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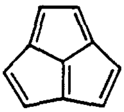
READY ACCESS TO BRIDGEHEAD OLEFINIC ISOMERS OF THE TRIQUINACENE SKELETON

Holger Butenschön and Armin de Meijere*

Institut für Organische Chemie und Biochemie der Universität
Martin-Luther-King-Platz 6, 2000 Hamburg 13

Abstract: 1-Halo- and 1,4-dihalotriquinacenes readily react with secondary amines and alkyl lithium compounds to yield bridgehead olefinic and double bridgehead olefinic derivatives of the tricyclo[5.2.1.0^{4,10}]decatriene system, probably by an S_N2' type attack of the soft nucleophile.

The long searched-for acepentalene (**1**) possesses the same carbon skeleton as triquinacene (**2**), and therefore the latter has been suggested as a potential precursor to **1** [1]. With regard to its thermodynamic stability **1** probably not only suffers from an unfavorable π-electronic system[2], but also from a considerable amount of bond and angle strain. Among the 16 isomeric tricyclo[5.2.1.0^{4,10}]decatrienes **2** is the only one without a bridgehead double bond. According to force field calculations[3] performed on the three isomeric monoolefins **3** - **5**[4] all other 15 isomers of **2** are predicted to be less stable than triquinacene (**2**). In fact, **3** was calculated to be 4.1 kcal/mol more stable than the bridgehead olefin **4**, and **4** in turn 12.2 kcal/mol more stable than the twofold bridgehead olefin **5**, in which all four substituents on the double bond must be bent out of plane.



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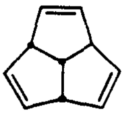

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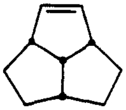

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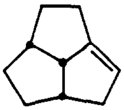

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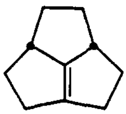

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ΔH_f(kcal/mole) 6.83 10.96 23.16

Under these circumstances it is of particular interest that bridgehead olefinic tricyclo[5.2.1.0^{4,10}]decatriene derivatives are readily accessible from the less strained triquinacene system. Reaction of bridgehead mono- and dihalo-triquinacenes **6**[5,6] with a number of secondary amines and with alkyl lithium reagents in general lead to the allyl-rearranged bridgehead olefinic derivatives **7** (see scheme 1 and table 1).

Scheme 1. (For conditions see table 1)

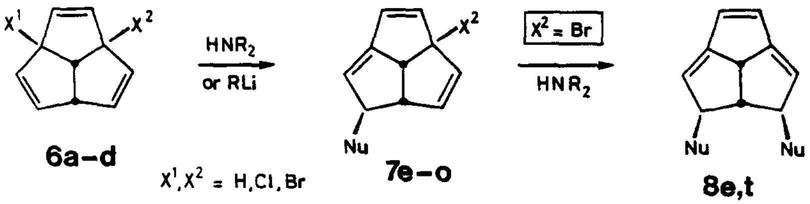

Table 1. Products[7], yields and conditions for reactions of halides **6** with secondary amines and alkyl lithium compounds.

Educt	X^1	X^2	Nucleophile	Product	Nu	Yield (%)	Conditions[*]
6a	Cl	H	dimethylamine	**7e**	NMe_2	35	I,II,III,IV
6a	Cl	H	piperidine	**7f**	$N(CH_2)_5$		II
6a	Cl	H	morpholine	**7g**	$N(CH_2)_2O(CH_2)_2$	89	II
6a	Cl	H	methyllithium	**7h**	Me	11	IV,V,VI
6a	Cl	H	*n*-butyllithium	**7i**	n-Bu	100	IV,VII
6b	Cl	Cl	dimethylamine	**7j**	NMe_2	38	I,IV,VIII
6b	Cl	Cl	piperidine	**7k**	$N(CH_2)_5$	91	II
6b	Cl	Cl	morpholine	**7l**	$N(CH_2)_2O(CH_2)_2$	53	II
6c	Br	H	*t*-butyllithium	**7m**	t-Bu	12	IV,IX,X
6c	Br	H	piperidine	**7f**	$N(CH_2)_5$	87	VIII
6d	Br	Br	dimethylamine	**7n**	NMe_2	96	I,XI
6d	Br	Br	dimethylamine	**8e**	NMe_2	95	I,II
6d	Br	Br	piperidine	**7o**	$N(CH_2)_5$	94	X
6d	Br	Br	piperidine	**8f**	$N(CH_2)_5$	97	XII

