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Preparation and Some Properties of 7,7-Dilithionorbornane

Cornelis P. Vlaar and Gerhard W. Klumpp*

Scheikundig Laboratorium Vrije Universiteit, De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands

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Abstract: 7,7-Dilithionorbornane 4a is formed from 7,7-dibromonorbornane 4b by reduction with 4.5 equiv of lithium p,p'-di-text-butylbiphenyl at -100 C, at which temperature it adds to ethylene. On warming it rearranges to 1-lithio-5-(2-lithioethyl)cyclopentene 5.

Our simple procedure for the generation of THF solutions of R_2CLi_2-2 LiHal, exhaustive reduction of R_2CHal_2 by lithium p,p'-di-*tert*-butylbiphenyl¹ (LiDBB), shows promise as a complement or alternative of existing more demanding routes to gem-dilithioalkanes.² So far we have prepared bis(trimethylsilyl)-stabilized $1^{3,4a}$, diphenyl-stabilized 2^{4b} and dilithiomethane $3^{4c,5}$. We now report the preparation of an unstabilized aliphatic geminal dilithium compound, 7,7-dilithionorbornane 4a.

$\mathbf{K}_2 \mathbf{C} \mathbf{L} \mathbf{I}_2$	$R^{2} \sim R^{1}$		я	b	с	d	e	f	ø	h	i	i	k	1
$1 \cdot R = Me_Si$	·· X ··			~	•		•	-	8	••	•	3		•
1 . D DL		R'	Li	Br	D	D	COOCH ₃	CH ₃	COOCH ₃	CH ₃	Li	CH ₂ CH ₂ D	Br	Li
$\mathbf{Z}; \mathbf{K} = \mathbf{P}\mathbf{\Pi}$		-2							- 2	. 5				
3: R = H		R″	Li	Br	D	Н	COOCH ₃	CH_3	Н	Н	Н	D	D	Br

In a typical experiment 4.5 equiv of LiDBB (THF, 0.45 M) was added slowly by syringe to a stirred solution of 7,7-dibromonorbornane **4b** in diethyl ether at -100 °C. After stirring for an additional 10 minutes at -100 °C the reaction mixture was quenched with CH₃OD to give after usual work-up an 85-100% yield^{6a} of a mixture containing **4c** (85-90%) and **4d** (10-15%). Quenching with CO₂ followed by acid-work-up and esterification with diazomethane gave the diester **4e** (85-90%)^{6b} and addition of excess dimethyl sulfate led to 7,7-dimethylnorbornane **4f** (75%)^{6b}. Based on our earlier studies^{4a-c}, the formation of **4c**, **e**, **f** is taken to reflect the formation of **4a** from **4b**. The disubstitution products were accompanied by 7-deuterionorbornane **4d**, 7-carbomethoxynorbornane **4g** (10-15%)^{6b} and 7-methylnorbornane **4h** (25%)^{6b}, respectively, which arise from 7-lithionorbornane **4i** that is formed by the reaction of **4a** or one of the intermediates leading to **4a** with the solvent. Extensive reaction of **4a** with the solvent takes place upon warming to 0 °C. Subsequent quenching with CH₃OD gave almost no dideuteronated norbornane **4c** while 7-deuterionorbornane **4d** was found in 40%^{6a} yield. Besides reaction with the solvent, warming of **4a** gave rise to ring opening, resulting in dilithioethylcyclopentene **5** (eq. 1), as shown by the formation of strain in the norbornane skeleton



and charge repulsion on C-7. The fact that 7-lithionorbornane 4i does not undergo ring opening is indicative of the charge effect. The enhanced reactivity of 4a as compared to 4i is also apparent in its reactivity towards ethylene:⁷ at -100 °C 4a adds to ethylene leading to the 1,3-dilithioalkane 6 (eq. 2, CH₃OD \rightarrow 54% ^{6a} 4j), member of a class of lithium compounds that is accessible by other means only with difficulty.⁸ Under the same conditions 4i is unreactive. With adamantanone, 4a formed the olefin 7⁹ (40 % ^{6a}, eq. 3).



Successful reduction of R_2CHal_2 by our method depends on the stability of the intermediate carbenoid $R_2CLiHal^{4b}$. When, under the conditions given above, **4b** was treated with 2 equiv of LiDBB, the only product found after deuterolysis was **4k**, indicating that the carbenoid **4l** is stable under the reaction conditions. By contrast, when di-*tert*-butyldibromomethane was reacted with 4 equiv of LiDBB under the conditions given above, no *gem*-dilithium compound was formed. The intermediate carbenoid eliminated LiBr and carbene rearrangement led to dimethyl-*tert*-butylcyclopropane (eq. 4).



In the case of 2,2-dibromoadamantane a carbenoid of intermediate stability is generated by LiDBB. Besides 2,2-dilithioadamantane, evidenced by its deuterolysis product, 2,2-dideuterioadamantane $(43\%^{6a})$, the carbene coupling product adamantylideneadamantane was found (*ca.* 45%).

In conclusion: together, our earlier studies^{4a-c} and the present work show that the $R_2CHal_2-LiDBB$ reaction affords *gem*-dilithioalkanes in good yields if the intermediate carbenoid $R_2CLiHal$ is stable under the reduction conditions. In these cases, their easy availability now sets the stage for comprehensive study of *gem*-dilithioalkanes dissolved in THF containing LiHal.

References and note

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