystallized from ethanol. The GC–MS analysis of the volatile compounds showed 10 mg (0.1 mmol) of 1,1-diphenylethene (**6**), 130 mg (0.7 mmol) of 1,1-diphenyl-1-propene (**7**), 600 mg (2.9 mmol) of 2-methyl-1,1-diphenyl-1-propene (**8**), 110 mg (0.5 mmol) of (*E*)-1-(2-methylphenyl)-1-phenyl-1-propene (**9**) and 10 mg (0.1 mmol) of (*Z*)-1-(2-methylphenyl)-1-phenyl-1-propene (**10**). The residue contained 460 mg of (1.2 mmol) 2,2,5,5-tetraphenyl-3-hexyne (**11**) and 20 mg (0.1 mmol) of (*E*)-2,2,5,5-tetraphenyl-3-hexene (**12**).

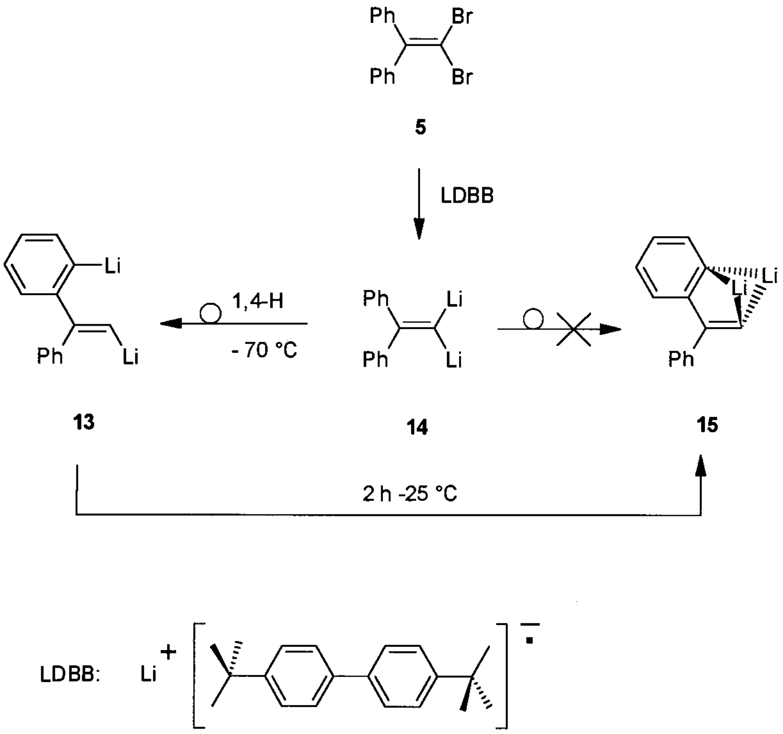
For spectroscopic data of 1,1-diphenyl-1-propene (**7**), 2-methyl-1,1-diphenyl-1-propene (**8**) and (*E*)-1-(2-methylphenyl)-1-phenyl-1-propene (**9**), see above.

1,1-Diphenylethene (**6**) [14]: MS (70 eV): *m*/*z* 180 (M$^+$, 94), 179 (69), 178 (59), 165 (100), 89 (35), 77 (29), 76 (26), 51 (77), 50 (42), 39 (26).

(*Z*)-1-(2-Methylphenyl)-1-phenyl-1-propene (**10**) [13]: MS (70 eV): *m*/*z* 208 (M$^+$, 30), 180 (15), 179 (100), 178 (35), 165 (8), 115 (35), 91 (13), 89 (16), 51 (9), 39 (9).



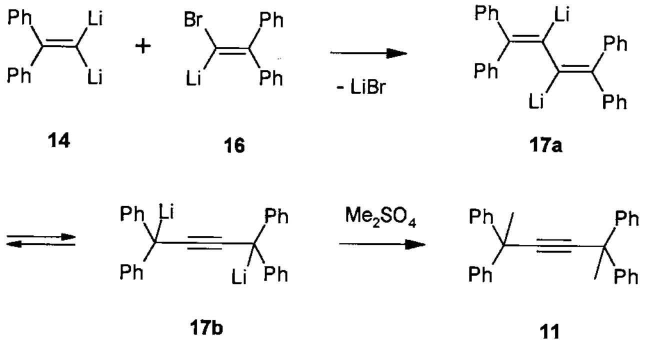
Scheme 2.



