240. Norbornanes[1]). Part 10. Solvolysis of the Stereoisomeric 6-Cyano-2-norbornyl *p*-Toluenesulfonates. A Correction

by **Cyril A. Grob** and **Danielle Herzfeld**

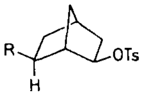
Institute of Organic Chemistry, University of Basel, St. Johanns-Ring 19, CH-4056 Basel

(21.IX.82)

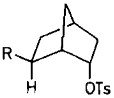
Summary

The solvolysis products of the stereoisomeric 6-cyano-2-norbornyl *p*-toluenesulfonates **1**-**4** (R = CN) in dioxane/water 7:3 have been determined. In contrast to an earlier report the 6*exo*-cyano-2*exo*-norbornyl *p*-toluenesulfonate (**1**; R = CN) yields 30% of the 2*endo*-alcohol **9** (R = CN) beside the 2*exo*-alcohol **10** and the norbornenes **12** and **13**. The results confirm that –I substituents at C(6) reduce 1,3-bridging in the intermediate norbornyl cation and hence its rate of rearrangement. The relatively high rate constants for some 6-fluoro- and 6-cyano-2*exo*-norbornyl *p*-toluenesulfonates are ascribed to C,C-hyperconjugation assisted by the conjugative effects of the 6-fluoro and cyano substituents.

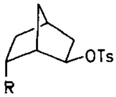
According to recent studies of the solvolysis rates and products of the stereoisomeric 6-substituted 2-norbornyl *p*-toluenesulfonates **1** [1], **2** [1], **3** [2] and **4** [3], electron-attracting substituents R – relative to the incipient cationic center at C(2) – lead to weakly bridged or unbridged intermediate 2-norbornyl cations **5** and **6**, whereas electron-donating substituents cause graded 1,3-bridging in the intermediate cations **7** and **8**[2])[3]).



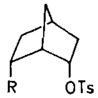
1



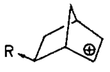
2



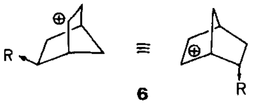
3



4

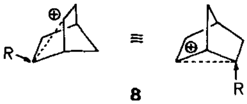


5



6

7



8

---

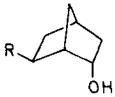
[1]) According to IUPAC nomenclature 'norbornane' is now called 8,9,10-trinorbornane.

[2]) For a review of this work see [4].

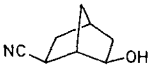
[3]) The terms 'classical' and 'nonclassical' for bridged and unbridged carbocations were avoided because they suggest a dichotomy not warranted by experiment.

0018-019X/82/8/2443-05$01.00/0

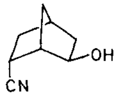
This follows from the large changes in reaction rates, *exo/endo* rate ratios (*i.e.* k_1/k_2 and k_3/k_4) and of the solvolysis products caused by varying the substituent R, in that 2*exo*-norbornanols *only* were obtained when R was an electron donor, whereas 2*exo*- and 2*endo*-substitution products resulted when R was an acceptor. Thus, due to the electron-attracting fluorine substituent, **1**-**3** (R=F) yielded 57, 7 and 4%, respectively, of 6*exo*-fluoro-2*endo*-norbornanol (**9**; R=F) beside the corresponding 2*exo*-alcohol when reacted in dioxane/water 7:3 (*w/w*) [1] [2]. Furthermore, considerable *endo*-cyclization took place when R was a nucleophilic substituent such as COOH, $COOCH_3$ or CH_2OH. These findings are in accordance with the view that nucleophilic attack on bridged norbornyl cations occurs predominantly on the unbridged *exo*-side of C(2), whereas attack can occur on both sides of C(2) in unbridged or weakly bridged norbornyl cations [1] [2].



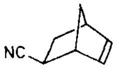
9



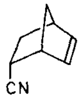
10



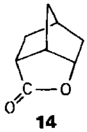
11



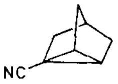
12



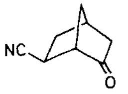
13



14



15



16

In contradiction to this view no *endo*-alcohol **9** (R=CN) was detected among the solvolysis products of the cyano *p*-toluenesulfonates **1**-**3** (R=CN) [1] [2], although the cyano group ($\sigma_{\mathrm{I}}^{q}=3.05$) is considerably more electron-attracting than the fluorine atom ($\sigma_{\mathrm{I}}^{q}=2.57$). Instead, large amounts of the 'nortricyclenecarbonitrile' **15** were reported beside the 2*exo*-norbornanols **10** and **11**, the olefins **12** and **13** and small amounts of the lactone **14**. Consequently, it became necessary to reinvestigate the hydrolysis of the cyano *p*-toluenesulfonates **1**-**3**[4]) and to include the hitherto unreported 6*endo*-cyano-2*endo*-norbornyl *p*-toluenesulfonate (**4**; R=CN)[5]). As shown below, the *endo*-alcohol **9** (R=CN) is indeed formed, but only traces of **15**. The abnormally high rate constant for the 6*exo*-cyano-2*exo*-norbornyl *p*-toluenesulfonate (**1**; R=CN)[6]) was originally thought to be connected with the supposedly

