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3,3,3',3'-TETRAMETHYL-2,2'-BISTRIMETHYLSILYL-1,1'-BICYCLOPROPENYL: SYNTHESIS AND ISOMERIZATION

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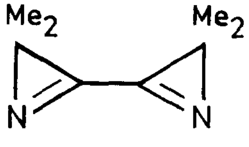
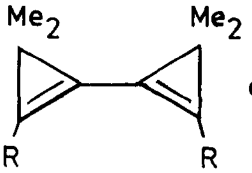
Summary: Oxidative dimerization of the cuprate 4 afforded a 30% yield of the 1,1'-bicyclopropenyl derivative 2a, which was converted thermally or by silver(I) ions to the octa-2,6-dien-4-yne 6b.

Thermal, photochemical and catalyzed isomerizations of 3,3'-bicyclopropenyl derivatives have been the object of intensive studies.[1-4] Recently, several 1,3'-bicyclopropenyls have been obtained by Padwa and his group, and the thermal and photochemical ring-opening reactions of these compounds have been investigated.[5] Although there have been promising attempts towards the synthesis of 1,1'-bicyclopropenyls,[6,7] derivatives of this ring system have to the best of our knowledge not been isolated so far. The 2,2'-bisazirinyl 1, however, has been found to be stable at room temperature.[8] Herein we report on the synthesis of 1,1'-bicyclopropenyl 2a and on the results of some isomerisation reactions of 2a.

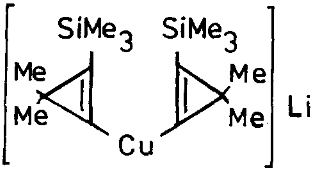


1



2

a: R = $SiMe_3$
b: R = H



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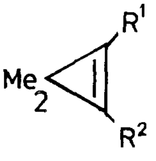


3

3	a	b	c	d
R^1	H	Li	$SiMe_3$	Li
R^2	H	H	H	$SiMe_3$

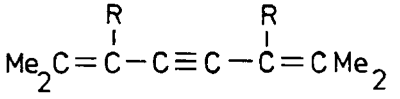
$[CuI \cdot P(n\text{-}Bu)_3]_4$

5

The silane 3c, obtained from 3a[9] via 3b and chlorotrimethylsilane in 85% yield, was metalated by lithium diisopropylamide in ether at -25°C to give 3d, which was converted to the cuprate 4 by addition of 0.125 equiv. of complex 5. Oxidation of 4 with oxygen[10] at -78°C, followed by aqueous workup and distillation of the oily residue of the organic phase at 40-50°C (0.05 torr), afforded a 30% yield of **2a** as a crystalline solid (mp 41°C), the spectroscopic data of which are in accord with structure **2a**: IR (KBr): 1677 cm^{-1} (C=C). ^1H NMR ($CDCl_3$): δ 0.18 and 1.18 (2 s of intensity 3:2). ^{13}C NMR ($CDCl_3$): δ -0.94 (q, $(CH_3)_3Si$), 20.87 (s, C-3), 27.11 (q, CH_3), 129.54 and 134.60 (2 s, C-2 and C-1). MS (70 eV): m/e 278 (74%, M^+).

The trimethylsilyl groups seem to be essential for the stability of **2a**. The attempt to desilylate **2a** with cesium fluoride in DMSO-d_6 at 25°C led to the formation of 2,7-dimethylocta-2,6-dien-4-yne (**6a**)[7,11] as the sole product. Likewise, when the reaction sequence giving rise to **2a** was carried out with **3a** instead of **3c**, only **6a** was isolated in 10% yield. Presumably, in both reactions **2b** is formed but rearranges to **6a** under the reaction conditions.

A solution of **2a** in benzene-d_6 sealed in an NMR tube remained unchanged after heating in a 90°C-bath for 10 min. When **2a** was distilled at 0.05 torr through a quartz tube kept at 400°C, **6b** was obtained as the only product. **6b** was also formed along with some polymeric material, when a solution of **2a** in ether was irradiated with a 150 W high-pressure mercury lamp for 5 hours. In addition, **2a** was spontaneously and quantitatively isomerized to **6b** by a solution of silver tetrafluoroborate in CCl_4.



$Me_2C=\overset{R}{\overset{|}{C}}-C\equiv C-\overset{R}{\overset{|}{C}}=CMe_2$

6

a: R = H
b: R = $SiMe_3$

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