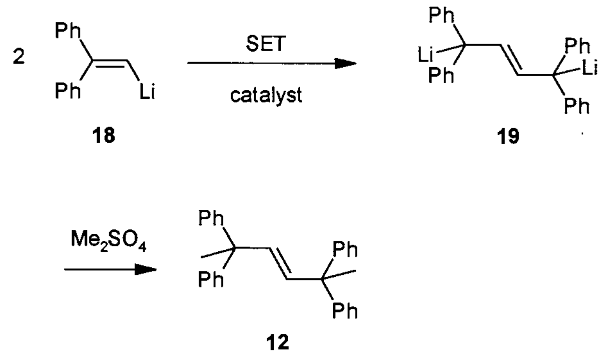
Scheme 3.

^{1}H-NMR (200 MHz, CDCl$_3$): δ 1.61 (d, $^3J = 8.9$ Hz, 3 H, allyl), 2.08 (s, 3 H, benzyl), 6.32 (q, $^3J = 8.9$ Hz, 1 H, vinyl), 7.25 (m, 9 H, aromatic H).

2,2,5,5-Tetraphenyl-3-hexyne (**11**) [15]: MS (70 eV): m/z 386 (M$^+$, 18), 371 (42), 293 (54), 281 (84), 278 (38), 215 (55), 181 (100), 165 (44), 91 (38), 77 (39).

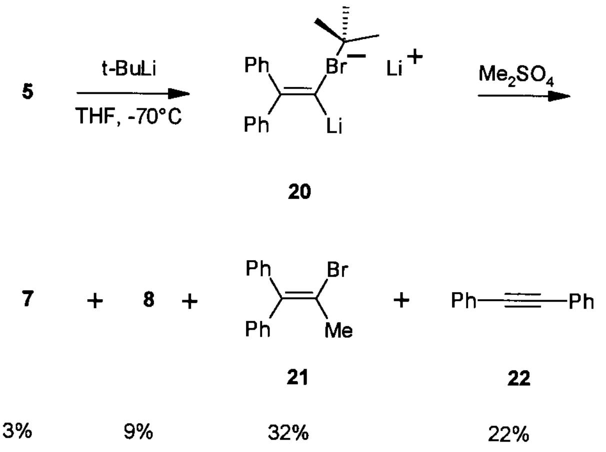


Scheme 4.

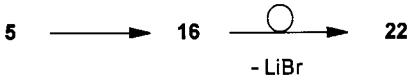


Scheme 5.

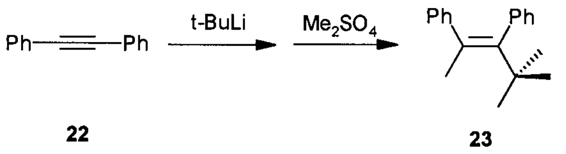
^{1}H-NMR (200 MHz, CDC13): δ 2.00 (s, 6 H, methyl), 7.35 (m, 20 H, aromatic H). ^{13}C-NMR (50 MHz, $CDCl_3$): δ 30.7, 44.8, 89.9, 126.4, 127.0, 128.1, 146.9. For spectroscopical data of 2,2,5,5-tetraphenyl-3-hexene (**12**) see below.



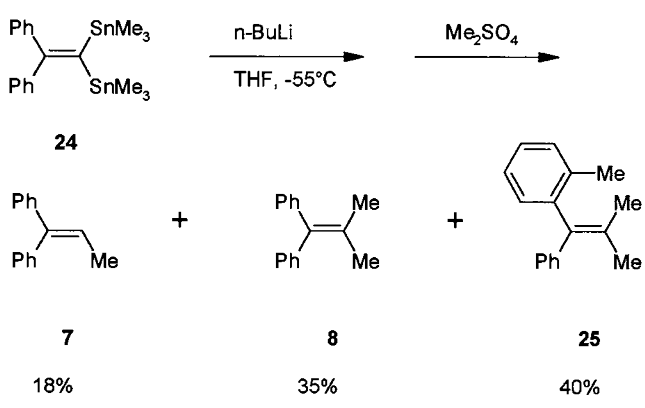
Scheme 6.



