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ON THE INTERMEDIACY OF 3-tert-BUTOXY-1,2-DEHYDROQUADRICYCLANE

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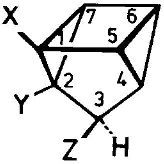
*Summary: The reaction of n-butyllithium with 3-tert-butoxy-2-chloroquadricyclane (**1j**) led to the 1-butyl-3-tert-butoxyquadricyclanes **8** and **9**. syn-3-tert-Butoxy-1,2-dehydroquadricyclane (**6b**) and the anti-isomer **7b** are proposed as intermediates.*

Whereas quadricyclane (**1a**) is metalated exclusively at C-1 by the *n*-BuLi/TMEDA complex [1,2], 3-quadricyclanol (**1b**) has been reported to give **1c** in high yield with two equiv. of 2-propyllithium [3]. In contrast, the kinetic acidity of position 1 (and 5) in 3-*tert*-butoxyquadricyclane (**1d**) is comparable to that of position 2 (and 4): **1d** and the BuLi/TMEDA complex in hexane led to a 1:1 mixture of **1e** and **1f**. This conclusion was reached after deuterium oxide addition to the **1e**/**1f** mixture, isomerization of the deuterated quadricyclanes **1g** and **1h** with the rhodium complex **3** to the mixture of the corresponding norbornadienes **2g** and **2h**, followed by ^{1}H NMR investigation of the product mixture. A higher selectivity towards C-2 lithiation was observed when BuLi in ether was used as a base for the metalation of **1d**. The above-mentioned work-up procedure led to a 1:4 mixture of **2g** and **2h**. Accordingly, the chlorination of the **1e**/**1f** mixture with p-toluenesulfonyl chloride [4] in THF afforded, depending on the metalating agent (BuLi/TMEDA in hexane or BuLi in ether) a 1:1 or, approximately, a 1:4 mixture of the chlorides **1i** and **1j** (total yield around 60%). The structures of **1i** and **1j** are based on the NMR spectra of the corresponding chloronorbornadienes **2i** and **2j**. These compounds were obtained by isomerization of **1i** and **1j** with **3** and were separated by preparative g. c. (column 6 m, Carbowax 20 M on kieselguhr, 150°C). Attempts to separate the chloroquadricyclanes **1i** and **1j** by g. c. were unsuccessful. However, the spinning band column distillation of the 1:4 mixture of **1i**/**1j** led to a fraction of **1j**, which only contained 5% of **1i**.



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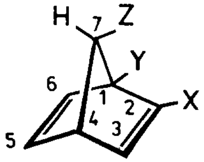

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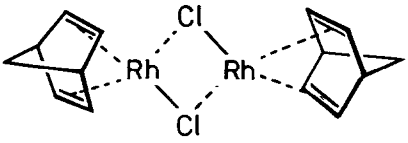
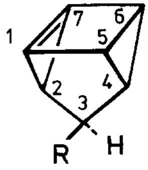


3

1, 2	a	b	c	d	e	f	g	h	i	j
X	H	H	Li	H	Li	H	D	H	Cl	H
Y	H	H	H	H	H	Li	H	D	H	Cl
Z	H	OH	OLi	O-t-Bu	O-t-Bu	O-t-Bu	O-t-Bu	O-t-Bu	O-t-Bu	O-t-Bu

We have recently found that 1-chloroquadricyclane on reaction with strong bases eliminates hydrogen chloride generating 1,7-dehydroquadricyclane (4a) as a reactive intermediate, which can be trapped by nucleophiles and 1,3-dienes. In addition, these investigations have revealed indications of the formation of 1,5-dehydroquadricyclane (5a) as a second reactive component. The isomeric bridgehead olefin 6a, however, could not be detected $^{1,2)}$.



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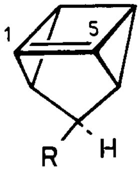

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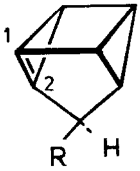

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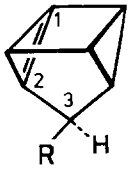


7

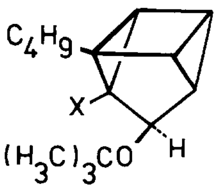
a: R = H

b: R = $OC(CH_3)_3$

The reaction of 1j with BuLi in ether provided clear evidence for the formation of 6b and 7b as short-lived species. When the mixture of 1j and 2.5 equiv. of BuLi after 20 h at room temperature was worked up with water a mixture of the butyl derivatives 8a and 9a was obtained (total yield 61%). This mixture was isomerized by 3 to a 5:1 mixture of 10a and 11a, which could be separated by preparative g. c. (Carbowax 20 M, 175°C). The structures of these norbornadienes followed from their ^{1}H NMR spectra. In accordance with the analyzed spectrum of 2d $^{5)}$ the signal of 3-H in **10** appeared at higher field than that of 3-H in **11** (δ 5.75 versus 5.90).

When the mixture of **1j** and 3.5 equiv. of BuLi in ether, after a reaction time of 10 h, was worked up with deuterium oxide, the ^1H NMR spectra of the separated 2-butyl-7-*tert*-butoxynorbornadienes showed that the respective 1-position was fully deuterated, as indicated in **10b** and **11b**. This result and the fact that **8** and **9** are products of a *cine* substitution $^{6)}$ form strong evidence for an elimination addition mechanism with the bridgehead olefins **6b** and **7b** as intermediates.

a: X = H
b: X = D



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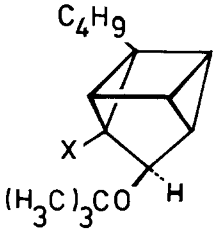

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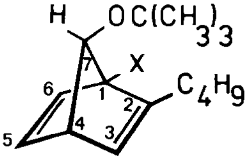
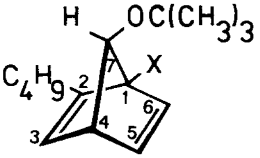


10



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The remarkably high regioselectivity of the BuLi addition to the CC double bonds of **6b** and **7b** probably results from a complexation of the lithium to the ether oxygen, which directs the butyl group to the more distant olefinic carbon atom.