---

[4]) The solvolysis of these compounds in 97% hexafluoroisopropyl alcohol was recently described by *Wilcox & Tuszynski* [5]. The stereoisomeric 5-cyano-2-norbornyl *p*-bromobenzenesulfonates have been studied by *Apeloig et al.* [6].

[5]) The rates and products of several 6*endo*-R-substituted 2*endo*-norbornyl *p*-toluenesulfonates are discussed in the preceding paper [3].

[6]) *p*-Toluenesulfonate **1** (R=CN) reacts eight times faster than anticipated on the basis of the inductive substituent constant for the cyano group [1].

high yield of **15**, a conclusion which is now shown to be incorrect. An alternative explanation for the high rate of **1** (R = CN) is therefore discussed below.

Results. The preparation of all four cyano *p*-toluenesulfonates **1** [7], **2** [8], **3** [9] and **4** [10] have been reported. Meanwhile, the preparation of 6*exo*-cyano-2*endo*-norbornanol[7]) (**9**; R = CN) and its *p*-toluenesulfonate **2** (R = CN) from **10** has been improved. The latter was oxidized with the CrO_3/pyridine complex and the resultant ketonitrile **16** reduced with $NaBH_4$ to yield **9** (R = CN), which was converted to the known **2** (R = CN) with *p*-toluenesulfonyl chloride in pyridine.

The preparative solvolyses of the cyano *p*-toluenesulfonates **1**–**4** (R = CN) were carried out in dioxane/water 7:3 (*w/w*) in the presence of two mol-equiv. of triethylamine as described before [11]. The reaction mixtures were analyzed by gas chromatography (s. *Exper. Part*). Products were identified by their retention times and by peak area amplification following the addition of authentic samples. Products and their yields are listed in the *Table.*

Table. *Reaction conditions and yields* (in %, accuracy ± 1.5) *of solvolysis products of the* p-*toluenesulfonates* **1**–**4** *(R = CN) in dioxane/water 7:3* (w/w)

Reactant	Reaction time [h]	Temperature [°C]	Yields [%][a]) **9** (R = CN)	**10**	**11**	**12**	**13**	**14**	**15**
1	38	130	30	11	tr.	52	5	2	tr.
2	40	130	3	83	1	12	tr.		tr.
3	75	130	tr.	2	70	tr.	13	2	1
4	312	140	2	4	76	1	13	4	tr.
GC. retention time [min][b])			16.11	15.54	14.74	2.74	3.63	9.66	3.42

[a]) tr. = Traces.

[b]) For GC. conditions, s. *Exper. Part.*

Discussion. The 6*exo*-cyano-2*exo*-norbornyl *p*-toluenesulfonate (**1**; R = CN) yielded 30% of the 2*endo*-alcohol **9** (R = CN; *Table*), proving that *endo*-attack at C(2) occurs, as in the case of the corresponding fluoro derivative **1** (R = F) [1]. In addition to **9** (R = CN), 11% of the *exo*-alcohol **10** were obtained with retention of configuration at C(2). The main product, however, was the olefin **12** (52%) accompanied by small amounts of the rearranged olefin **13**[8]).

These products are most easily explained as arising in a k_c-process, *i.e.* by way of a cationic intermediate. It has already been shown that 2*exo*- and 2*endo*-norbornyl derivatives fail to react by a displacement (S_N2) mechanism [12] even with large excesses of strong nucleophiles such as KOH and C_6H_5SNa in 90% ethyl alcohol and methyl cellosolve, respectively. This inertness to direct nucleophilic attack was ascribed to steric hindrance of rearside *exo*- and *endo*-attack at C(2), but does not apply to the cations from **1**–**4** (R = CN) as the formation of 2*endo*- and 2*exo*-norbornanols shows.

The cyano *p*-toluenesulfonates **2** and **4** (R = CN) yielded much less *endo*-alcohol **9** (R = CN), the main products being the inverted alcohols **10** and **11**, re-

---

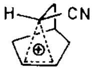
[7]) The systematic name of **9** is 6*endo*-hydroxy-8,9,10-trinorbornane-2*exo*-carbonitrile.