[*] I: Thick-wall closed reaction vessel. II: Neat, 5d, 25°C. III: Byproduct 10% 1-dimethylaminotriquinacene[8]. IV: Isolation by glc. V: *n*-Hexane/ether, N_2, 12h, 25°C. VI: Byproduct 3% 1-methyltriquinacene. VII: *n*-Hexane, N_2, 1h, -78°C. VIII: Neat, 3d, 25°C. IX: Byproduct 3% 1-*t*-butyltriquinacene. X: *n*-Hexane, N_2, 2h, -78°C. XI: Neat, 25min, 25°C. XII: Neat, 14d, 25°C.

Only 1,4-dibromotriquinacene (**6d**), not the dichloride **6b**, reacted with 2 equivalents of the secondary amine to give the interesting conjugated trienes **8** by a twofold allyl shift. The structural assignments of all compounds **7** and **8** could readily be made on the basis of their ^{1}H-nmr spectra[7] (see table 2). The unsubstituted tricyclo[5.2.1.0^{4,10}]-deca-1,5,8-triene was prepared for comparison according to a procedure developped by L.A. Paquette and J. Kramer[9]. The *exo*-configuration of compounds **7** and **8** follows from the coupling constants between the protons on C-3 and C-4, which were found to be smaller than 2.6 Hz in all cases, indicating a dihedral angle between 60 and 90°. In contrast the coupling constant ^3J between protons *exo*-3-H and 4-H in the unsubstituted compound[9] was 5.8 Hz, corresponding to a dihedral angle $<60°$.

Table 2. NMR-spectroscopic data of selected compounds **7** and **8**, δ_{TMS} in ppm, J in Hz

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7e ^{1}H-NMR (270 MHz, CDCl$_3$): 2.26(s, 6H, N(CH$_3$)$_2$), 3.03(mc, 4-H, $J_{3,4}$ = 2.2, $J_{4,5}$ = 1.8, $J_{4,6}$ = 1.9, $J_{4,10}$ = 5.7), 3.33(mc, 7-H, $J_{6,7}$ = 1.6, $J_{5,7}$ = 2.0, $J_{7,8}$ = 2.6, $J_{7,9}$ = 1.1, $J_{7,10}$ = 7.8), 3.60(dd, 3-H, $J_{2,3}$ = 3.4), 3.74(mc, 10-H, $J_{2,10}$ = 2.7, $J_{5,10}$ = 0.6, $J_{6,10}$ = 0.6), 5.24(dd, 2-H), 5.26(mc, 5-H, $J_{5,6}$ = 5.4), 5.43(ddd, 6-H), 6.04(dd, 8-H, $J_{8,9}$ = 4.7), 6.10(dd, 9-H).

