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Phenolysis of *exo*- and *endo*-2-Norbornyl *p*-Toluenesulfonates. Rates and Product Distributions

Kunio OKAMOTO, Tomomi KINOSHITA, and Yuji ITO

Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606

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Although norbornyl arenesulfonate solvolysis has been extensively studied with regard to the non-classical nature of the norbornyl cation,[1,2] the system has never been subjected to solvolytic study with the use of a phenolic solvent, which is suitable for S_N1-solvolysis.[3]

This study was carried out in order to compare the results of 2-norbornyl tosylate (ROTs) phenolysis with those of the previous studies[1b] in common solvolytic solvents with regard to the *exo*/*endo* rate ratio and epimeric nature of the products, and to examine the distribution of the O- and C-norbornylated phenols for information on the non-classical nature of the solvolysis intermediates from *exo*- and *endo*-ROTs in the phenolic solvent.

Titrimetric first-order rate constants (k_1) for the two epimeric ROTs's in a phenol–benzene (1:1 by wt.) solvent are given in Table 1. The *exo*/*endo* rate ratios for the phenolysis are 591 at 25 °C and 622 at 50 °C, being comparable with the acetolysis rate ratio of 185 at 50 °C,[1a] and also with the ethanolysis rate ratio of 171 at 50 °C.[2]

Phenolysis of 2-norbornyl tosylates gives the phenyl ether (ROC_6H_5), and *o*- and *p*-norbornylated phenols (*o*- and *p*-RC_6H_4OH), and a mixture of nortricyclene and norbornene. The results for representative runs are given in Table 2. Using capillary gas chromatography, we have examined the *exo*/*endo* epimer ratio of the substitution products. Control experiments showed 0.1% *endo*-epimer in ROC_6H_5 and 0.02% *endo*-epimer in both *o*- and *p*-RC_6H_4OH to be detectable. However, neither *endo*-ROC_6H_5 nor *endo*-RC_6H_4OH were observed in the phenolysis products from *exo*- and *endo*-ROTs, the *endo*-epimer content being definitely <0.1% for ROC_6H_5 and <0.02% for *o*- and *p*-RC_6H_4OH.

Table 1. Titrimetric phenolysis rates of 2-norbornyl tosylates[a]

	Tosylate M	NaOPh M	Temp. °C	k_1 sec^{-1}	*exo*/*endo*
exo	0.0998	0.1040	0.0	1.58×10^{-4}	
	0.1004	0.1040	25.0	3.78×10^{-3}	591
			50.0	5.55×10^{-2} [b]	622
endo			25.0	6.40×10^{-6} [b]	
	0.1009	0.1041	50.0	8.92×10^{-5}	
	0.1009	0.1041	75.0	8.65×10^{-4}	

a) Solvent: PhOH–Benzene (1:1 by wt.). b) Extrapolated from data at other temperatures.

Product distributions for the phenolysis of epimeric tosylates in the presence of sodium phenoxide (0.007—0.095 M) were determined in the phenoxide/substrate concentration ratios 7.6—9.5 at 50.0 °C. The distribution of products resulting from the reaction of phenol molecule with phenolysis intermediate can be estimated by the graphic extrapolation of the distribution curve to the zero phenoxide concentration, as in the case for 1-adamantyl,[3a] 2-octyl,[3b] and tetrahydrolinalyl systems;[3b] the distribution of products resulting from the reaction of phenoxide ion with phenolysis intermediate has been calculated by the method previously reported.[3] The results are given in Table 3.

The calculated product distributions for the *exo*-

Table 3. Calculated product distributions for the reactions of the phenol molecule and the phenoxide ion[a]

Substrate	Product distribution %			
	ROC_6H_5	*o*-RC_6H_4OH	*p*-RC_6H_4OH	Hydrocarbons
Reaction of the phenol molecule				
exo-ROTs	81.5	4.0	0.86	13.6
endo-ROTs	82.3	6.5	1.1	10.1
Reaction of the phenoxide ion				
exo-ROTs	51.8	42.1	6.3	0.0
endo-ROTs	50.1	44.3	5.9	0.0
Values of k_2'/k_2 [b]				
exo-ROTs	223	217	78	87
endo-ROTs	268	288	79	97

a) Solvent: PhOH–Benzene (1:1 by wt). Temperature: 50.0 °C. b) *Cf.* Ref. 2.