[8]) Separation of the olefinic and tricyclic nitriles **12**, **13** and **15**, respectively, was incomplete with the GC. technique employed previously [1] and led to erroneous peak assignments.

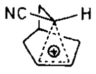
spectively. The *Table* also reveals that only small amounts of the lactone **14** and traces of the 'nortricyclenecarbonitrile' **15** were formed. Furthermore, less than 8% of the products are derived from a *Wagner-Meerwein* rearrangement of the type **5**→**6** or **6**→**5** which confirms that –I substituents hinder 1,3-bridging and hence also rearrangement [2].

17

18



17a



17b

It is also noteworthy that the *p*-toluenesulfonates **1** and **3** (R=CN) should yield identical product mixtures if they reacted *via* bridged carbocations of the *Wilson-Winstein*-type **17a** and **17b**, respectively [4], for these are enantiomers. In fact the yields of products from **1** and **3** are quite different *(Table)*, which proves that they are derived from the unbridged carbocations **5** and **6**, respectively.

Earlier kinetic studies have shown that the logarithms of the rate constants for the 6-substituted 2-norbornyl *p*-toluenesulfonates **1**–**3** correlate well with the inductive substituent constant σ_I^q of R except when the latter is a F-atom in the series **1** and **2** and the cyano group in the series **1** [1] [2]. In these cases solvolysis rates were faster by factors of 3 to 8 than calculated from the inductive regression line. The enhanced rate of the fluoro *p*-toluenesulfonate **1** (R=F) was ascribed to C,C-hyperconjugation of the C(1)–C(6) bond including an n-electron pair of the F-substituent as in **17** [1][9]. On the other hand, participation of the 'loosened' C(6),H*endo*-bond was favored in the case of the cyano *p*-toluenesulfonate **1** (R=CN) because of the putative high yields of the nortricyclene derivative **15**. Now that this has been disproved, C,C-hyperconjugation involving the π-electrons of the cyano group appears to be a better explanation. In fact recent work by *Gassman* and others[10] has shown that the conjugative effect of a cyano group can partially balance its strong –I effect when attached to an incipient cationic center. This could also apply, albeit to a lesser degree, to the partial positive charge transferred to C(6) in the 6*exo*-cyano-2-norbornyl cation **18**.

This work was supported by the *Swiss National Science Foundation*.

Experimental Part[11]

General remarks. The reaction mixtures were analyzed by gas chromatography (*Hewlett-Packard* model *5880 A*) employing a freshly prepared column packed with 3% *Carbowax 20 M* on *Chromosorb W 80/100 mesh* with a N_2 stream of 30 ml/min, a temperature program 130–200° and an injection temperature of 200°. This procedure led to satisfactory peak separation and integration. Melting points (m.p.) were determined on a *Kofler* block and are corrected (±1°).

---

[9] Conjugation of the n- and π-electrons of F and CN, respectively, demands hyperconjugation of the C(1),C(6)-bond in **17** and **18** if the octetts around C(6) are to be preserved. Stronger n-electron donors, such as R_2N and RO, lead to fragmentation [1].

[10] *Cf.* [13] and further lit. cit. therein.

[11] The following reactions were first carried out by Dr. *R. Hanreich*.

*Preparation of 6-oxo-2*exo*-norbornanecarbonitrile* (**16**). To a suspension of 9.9 g (35 mmol) of the CrO_3/pyridine complex [14] in 75 ml abs. CH_2Cl_2 were added 800 mg (5.8 mmol) of 6*exo*-hydroxy-2*exo*-norbornanecarbonitrile (**10**) [8] in 2 ml of abs. CH_2Cl_2. After stirring for 30 min, the supernatant solution was decanted and washed with 2N HCl, 2N Na_2CO_3 and then with a sat. aq. NaCl-solution. Drying over Na_2SO_4 and evaporation of the solvent yielded 670 mg (85%) of **16**, m.p. 44-45° (ether/hexane). - IR. (KBr): 2230 (C≡N), 1750 (C=O).