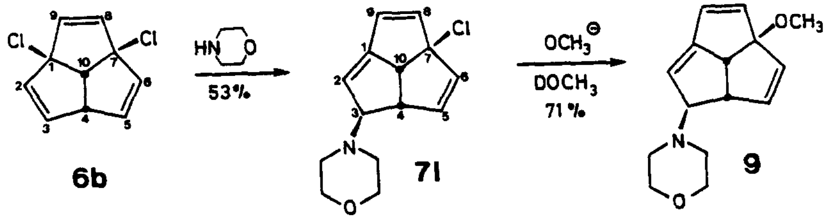
7i ^{1}H-NMR (270 MHz, CDCl$_3$): 0.89(t, 4'-H$_3$, $J_{3',4'}$ = 7.0), 1.32(m, 2'-H$_4$, 3'-H$_2$), 1.49(m, 1'-H$_2$, $J_{1',3}$ = 7.0), 2.79(ddt, 3-H, $J_{3,4}$ = 2.3, $J_{2,3}$ = 3.6), 2.86(ddd, 4-H, $J_{4,5}$ = 1.8, $J_{4,6}$ = 2.0, $J_{4,10}$ = 5.6), 3.39(mc, 7-H, $J_{5,7}$ = 2.1, $J_{6,7}$ = 1.1, $J_{7,8}$ = 2.8, $J_{7,9}$ = 1.1, $J_{7,10}$ = 7.8), 3.83(m, 10-H, $J_{2,10}$ = 2.5, $J_{5,10}$ = 0.6, $J_{6,10}$ = 0.6), 5.38(m, 5-H, $J_{5,6}$ = 5.4), 5.41(dd, 2-H), 5.56(dt, 6-H), 6.06(dd, 8-H, $J_{8,9}$ = 5.6), 6.19(dd, 9-H). - ^{13}C-NMR (67.89 MHz, CDCl$_3$): 14.07(q, C-4'), 22.94(t, C-3'), 30.64(t, C-2'), 35.05(t, C-1'), 51.66(d, C-3, $^1J_{C,H}$ = 142.0), 53.91(d, C-4, $^1J_{C,H}$ = 142.1), 56.79(d, C-10, $^1J_{C,H}$ = 131.9), 57.95(d, C-7, $^1J_{C,H}$ = 146.1), 122.46(d, C-8, $^1J_{C,H}$ = 167.4), 128.02(d, C-2, $^1J_{C,H}$ = 162.4), 128.08(d, C-5 or C-6, $^1J_{C,H}$ = 162.4), 136.32(d, C-5 or C-6, $^1J_{C,H}$ = 163.1), 139.38(d, C-9, $^1J_{C,H}$ = 164.4), 155.43(s, C-1).

7j ^{1}H-NMR (270 MHz, CDCl$_3$): 2.30(s, 6H, N(CH$_3$)$_2$), 3.28(mc, 4-H, $J_{3,4}$ = 2.2, $J_{4,5}$ = 1.9, $J_{4,6}$ = 2.2, $J_{4,10}$ = 5.2), 3.70(dd, 3-H, $J_{2,3}$ = 3.4), 3.89(mc, 10-H, $J_{2,10}$ = 2.6, $J_{5,10}$ = 2.2, $J_{6,10}$ = 1.9), 5.35(dd, 2-H), 5.50(ddd, 5-H, $J_{5,6}$ = 5.3), 5.60 (ddd, 6-H), 6.10(d, 8-H, $J_{8,9}$ = 5.6), 6.28(d, 9-H). - ^{13}C-NMR (15.08 MHz, CDCl$_3$): 41.67(N(CH$_3$)$_2$), 43.74(C-4), 46.85(C-10), 69.24(C-3), 79.33(C-7), 118.28(C-2 or C-8), 129.15(C-2 or C-8), 129.41(C-5 or C-6), 137.17(C-5 or C-6), 142.22(C-9), 155.93(C-1).