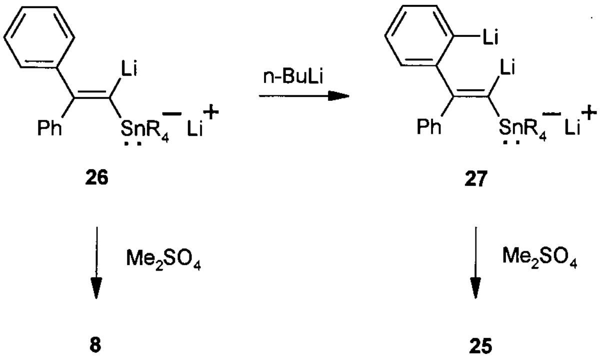
Scheme 7.



Scheme 8.



Scheme 9.



Scheme 10.

2.4. Preparation of 2,2,5,5-tetraphenyl-3-hexene (12) by dimerization of 1-lithio-2,2-diphenylethene

A solution of 1.90 g (5.6 mmol) of 1,1-diphenyl-2-trimethylstannylethene [16] in 30 ml of THF was treated at − 100°C over 15 min with 3.8 ml (5.7 mmol) of a 1.6 M solution of methyllithium in ether. The stirring was continued for an additional 2 h. The solvent was removed under reduced pressure at ambient temperature. The residue was resolved in pentane. After removing the solvent again, the lithium compound was dissolved in ether and recooled to − 100°C. At this temperature 3.5 ml (5.6 mmol) of a 1.6 M solution of *t*-butyllithium in pentane was added over 15 min. After 3 h stirring at the same temperature, the mixture was quenched with dimethyl sulphate at − 20°C. After work-up as described above the solvent was removed. The distillation yielded 0.3 g (1.6 mmol) of 1,1-diphenyl-1-propene (**7**). The residue of the distillation was recrystallized from butyl acetate. One obtained 0.3 g (0.7 mmol) of 2,2,5,5-tetraphenyl-3-hexene (**12**) (m.p. 128–130°C): MS (70 eV): m/z 194 (100), 181 (21), 179 (33), 178 (16), 167 (17), 165 (21), 129 (19), 105 (20), 103 (18), 91 (20). ^{1}H-NMR (200 MHz, $CDCl_3$): δ 1.82 (s, 6 H, methyl), 5.82 (s, 2 H, vinyl), 7.24 (m, 20 H, aromatic H). ^{13}C-NMR (50 MHz, $CDCl_3$): δ 28.1, 49.3, 125.8, 127.8, 127.9, 137.5, 148.6. –$C_{30}H_{28}$ (388.56): calcd. C 92.74, H 7.26; found: C 92.60; H 7.31.

*2.5. Conversion of (E)-1-lithio-2-(2-lithiophenyl)-2-phenylethene **(13)** into the (Z)-compound **15***

The crude (*E*)-compound **13** was prepared from 3.4 g (10 mmol) 1,1-dibromo-2,2-diphenylethene (**5**) and 0.7 g (100 mmol) lithium dust as described above. The excess of lithium was filtered off and the resulting solution stirred for 2 h at −25°C. After quenching with dimethyl sulphate and usual work-up, the resulting slurry was recondensed in a cooled trap. In the volatile part 5 mg (0.03 mmol) 1,1-diphenylethene (**6**), 5 mg (0.03 mmol) 1,1-diphenyl-1-propene (**7**), 5 mg (0.03 mmol) (*E*)-1-(2-methylphenyl)-1-phenyl-1-propene (**9**), and 455 mg (2.2 mmol) (*Z*)-1-(2-methylphenyl)-1-phenyl-1-propene (**10**) are obtained.

*2.6. Reaction of 1,1-dibromo-2,2-diphenylethene **(5)** with t-butyl lithium at −90°C*

A solution of 3.38 g (10 mmol) of 1,1-dibromo-2,2-diphenylethene (**5**) in 30 ml of THF was treated at −90°C and over 15 min with 30 ml (45 mmol) of a 1.5 M solution of *t*-butyllithium in pentane. The stirring was continued for an additional 30 min and then the solution was allowed to warm up to −70°C. At this temperature the mixture was quenched with a solution of 5 ml (53 mmol) dimethyl sulphate in 10 ml THF. The excess of dimethyl sulphate was destroyed by stirring with aqueous ammonia at r.t. The organic layer was separated, washed with 2 M hydrochloric acid, saturated sodium hydrogencarbonate solution, and brine. After drying over magnesium sulphate and removing the solvent, the residue was recondensed in a cooled trap. The following products were found by gas chromatographical investigation: 56 mg (0.3 mmol) of 1,1-diphenyl-1-propene (**7**), 141 mg (0.9 mmol) of 1,1-diphenyl-2-methyl-1-propene (**8**), 382 mg (2.2 mmol) of tolane (**22**), and 870 mg (3.2 mmol) of 2-bromo-1,1-diphenyl-1-propene (**21**).