C_8H_9NO (135.17) Calc. C 71.09 H 6.71 N 10.36% Found C 70.91 H 6.83 N 10.43%

*Preparation of 6*endo*-hydroxy-2*exo*-norbornanecarbonitrile* (**9**; R = CN). To a solution of 481 mg (3.6 mmol) of **16** in 10 ml of moist ether were added 68 mg (1.8 mmol) of $NaBH_4$. After stirring for 2 h, 2N HCl was added until the pH was 1. The mixture was extracted with ether, which was washed with aq. sat. $NaHCO_3$-solution, dried over Na_2SO_4 and evaporated. The oily residue, 426 mg (87%), consisted of 85% of **9** (R = CN) and 15% of **10** according to GC. analysis. Chromatography on silica gel with CH_2Cl_2/ether 4:1 yielded pure (but extremely hygroscopic) **9** (R = CN), as shown by spectral analysis. - IR. (film): 3425 (OH); 2240 (C≡N). - ^{1}H-NMR. ($CDCl_3$): 0.7-2.0 (*m*, 6 H, 3 CH_2); 2.3 (*m*, 2 H, H-C(1), H-C(4)); 2.6 (*d*, 1 H, HO; exchangeable with D_2O); 3.2 (*t*, 1 H, H-C(2)); 4.3 (*m*, 1 H, H*exo*-C(6)).

*Preparation of 6*exo*-cyano-2*endo*-norbornyl* p*-toluenesulfonate* (**2**; R = CN). A solution of 109 mg (0.8 mmol) of **9** (R = CN) and 230 mg (1.2 mmol) of *p*-toluenesulfonyl chloride in 3 ml of abs. pyridine were kept for 3 days at 22°. Ice, and after 15 min, 2N HCl were added to the solution which was then extracted with CH_2Cl_2. This was washed with 2N $NaHCO_3$, dried over Na_2SO_4 and evaporated *i.v.* Crystallization of the residue from ethyl acetate/hexane gave 171 mg (74%) of **2** (R = CN) as needles, m.p. 102-103° ([8]: m.p. 102-103°).

REFERENCES

[1] *W. Fischer, C.A. Grob & G. von Sprecher,* Tetrahedron Lett. *1979*, 473; *W. Fischer, C.A. Grob, G. von Sprecher & A. Waldner,* ibid. *1979*, 1901, 1905; *W. Fischer, C.A. Grob, R. Hanreich, G. von Sprecher & A. Waldner,* Helv. Chim. Acta *64*, 2298 (1981).

[2] *C.A. Grob, B. Günther, R. Hanreich & A. Waldner,* Tetrahedron Lett. *22*, 835 (1981); *C.A. Grob, B. Günther & R. Hanreich,* Helv. Chim. Acta *64*, 2312 (1981).

[3] *C.A. Grob, B. Günther & R. Hanreich,* Helv. Chim. Acta *65*, 2110 (1982); *C.A. Grob, B. Günther & R. Hanreich,* Tetrahedron Lett. *22*, 1211 (1981).

[4] *C.A. Grob,* Angew. Chem. *94*, 87 (1982); Int. Ed. *21*, 87 (1982).

[5] *C.F. Wilcox & W.J. Tuszynski,* Tetrahedron Lett. *23*, 3119 (1982).

[6] *Y. Apeloig, D. Arad, D. Lenoir & P. von R. Schleyer,* Tetrahedron Lett. *22*, 879 (1981).

[7] *W. Fischer, C.A. Grob & G. von Sprecher,* Helv. Chim. Acta *63*, 806 (1980).

[8] *W. Fischer, C.A. Grob, G. von Sprecher & A. Waldner,* Helv. Chim. Acta *63*, 816 (1980).

[9] *C.A. Grob, B. Günther & A. Waldner,* Helv. Chim. Acta *64*, 2709 (1981).

[10] *C.A. Grob, B. Günther & R. Hanreich,* Helv. Chim. Acta *65*, 2288 (1982).

[11] *W. Fischer, C.A. Grob, G. von Sprecher & A. Waldner,* Helv. Chim. Acta *63*, 928 (1980).

[12] *C.A. Grob & E. Lutz,* Helv. Chim. Acta *64*, 153 (1981).

[13] *P.G. Gassman & J.J. Talley,* J. Am. Chem. Soc. *102*, 1214, 4138 (1980); *P.G. Gassman, K. Saito & J.J. Talley,* ibid. *102*, 7613 (1980); *P.G. Gassman & K. Saito,* Tetrahedron Lett. *22*, 1311 (1981); *P.G. Gassman & M.M. Doherty,* J. Am. Chem. Soc. *104*, 3742 (1982); *G.A. Olah, G.K.S. Prakash & M. Arvanaghi,* ibid. *102*, 6640 (1980); *A.D. Allen, F. Shahidi & T.T. Tidwell,* ibid. *104*, 2516 (1982).

[14] *R. Ratcliffe & R. Rodehurst,* J. Org. Chem. *35*, 4000 (1970).