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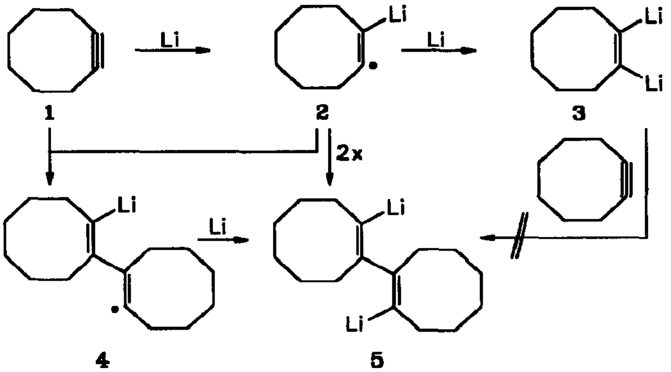
2,2′-Dilithio-1,1′-bicyclooctenyl: Synthesis and Reactions with Electrophiles

Adalbert Maercker and Ulrich Girreser*
Institut für Organische Chemie der Universität Siegen, D-57068 Siegen (Germany)

Abstract: Reaction of cyclooctyne (1) with commercially available lithium sand affords the 1,4-dilithio-1,3-butadiene derivative 5 in 57% yield. Upon treatment with sulphur dichloride the thiophene derivative 6 is formed. When using methyl iodide as electrophile an interesting lithium iodine exchange takes place to the vinyl iodide 7, which allows further functionalization of the 1,1′-bicyclooctenyl framework.

1,4-Dilithio-1,3-butadienes permit easy access to heterosubstituted 5-membered aromatic rings.[1] The first member of this interesting class of compounds, 1,4-dilithio-1,2,3,4-tetraphenyl-1,3-butadiene, was obtained already 65 years ago by Schlenk and Bergmann when reacting diphenylacetylene with lithium metal in diethyl ether.[2] Cyclooctyne (1) reacts with very reactive lithium dust in diethyl ether to (Z)-1,2-dilithiocyclooctene (3)[3], as by-product the dimer 5 with a stabilized doubly bridged structure[ref. 76 in [1]] is formed (entry 1 in the table overleaf). Studying the formation of 5 we found that the yield remarkably increases by either the use of an unpolar solvent like cyclopentane (entry 2)[ref. 10 in [3]] or by using less reactive lithium sand (entry 3). 5, however, is neither formed by reacting the dilithioalkene 3 with the starting alkyne 1 (entry 4) nor by using equimolar amounts of lithium metal (entry 5), thus demonstrating the intermediacy of the radical anion 2.



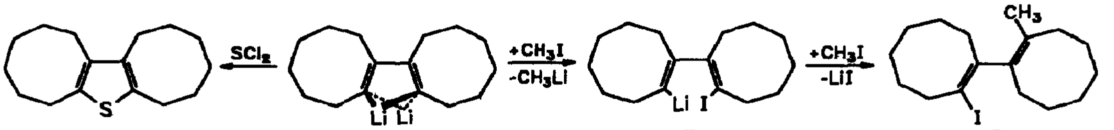
Upon quenching of a solution of 5 in diethyl ether with sulphur dichloride (purified by distillation with phosphorous trichloride[4]) 1,2,3,4,5,6,8,9,10,11,12,13-dodecahydrodicycloocta[b,d]thiophene (6) is formed as the main product (44 %),[5] which is characterized by ^{1}H NMR, ^{13}C NMR, and mass spectral data.[6] Besides 32% of non-volatile material, GC/MS analysis suggested the formation of the following compounds: cyclooctathione (2%), 1-chlorothio-1-cyclooctene (2%), 1-chloro-2-chlorothio-1-cyclooctene (1%), 2-chloro-1,1′-bicyclooctenyl (2%), 2,2′-dichloro-1,1′-bicyclooctenyl (1%), 1,2,3,4,5,6,8,9,10,11,12,13-dodecahydro[b,e]-1,4-dithiine[6] (2%); 14% not identified.

Table: Hydrocarbons obtained upon derivatization with methanol-d_1 and dimethyl sulfate (entry 2) under various conditions as determined by GC/MS coupling using n-dodecane as internal standard (yields in %).

entry	reaction conditions	1	3	5	not identified	non-volatile
1	-40°C, excess lithium dust[a]	-	72 (92%d_2,6%d_1,4%d_0)	22 (90%d_2,6%d_1,4%d_0)	-	6
2	-10°C, excess lithium dust[b]	5	15 (87%Me_2,13%Me_0)	61 (82%Me_2,12%Me_1,6%Me_0)	-	19
3	addition of 1 equivalent of 1[a]	7	14 (69%d_2,15%d_1,16%d_0)	23 (86%d_2,10%d_1,4%d_0)	6	50
4	as in entry 1, excess lithium sand[a,c]	12	10 (80%d_2,12%d_1,8%d_0)	57 (92%d_2,7%d_1,1%d_0)	-	21
5	using 1 equivalent of lithium dust[a]	66	10 (87%d_2,9%d_1,4%d_0)	13 (90%d_2,6%d_1,4%d_0)	-	11

[a] in diethyl ether as solvent, [b] in cyclopentane as solvent, [c] commercially available (Metallgesellschaft)

Upon derivatization of **5** with methyl iodide, the corresponding 2,2′-dimethyl-1,1′-bicyclooctenyl[ref. 10 in [3]] could not be isolated. Instead, vinyl iodide **8** is the main product (28%),[7] presumably formed through the intermediate **7**,[8] which does not eliminate lithium iodide through an intramolecular pathway. The formation of methyllithium was proved by adding trimethylsilyl chloride to the reaction mixture and the detection of tetramethylsilane by GC/MS coupling.



6 **5** **7** **8**

References and Notes

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4. Steudel, R.; Jensen, D.; Plinke, B. *Z. Naturforsch.* **1987**, *42B*, 163-168.
5. For a different approach to thiophenes starting from cycloalkynes see: Krebs, A.W.; Franken, E.; Müller, M.; Cholcha, W.; Wilken, J.; Ohrenberg, J.; Albrecht, R.; Weiss, E. *Tetrahedron Lett.* **1992**, *33*, 5947-5950.
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7. Experimental: A solution of **5** in diethyl ether was prepared starting from 4.5 g (42 mmol) of **1** and an excess of commercially available lithium sand (Metallgesellschaft) at -15°C as described before.[ref. 11 in [3]] To this mixture a solution of 15.0 g (106 mmol) of methyl iodide in diethyl ether was added at -40°C. After the workup **8** was isolated by bulb to bulb destillation, several washings with a diluted sodium thiosulfate solution, filtration through basic alumina and fractional distillation: 2.1 g (5.9 mmol) of a light-sensitive oil, b.p. 140-150°C (0.002 Torr). ^{1}H NMR (80 MHz, $CDCl_3$): δ 1.57 (m, 16 H, methylene), 1.64 (s, 3H, methyl), 2.25 (m, 6H, allyl), 2.80 (m, 2H, allyl vicinal to I). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.9, 140.3, 130.4, 100.6, 40.9, 33.6, 32.0, 31.9, 30.2, 29.6, 28.1, 27.9, 27.3, 27.1, 26.2, 25.5, 20.3. MS (70 eV): m/z 358 (M^+, 51), 232(100), 149(42), 135(53), 94(47), 72(53), 68(53), 56(42), 41(32).
8. Methylene iodide has been used for the synthesis of iodides starting from the corresponding organolithium compounds: Gay, R.L.; Crimmins, T.F.; Hauser, C.R. *Chem. & Ind.* **1966**, 1635.

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