See above for spectroscopical data of 1,1-diphenyl-1-propene (**7**) and 1,1-diphenyl-2-methyl-1-propene (**8**). Tolane (**22**) [17]: MS (70 eV): m/z 179 (15), 178 (M +, 100), 177 (11), 176 (22), 152 (18), 151 (12), 89 (12), 76 (16), 51 (14), 50 (14).

2-Bromo-1,1-diphenyl-1-propene (**21**) [18]: MS (70 eV): m/z 274 (18) 272 (M^+, 18), 193 (11), 178 (25), 165 (16), 115 (100), 91 (23), 51 (28), 50 (14), 39 (14). ^{1}H-NMR (80 MHz, $CDCl_3$): δ 2.38 (s, 3 H, methyl), 7.25 (m, 10 H, aromatic H).

*2.7. Reaction of 1,1-dibromo-2,2-diphenylethene **(5)** with t-butyllithium and warming to −10°C*

A sample of 3.38 g (10 mmol) 1,1-dibromo-2,2-diphenylethene (**5**) were treated with 30 ml (45 mmol) of a 1.5 M solution of *t*-butyllithium in pentane, as described above. The solution was allowed to warm to −10°C over a period of 2 h. Then the solution was cooled down to −70°C, quenched with dimethyl sulphate, and the work-up was performed as usual. The following products were detected by gas chromatographic investigation: 170 mg (0.9 mmol) of 1,1-diphenyl-1-propene (**7**) and 780 mg (3.5 mmol) of (*Z*)-4,4-dimethyl-2,3-diphenyl-2-pentene (**23**).

See above for spectroscopical data of 1,1-diphenyl-1-propene (**7**), see next experiment for spectroscopical data of (*Z*)-4,4-dimethyl-2,3-diphenyl-2-pentene (**23**).

*2.8. Confirming the formation of (Z)-4,4-dimethyl-2,3-diphenyl-2-pentene **(23)***

A solution of 1.78 g (10 mmol) of tolane (**22**) in 50 ml of THF was treated at −70°C over 30 min with 30 ml (45 mmol) of a 1.5 M solution of *t*-butyllithium in pentane. After stirring for an additional 30 min the solution was quenched with dimethyl sulphate and worked-up as usual. Yield: 1.35 g (5.4 mmol) (*Z*)-4,4-dimethyl-2,3-diphenyl-2-pentene (**23**) m.p. 50.5–51°C. MS (70 eV): m/z 250 (M^+, 32), 178 (30), 157 (68), 145 (34), 115 (99), 105 (52), 91 (100), 51 (31), 41 (53), 39 (28). –$C_{19}H_{22}$ (250.38): calcd. C 91.14, H 8.86; found: C 91.32; H 8.88. ^{1}H-NMR (80 MHz, $CDCl_3$): (1.28 (s, 9 H, *t*-butyl), 2.28 (s, 3 H, methyl), 6.90 (m, 5 H, aromatic H). The (*Z*)-structure was confirmed by NOE-difference spectroscopy (*t*-butyl/methyl).