So far, the chloride **1i** has not been obtained pure. However, the main path of its reaction with BuLi could be deduced from the result of the reaction of a 1:1 mixture of **1i** and **1j** with this base. After work-up with water or deuterium oxide and after isomerization of the quadricyclanes to the corresponding norbornadienes by the rhodium complex **3**, preparative g. c. separation of the product mixture afforded only **10a** and **11a** and **10b** and **11b**, respectively. The ratio of **10**:**11** was 8:1. The main course of the base promoted hydrogen chloride elimination from **1i**, therefore, proceeds via **6b**.

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Tab. 1. NMR Data of **1j**, **2i**, **2j**, **10a**, and **11a** [a)]

1j: ^{1}H NMR (CCl_4): δ = 1.29 (s; 9 H, CMe_3), 1.60-2.03 (m; 5 H), 4.52 (m; 1 H, 3-H). - ^{13}C NMR ($CCl_4/CDCl_3$): δ = 16.8 (d), 20.4 (d), 22.7 (d), 26.9 (d), 28.6 (q), 50.2 (s), 73.8 (s), 78.8 (d).

2i: ^{1}H NMR (CCl_4): δ = 1.12 (s; 9 H, CMe_3), 3.03 (m; 1 H, 1-H), 3.27 (m; 1 H, 4-H), 3.75 (m; 1 H, 7-H), 6.04 (m; 1 H, 3-H), 6.60 (m; 2 H, 5-H, 6-H). - ^{13}C NMR ($CCl_4/CDCl_3$): δ = 28.3 (q), 55.6 (d; C-4), 61.8 (d; C-1), 73.7 (s; $\underline{C}Me_3$), 103.2 (d; C-7), 128.3 (d; C-3), 138.0 and 139.3 (2 d; C-5 and C-6 in unknown order), 143.2 (s; C-2).

2j: ^{1}H NMR (CCl_4): δ = 1.13 (s; 9 H), 3.28 (m; 1 H, 4-H), 3.72 (m; 1 H, 7-H), 6.30 (m; 2 H, 2-H, 3-H), 6.52 (m; 2 H, 5-H, 6-H). - ^{13}C NMR ($CCl_4/CDCl_3$): δ = 28.4 (q), 55.1 (d; C-4), 74.2 (s; $\underline{C}Me_3$), 77.9 (s; C-1), 109.1 (d; C-7), 136.8, 138.2, 139.7, 142.8 (4 d; C-2, C-3, C-5, C-6 in unknown order).

10a: ^{1}H NMR (CCl_4): δ = 0.87-1.33 (m; 7 H, CH_3-CH_2-CH_2), 1.07 (s; 9 H, CMe_3), 2.12 (m; 2 H, CH_2), 2.93 (m; 1 H, 1-H), 3.15 (m; 1 H, 4-H), 3.58 (m; 1 H, 7-H), 5.75 (m; 1 H, 3-H), 6.47 (m; 2 H, 5-H, 6-H). - ^{13}C NMR ($CCl_4/CDCl_3$): δ = 13.9 (q), 22.3 (t), 28.4 (q), 29.4 (t), 31.1 (t), 55.0 (d), 58.7 (d), 73.1 (s), 102.7 (d), 127.1 (d), 139.0 (d), 140.3 (d), 152.3 (s). - In the ^{1}H NMR spectrum of **10b** the δ = 2.93 signal was lacking; in the proton decoupled ^{13}C NMR spectrum of **10b** instead of the δ = 58.7 singlet there appeared a 1:1:1 triplet of low intensity.

11a: ^{1}H NMR (CCl_4): δ = 0.87-1.24 (m; 7 H, CH_3-CH_2-CH_2), 1.05 (s; 9 H, CMe_3), 2.10 (m; 2 H, CH_2), 2.96 (m; 1 H, 1-H), 3.15 (m; 1 H, 4-H), 3.62 (m; 1 H, 7-H), 5.90 (m; 1 H, 3-H), 6.33 (m; 2 H, 5-H, 6-H). - In the ^{1}H NMR spectrum of **11b** the δ = 2.96 signal was lacking.

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a) Elemental analyses and mass spectra of these compounds are consistent with the proposed structures.

Literature:

1) J. Harnisch, O. Baumgärtel, G. Szeimies, M. Van Meerssche, G. Germain, and J.-P. Declercq, J. Am. Chem. Soc. **101**, 3370 (1979).

2) O. Baumgärtel and G. Szeimies, Chem. Ber. **116**, 2180 (1983). O.Baumgärtel, J. Harnisch, G. Szeimies, M. Van Meerssche, G. Germain, and J.-P. Declercq, Chem. Ber. **116**, 2205 (1983).

3) G. W. Klumpp, M. Kool, M. Schakel, R. F. Schmitz, and C. Boutkan, J. Am. Chem. Soc. **101**, 7065 (1979).

4) G. Szeimies, F. Philipp, O. Baumgärtel, and J. Harnisch, Tetrahedron Lett. **1977**, 2135.

5) E. I. Snyder and B. Franzus, J. Am. Chem. Soc. **86**, 1166 (1964).

6) For definition see P. Martin, H. Greuter, G. Rihs, T. Winkler, and D. Bellus, Helv. Chim. Acta **64**, 2571 (1981), and references therein.

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