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Stereoselectivity in Reactions of Bicyclo[3.3.0]oct-1-enes

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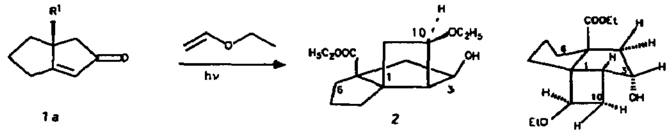
Abstract: The derivatives of trans-bicyclo[3.3.0]octane **3** and **6** have been obtained the bicyclo[3.3.0]oct-1-enes, sterically hindered at the exo-side, via photoinduced [2+2]cycloaddition of **1** with ethylvinyl ether and by hydroboration-oxidation of **5d**, respectively.

The synthesis of polyquinanes has uniquely been concerned with the construction of annulated cylopentanes where all bicyclo[3.3.0]octane subunits are cis-fused (cf. formula **7**)[1]. In contrast to the plethora of such compounds only a few examples of trans-bicyclo[3.3.0]octanes (cf. formula **4**) have been reported [2]. Recently we [3,4] and others [5-8] have reported the preparation of bicyclic and polycyclic polyquinanes containing a trans-fused bicyclo[3.3.3]octane substructure. Key step in these procedures was either the intramolecular olefin-enone-photocycloaddition [3,4] or the direct transformation of 1,6-dienes into bicyclics [5,6] or the reaction of bi- and tricyclic compounds containing a bridgehead double bond and sterically demanding groups on the concave side of the bicyclo[3.3.0]oct-1-ene substructure [7-9].

With **1a,b** in hand[10,11], we explored several reaction protocols with a strong propensity for stereoselectivity. The wealth of intermolecular, face-selective [2+2] cycloadditions between an enone and an olefin [13,14] and our experience that an intramolecular [2+2]cycloaddition at the endo-side of the bicyclo[3.3.0]oct-1-en-3-one substructure is a highly efficient process[3] lead us to explore the photoreaction of **1a** with ethylvinyl ether. After $NaBH_4$-$CeCl_3$ reduction of the four photoproducts, formed in a ratio of 1:1.3:1.5:1.5 the two adducts **2** and **3** could be isolated in a yield of 35 and 43%, respectively. Whereas **2** is clearly formed by a head-to-head addition of the olefin to the exo-side of **1**, the head-to-tail product **3** contains the trans configuration[15].

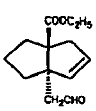


1a

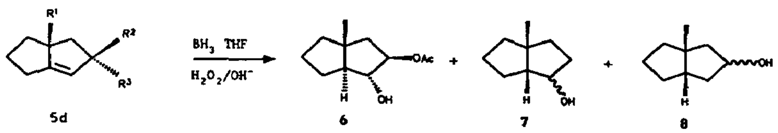
2

3

1 a) R^1= $COOC_2H_5$
b) R^1= CH_3



4



5d

6

7

8

a) R^1= $COOC_2H_5$,
R^2= H, R^3= OH
b) R^1= $COOC_2H_5$
R^2= H, R^3= OCH=CH_2

c) R^1= CH_3
R^2= H, R^3= OH
d) R^1= CH_3
R^2= OAc, R^3= H

Only **5a** rather than the expected trans-1,5-disubstituted bicyclo[3.3.0]octane **4** was observed, when **5b** was submitted to Griecos conditions[16] for the Claisen rearrangement[17]. The hydroboration of **5d**[18] with H_3B·THF provided after oxidation with H_2O_2 a complex mixture, from which **6** could be obtained in a yield of 26%[15]. In addition, a mixture of the cis-fused products **7** and **8** was obtained.

It is evident from these results and the literature cited that only a few procedures are known, which lead to trans-bicyclo[3.3.0]octanes. This is in contrast to the rather high number of synthetic routes to trans-bicyclo[4.3.0]nonanes (trans-hydrindanes)[20].

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15. The structures **2** and **3** as well as of **6, 7** and **8** were established by NMR spectroscopy. The configuration of **3** and **6** was determined by NOE-measurements. NMR data: [$^1H/^{13}C$ (δ[ppm], $CDCl_3$, J [Hz] side chains ommitted; sequence of data: *assignment*: $\delta(^{13}C)$; $\delta(^1H)$, multiplicity). NOE results: irradiated at **C(X)H$_{c,t}$**: signal enhancement at C(Y)$H_{x,t}$ with c=cis and t = trans to the bridgehead -CH_3 and -COOEt respectively.
    <u>NMR data of 3:</u> **C(1)**: 61.40(s); **C(2)**-H_c: 47.37(d), 2.20(m); **C(3)**H_c: 73.07(d), 4.25(dd); **C(4)**H_2: 46.42(t), 1.70(ddd, H_c), 2.52(dd, H_c); **C(5)**:68.67(s); **C(6)H$_2$**: 32.23(t), 1.95(m); **C(7)**H_2: 23,14(t), 1.55(m, H_t), 1.80(m, H_c); **C(8)**H_2: 37.62(t), 1.60(m,H_t), 2.20(m, H_c); **C(9)**H: 75.95(d), 3.75(t); **C(10)**H: 24.50(t), 1.90(m, H_t), 2.15(m, H_c); NOE results: **C(2)H$_c$**: C(3)H_c, C(10)H_c; **C(9)H**: C(10)H_t, **C(10)H$_t$**; C(9)H, C(10)H_c. HR-MS: 250.1569 (cal. 250.1707 for M^+-H_2O). GC-MS studies with chemical ionisation (CH_4, $(CH_3)_3CH$) [19] are consistent with the constitution of **2** and **3.**
    <u>NMR data of 6:</u> **C(1)**: 50.47(s); **C(2)H$_2$**: 40.90(t), 1.63(dd, 13.76, 1.2, H_c), 1.94(dd, 13.76, 9.01, H_t; **C(3)H$_t$**: 91.58(d), 4.95(ddd, 9.16, 1.2, 3.37); **C(4)H$_c$**: 78.66(d), 3.86(dd, 3.3, 11.0) **C(5)H$_t$**: 59.07(d), 1.88(ddd, 12.50, 11.03, 6.97); **C(6)H$_2$**: 20.6(t), 1.40(~ddd, 12.43, 10.26, 7.51), 1.68(m, H_t), **C(7)H$_2$**: 27.10(t), 2.05(m), **C(8)H$_2$**: 35.34(t), 1.25(m, H_t), 1.37(m, H_c) **C(9)H$_3$**: 19.89(q), 0.91(t, 0.88). - NOE results: **C(2)H$_c$**: C(2)H_t, C(3)H_t, C(4)H_c, C(9)H_3; **C(3)H$_t$**: C(2)H_c, C(4)H_c, C(5)H_t; **C(4)H$_c$**: C(3)H_t, C(6)H_c, C(9)H_3; **C(8)H$_t$**: C(2)H_t, C(5)H, C(8)H_c; **C(9)H$_3$**: C(2)H_c , C(4)H_c, C(8)H_c. - $C_{11}H_{18}O_3$: Calc. C 66.64, H 9.15; found C 66.64, H 9.06%.
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