Table 2. Product distributions of *exo*- and *endo*-2-norbornyl tosylate phenolyses[a]

	Tosylate M	NaOPh M	Temp. °C	Time hr	ROC_6H_5[b]	*o*-RC_6H_4OH[c]	*p*-RC_6H_4OH[d]	Nortricyclene	Norbornene
exo	0.1006	0.1110	50.0	0.57	58.6	26.5	3.1	11.8	0.07
endo	0.1009	0.1061	50.0	23	54.3	23.6	2.6	23.0	0.44

a) Solvent: PhOH–Benzene (1:1 by wt.).
b, c, d) *exo*-% >99.9% for b; >99.98% for c; >99.96% for d.

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and *endo*-tosylates are in line with each other within experimental error in both phenol molecule and phenoxide ion reactions. The *endo*-tosylate initially produces the classical norbornyl ion and subsequently most the classical ion becomes non-classical before it is captured by the nucleophile.[1] The distribution character for the phenolysis products probably indicates that the life of the classical ion is relatively short in the phenolysis medium, and consequently most of the products from *endo*-ROTs stem from the non-classical norbornyl cation.

Experimental[4]

Materials. *exo*-2-Norbornanol[2] and *endo*-2-norbornanol (the *exo*-epimer content 8.1% by glc)[5-8] were prepared by known methods. *exo*- and *endo*-2-Norbornyl *p*-toluenesulfonates[1a] and nortricyclene[9] were obtained in the usual manner. Sodium phenoxide was prepared by the reported method.[3a] The other organic reagents employed were of analytical reagent grade and were fractionated just prior to use.

Syntheses of exo- *and* endo-*2-Norbornyl Phenyl Ethers.* A mixture of a potassium salt of *exo*-2-norbornanol (prepared from the alcohol and potassium in benzene) and bromobenzene in hexamethylphosphoric triamide was heated at 150 °C for 32 hr. The usual work up gave *exo*-2-norbornyl phenyl ether (bp 100—103 °C/1.8 mmHg, lit,[9] bp 98 °C/1 mmHg; the *exo*-epimer content >99.9% by glc). *endo*-2-Norbornyl phenyl ether was prepared from *endo*-2-norbornanol in a similar manner; bp 102—105 °C/2 mmHg; the *endo*/*exo* ratio 35.5/64.5 by glc. Found: C, 83.13; H, 8.82%. Calcd for $C_{13}H_{16}O$: C, 83.03; H, 8.52%.

Syntheses of exo- *and* endo-*2-Norbornylphenols.* *o*- and *p*-*endo*-2-Norbornylphenols were synthesized according to the method of Kheifits and Gol'dovskii;[10] the *o*-isomer, bp 124—126 °C/1.8 mmHg (lit,[10] bp 119—123 °C/0.3 mmHg); the *p*-isomer, bp 174—177 °C/4.0 mmHg (lit,[10] bp 125—129 °C/0.3 mmHg). *o*- and *p*-*exo*-2-Norbornylphenols were obtained by *exo*-2-norbornyl tosylate phenolyses; the *o*-isomer, mp 47.3—48.5 °C (corr.) (lit,[11] mp 49—50 °C); the *p*-isomer, mp 128.6—129.4 °C (corr.) (lit,[12] mp 133—135.5 °C).

Isolation of the Phenolysis Product. A flask containing the reaction mixture was placed in a constant-temperature bath for at least ten half-lives. After the work up[3] products were separated by column chromatography or by thin-layer chromatography (silica gel).

Kinetic Measurement. This was carried out by the usual sealed-ampoule and pipetting out technique.[3] In each case, smooth first-order rate plots were obtained over 70—80% reaction.

Product Analysis by Gas Chromatography. The product distribution was analysed by glc using a 2 m × 3 mm column with Apiezon Grease on Neopak 1A at 230 °C. The epimer analysis of each product was performed by glc using a Hitachi Golay column R-45 at 83 °C for 2-norbornanol (retention time: *exo*-epimer, 51.3 min; *endo*-epimer, 56.6 min) and a Hitachi Golay column Q-45 at 230 °C for 2-norbornyl phenyl ether (retention time: *exo*-epimer, 105.1 min; *endo*-epimer, 106.9 min). Norbornylphenols were converted into norbornylanisols by the use of dimethyl sulfate[13] prior to glc analysis, carried out using the column Q-45 at 230 °C: *o*-(2-norbornyl)anisol[10] (retention time: *exo*-epimer, 116 min; *endo*-epimer, 114 min); *p*-(2-norbornyl)anisol[10] (retention time: *exo*-epimer, 79 min; *endo*-epimer, 77 min).

4) A Hitachi Model 023-6003 gas chromatographic instrument, with a flame ionization detector, a Hitachi Model 215 IR spectrophotometer, and a Hitachi Model R-24 60 MHz NMR instrument were used for the analytical work.

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