Tricyclo[5.2.1.0^{4,10}]deca-1,5,8-triene ^{1}H-NMR (270 MHz, CDCl$_3$): 2.55(ddd, endo-3-H, $J_{endo-3,4}$ = 2.0, $J_{2,endo-3}$ = 3.7, $J_{endo-3,exo-3}$ = -16.6), 3.00(dm, exo-3-H, $J_{exo-3,4}$ = 5.8, $J_{2,exo-3}$ = 3.7), 3.16(dq, 4-H, $J_{4,5}$ = 2.0, $J_{4,6}$ = 2.0, $J_{4,10}$ = 5.8), 3.45(m, 7-H, $J_{5,7}$ = 1.9, $J_{6,7}$ = 1.8, $J_{7,8}$ = 2.8, $J_{7,9}$ = 0.5, $J_{7,10}$ = 8.7), 3.78(m, 10-H, $J_{2,10}$ = 2.2, $J_{6,10}$ = 0.6), 5.37(dt, 2-H), 5.41(dt, 5-H, $J_{5,6}$ = 5.4), 5.54(dt, 6-H), 6.07(dd, 8-H, $J_{8,9}$ = 5.7), 6.21(dd, 9-H). - ^{13}C-NMR (67.89 MHz, CDCl$_3$): 42.73(t, C-3, $^1J_{C,H}$ = 130.2), 47.72(d, C-4, $^1J_{C,H}$ = 140.8), 52.01(d, C-7, $^1J_{C,H}$ = 147.7), 59.92(d, C-10, $^1J_{C,H}$ = 128.0), 117.94(d, C-2, $^1J_{C,H}$ = 161.4), 127.91(d, C-8, $^1J_{C,H}$ = 167.4), 128.43(d, C-5 or C-6, $^1J_{C,H}$ = 162.7), 136.09(d, C-5 or C-6, $^1J_{C,H}$ = 163.4), 139.16 (d, C-9, $^1J_{C,H}$ = 165.4), 155.87(s, C-1).

8e ^{1}H-NMR (270 MHz, C$_6$D$_6$): 2.25(s, 12H, N(CH$_3$)$_2$), 2.34(dt, 4-H, $J_{3,4}$ = $J_{4,5}$ = 1.8, $J_{4,10}$ = 7.1), 3.74(ddd, 3-H, 5-H, $J_{2,3}$ = $J_{5,6}$ = 3.2) 4.04(dtt, 10-H, $J_{2,10}$ = $J_{6,10}$ = 2.4, $J_{3,10}$ = $J_{5,10}$ = 1.8), 5.02(dd, 2-H, 6-H), 6.26(s, 8-H, 9-H).

The exclusive formation of products **7** and **8** can only be rationalized on the basis of the HSAB principle[10], since mono- and dihalo-triquinacenes **2** react with hard nucleophiles such as hydroxide and methoxide to give bridgehead-substituted triquinacenes by ordinary S$_N$1 type reactions[5,8]. Softer nucleophiles such as secondary amines or lithium alkyls attack with predominating orbital instead of charge control and therefore cause allyl rearrangement in spite of a bridgehead double bond being formed. It seems plausible that these bridgehead double bonds are stabilized to some extent by conjugative interaction with the neighboring double bond. The ruling of the HSAB principle was most convincingly demonstrated by consecutive reaction of 1,4-dichloride **6b** with morpholine and methoxide in CH_3OD. The initial product **7l** gave only **9** in the second step; no deuterium was incorporated, which excludes an elimination-addition sequence.



6b **7l** **9**

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References and footnotes:

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3 Force field calculations were carried out with the MM1 and MM2 programs, cf. N.L. Allinger, J. Am. Chem. Soc. **99**, 8127 (1977) and ref. cited therein.

4 MM1 calculations for **5** were performed by P. von R. Schleyer and W. Maier; P. von R. Schleyer and W. Maier, private communication.

5 Chlorides were prepared according to: D. Bosse and A. de Meijere, Chem. Ber. **111**, 2243 (1978).

6 Bromides were obtained by bromination of **2** with N-bromosuccinimide in CCl_4, cf. G.K. Agopian, Ph. D. thesis, Univ. of Calif. at Los Angeles, 1975.

7 All new compounds were fully characterized by their ^1H- and (in part) ^{13}C-nmr as well as ir, mass spectra and gave satisfactory elemental analysis and/or high resolution mass spectroscopic molecular weights.

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10 Cf. Tse-Lok Ho, Hard and Soft Acids and Bases Principle in Organic Chemistry, Academic Press, New York 1977.

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