*2.9. Reaction of 1,1-diphenyl-2,2-bis(trimethylstannyl)-ethene **(24)** with n-butyllithium*

A solution of 2.53 g (5 mmol) of 1,1-diphenyl-2,2-bis(trimethylstannyl)ethene (**24**) [19] in 20 ml of THF was treated at −90° with 40 ml (65 mmol) of a 1.6 M solution of *n*-butyllithium in hexane. After warming up to −55°C, the stirring was continued for 24 h. The solution was again cooled to −70°C. At this temperature the mixture was quenched with a solution of 10 ml (105 mmol) of dimethyl sulphate in 20 ml of THF. The excess of dimethyl sulphate was destroyed by stirring with aqueous ammonia at ambient temperature. The organic layer was separated, washed with 2 N hydrochloric acid, saturated sodium hydrogencarbonate solution, and brine. After drying over magnesium sulphate and removal of the solvent, the residue was recondensed in a cooled trap. The following products were found by gas chromatographic investigation: approx. 2.4 g tetrabutyltin, 0.17 g (0.9 mmol) 1,1-diphenyl-1-propene (**7**), 0.365 g (1.8 mmol) 1,1-diphenyl-2-methyl-1-propene (**8**) and 0.44 g (2.0 mmol) 1-(2-methylphenyl)-2-methyl-1-phenyl-1-propene (**25**).

See above for spectroscopic data of 1,1-diphenyl-1-propene (**7**) and 1,1-diphenyl-2-methyl-1-propene (**8**). 1-(2-Methylphenyl)-2-methyl-1-phenyl-1-propene (**25**): MS (70 eV): m/z 222 (M^+, 50), 207 (13), 180 (16), 179 (100), 178 (37), 165 (23), 129 (39), 128 (21), 115 (28), 91 (27). ^{1}H-NMR (200 MHz, $CDCl_3$): δ 1.59 (s, 3 H, *Z*-allyl), 1.88 (s, 3 H *E*-allyl), 2.12 (s, 3 H, tolyl), 7.20 (m, 9 H, aromatic H).

3. Results and discussion

When a diluted solution of 1,1-dibromo-2,2-diphenylethene (**5**) in THF is added slowly at −70°C to a solution of the freshly prepared radical anion lithium-di-*t*-butylbiphenyl (LDBB) [7] in THF, 1,1-dilithio-2,2-diphenylethene (**14**) is obtained in a yield of 36%. The dilithio compound was characterized by quenching with dimethyl sulphate to yield 2-methyl-1,1-diphenyl-1-propene (**8**).

However, the main product of this reaction is (*E*)-1-(2-methylphenyl)-1-phenyl-1-propene (**9**) in a yield of more than 50%, a derivative of (*E*)-1-lithio-2-(2-lithiophenyl)-2-phenylethene (**13**). The latter is formed from 1,1-dilithio-2,2-diphenylethene (**14**) by a 1,4-proton shift.

Nearly the same product mixture is observed when the reaction of 1,1-dibromo-2,2-diphenylethene (**5**) is performed with lithium dust at −110°C in a mixture of THF, diethylether, and pentane, the so-called Trapp mixture [20]. Besides 29% of 2-methyl-1,1-diphenyl-1-propene (**8**) and 5% of (*E*)-1-(2-methylphenyl)-1-phenyl-1-propene (**9**) the following compounds could be identified: 1% of 1,1-diphenylethene (**6**), 7% of 1,1-diphenyl-1-propene (**7**), 1% of (*Z*)-1-(2-methylphenyl)-1-phenyl-1-propene (**10**) as well as 24% of 2,2,5,5-tetraphenyl-3-hexyne (**11**) and 2% of (*E*)-2,2,5,5-tetraphenyl-3-hexene (**12**) in the residue are obtained by quenching with dimethyl sulphate (Scheme 2).

On first sight it is surprising that the (*E*)-dilithio compound **13** is the product of the rearrangement and not the (*Z*)-dilithio compound **15**, because only the latter can adopt the more stable [21] bridged structure.

Only an intramolecular rearrangement can explain the formation of the (*E*)-isomer **13**, thus proving the existence of the *gem*-dilithio compound **14**. The formation of a QUADAC under these conditions of course is not possible, because reactions between LDBB and halides are similar to the direct lithium–halogen exchange employing lithium metal.

As a result of the experiments described above, we may keep in mind that in the case of successful formation of the *gem*-dilithioalkene **14**, (*E*)-1-lithio-2-(2-lithiophenyl)-2-phenylethene (**13**) is always present as a follow-up product, and so **13** indicates the intermediate formation of the *gem*-dilithioalkene **14**.

At higher temperatures an isomerization of (*E*)-1-lithio-2-(2-lithiophenyl)-2-phenylethene (**13**) into the (*Z*)-compound **15** is observed. This isomerization is almost complete after 2 h at −25°C. Thus, stirring for 2 h at −25°C before quenching with dimethyl sulphate affords 22% of (*Z*)-1-(2-methylphenyl)-1-phenyl-1-propene (**10**) as the main volatile product. Under these reaction conditions 2-methyl-1,1-diphenyl-1-propene (**8**) is not detected (Scheme 3).

2,2,5,5-Tetraphenyl-3-hexyne (**11**) is formed by the addition of 1,1-dilithio-2,2-diphenylethene (**14**) to the carbenoid intermediate **16** and quenching the resulting dilithio compound **17** with dimethyl sulphate (Scheme 4).

(*E*)-2,2,5,5-Tetraphenyl-3-hexene (**12**) is a product of a different type of dimerization and is formed via dimerization of monoprotonated **14**, followed by quenching with dimethyl sulphate, a reaction which was independently proved starting with 1-lithio-2,2-diphenylethene (**18**) and *t*-butyllithium or lithium as electron donor catalyst (Scheme 5).

Next, we will discuss the investigation of the system 1,1-dibromo-2,2-diphenylethene (**5**)/*t*-butyllithium: a solution of **5** in THF was treated with a more than stoichiometric amount of *t*-butyllithium (1:4.5) in pentane at −90°C and after 30 min with an excess of dimethyl sulphate at −70°C. Three percent of 1,1-diphenyl-1-propene (**7**), 9% of 2-methyl-1,1-diphenyl-1-propene (**8**), 22% of tolane (**22**), and 32% of 2-bromo-1,1-diphenyl-1-propene (**21**) have been obtained (Scheme 6).

Tolane (**22**) is formed via Fritsch–Buttenberg–Wiechell rearrangement of the carbenoid **16** [22] (Scheme 7).

In a further experiment under the same conditions, the mixture was allowed to warm to −10°C before quenching with dimethyl sulphate at −70°C. Only two volatile products were formed: 9% of 1,1-diphenyl-1-propene (**7**) and 35% of (*Z*)-4,4-dimethyl-2,3-diphenyl-2-pentene (**23**). The latter was formed by the known addition of *t*-butyllithium to tolane (**22**) [21] and reaction of the resulting lithium compound with dimethyl sulphate (Scheme 8).

In both experiments (*E*)-1-(2-methylphenyl)-1-phenyl-1-propene (*9*) could not be detected. This and the fact that (*Z*)-1-(2-methylphenyl)-1-phenyl-1-propene (**10**) was also not found after warming-up the reaction mixture is an indication for a stepwise formation of

2-methyl-1,1-diphenyl-1-propene (**8**) via the corresponding QUADAC **20** [4] in the first experiment of this section.

At last we asked whether our method of distinguishing between a true *gem*-dilithioalkene and a QUADAC is working also in the case of tinorganic compounds as precursor. A solution of 5 mmol of 1,1-diphenyl-2,2-bis(trimethylstannyl)-ethene (**24**) in THF was treated with 65 mmol of a 1.6 M solution of *n*-butyllithium in hexane at −90°C. The high excess of *n*-butyllithium is necessary, because the methyl groups of the trimethylstannyl substituents have to be substituted by butyl groups as well. On the other hand, methyllithium would be even less reactive for a double tin lithium exchange. After stirring for 24 h at −55°C, the mixture was quenched with dimethyl sulphate. The usual work-up yielded 18% of 1,1-diphenyl-1-propene (**7**), 35% of 2-methyl-1,1-diphenyl-1-propene (**8**), and 40% of 2-methyl-1-(2-methylphenyl)-1-phenyl-1-propene (**25**). (*E*)-1-(2-methylphenyl)-1-phenyl-1-propene (**9**) was not detected. That means that **8** is formed from the QUADAC **26** by a stepwise reaction and not via the *gem*-dilithioalkene **14** (Scheme 9).

These results showed us that the method for discrimination described above is also working in the case of tinorganic compounds as starting material. The formation of 2-methyl-1-(2-methylphenyl)-1-phenyl-1-propene (**25**) can be explained as a direct methylation of the lithiated ate-complex **27** (Scheme 10).

4. Conclusion

Our method shows a possibility to discriminate QUADACs from real *gem*-dilithioalkenes in the case of substituted diphenylethenes. Experiments [23] expanding these results to other systems, will be described in a further paper.[1]

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