

The Protonation of Some Methyl-naphthalen-1-ols in Fluorosulfonic Acid

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Abstract

The protonations of 4-methyl-, 3,4-dimethyl- and 4,5-dimethyl-naphthalen-1-ols have been examined for fluorosulfonic acid solutions at -50° . The C2/C4 protonation ratios are markedly dependent on the extent and position(s) of methyl substitution in the naphthalen-1-ol system.

Introduction

The study of the protonation of phenols and aromatic ethers in superacids has attracted much interest in recent years.¹ The relative extent of O- and C-protonation, and the position of C-protonation for these compounds is dependent on the nature of the solvent system, the temperature and on the detailed pattern of ring substitution.²

In 1974 we reported the results of the protonation of a series of polymethylphenols, in which we rationalized preferences for the formation of isomeric ions in terms of electronic and steric factors only, using the same solvent system (fluorosulfonic acid) throughout.³ We now report the results of our investigation of the protonation in fluorosulfonic acid of some methyl-substituted naphthalen-1-ols.

Results and Discussion

¹H n.m.r. data for C4- and C2-protonated naphthalen-1-ols are given in Table 1. The relative abundances of these two types of ions obtained for each substrate are given in Table 2. The chemical shifts for the methine and methyl protons for the C4- and C2-protonated species fall into clearly discernible patterns, and the assignments were made by analogy with data in the literature,⁴ and the observed multiplicities of signals.

For the naphthalen-1-ol systems the relative basicities of the hydroxyl group and the ring carbons are such that only C-protonation is observed in fluorosulfonic acid

¹ For reviews, see Brouwer, D. M., Mackor, E. L., and MacLean, C., in 'Carbonium Ions' (Eds G. A. Olah and P. v. R. Schleyer) Vol. 2 (John Wiley: New York 1970); Liler, M., *Adv. Phys. Org. Chem.*, 1975, **11**, 267.

² Larsen, J. W., and Eckert-Maksic, M., *J. Am. Chem. Soc.*, 1974, **96**, 4311, and references cited therein.

³ Blackstock, S. M., Richards, K. E., and Wright, G. J., *Can. J. Chem.*, 1974, **52**, 3313.

⁴ Koptuyug, V. A., Kamshii, L. P., and Mamatyuk, V. I., *Zh. Org. Khim.*, 1975, **11**, 128, and references cited therein.

at -50° . Naphthalen-1-ol itself is protonated exclusively at C4 but, as can be seen from Table 2, the introduction of a C4-methyl group promotes C2-protonation at the expense of C4-protonation. This observation parallels the earlier report of the effect on the *para/ortho*-protonation ratio of the introduction of a C4-methyl group into methylphenols.³ Comparison of the C4/C2 protonation ratios for 4-methylnaphthalen-1-ol and 3,4-dimethylnaphthalen-1-ol reveals the dramatic effect of the introduction of the C3-methyl group. This observation is strikingly similar to the effect on the C4/C6 protonation ratio of the introduction of a C5-methyl group into 2,3,4-trimethylphenol (Scheme 1). Because the electronic effect of the additional methyl group should apply equally to the adjacent *ortho* and *para* positions, it is

Table 1. ^1H n.m.r. data for C4- and C2-protonated species in fluorosulfonic acid at -50°
Chemical shifts are in ppm from Me_4Si by using Me_4N^+ as internal standard (see Experimental)

Naphthalen-1-ol	H2	3-Me	H3	4-Me	H4	5-Me	H5	H6	H7	H8
C4-protonated species										
Unsubstituted	7.56 ^A	—	8.74 ^A	—	4.63 ^B	—	— ^C	— ^C	— ^C	8.84 ^D
4-Methyl	7.37 ^E	—	8.67 ^F	1.78 ^G	4.43 ^H	—	7.77 ^I	— ^J	— ^J	8.62 ^F
3,4-Dimethyl	7.31 ^K	2.75 ^K	—	1.75 ^L	4.35 ^M	—	8.03 ^L	— ^N	— ^N	8.74 ^D
4,5-Dimethyl	7.32 ^A	—	8.73 ^O	1.57 ^P	4.60 ^P	2.70 ^B	—	7.70 ^D	8.00 ^Q	8.56 ^D
C2-protonated species										
4-Methyl	4.23 ^R	—	6.75 ^R	2.47 ^S	—	— ^J	— ^J	— ^J	— ^J	— ^T
4,5-Dimethyl	4.23 ^R	—	— ^T	— ^T	—	— ^T	—	— ^T	— ^T	— ^T

^A d, J 10 Hz. ^B 2H, singlet. ^C Part of multiplet 7.75–8.45. ^D d, J 8 Hz. ^E dd, J 10, 1 Hz.
^F dd, J 10, 3 Hz. ^G d, J 7.5 Hz. ^H ddq, J 3, 1, 7.5 Hz. ^I dd, J 8, 3 Hz. ^J Part of multiplet 7.78–8.68.
^K Singlet. ^L d, J 7 Hz. ^M q, J 7 Hz. ^N Part of multiplet 7.80–8.50.
^O dd, J 10, 4 Hz. ^P dq, J 4, 8 Hz. ^Q t, J 8, 8 Hz. ^R 2H, broad singlet. ^S d, J 1 Hz.
^T Position of signal obscured.

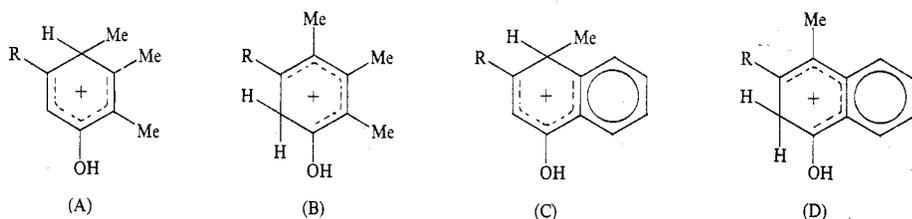
Table 2. Percentage of ions formed on C2- and C4-protonation in fluorosulfonic acid at -50°

Compound	C2	C4
Naphthalen-1-ol	0	100
4-Methylnaphthalen-1-ol	48	52
3,4-Dimethylnaphthalen-1-ol	0	100
4,5-Dimethylnaphthalen-1-ol	8	92

tempting to ascribe this effect *totally* to the relief of non-bonded interactions between the buttressed methyl groups, or the buttressed methyl groups and the adjacent benzene ring, when the C4-methyl group moves out of the plane of the ring system in C4-protonation. However, 4,5-dimethylnaphthalen-1-ol, being a derivative of 1,8-dimethylnaphthalene, should be considerably more strained than 3,4-dimethylnaphthalen-1-ol, a derivative of 1,2-dimethylnaphthalene.⁵ As C4-protonation does not occur exclusively for the more strained 4,5-dimethylnaphthalen-1-ol, it seems that steric

⁵ Bright, D., Maxwell, I. E., and de Boer, J., *J. Chem. Soc., Perkin Trans. 2*, 1973, 2101; Good, W. D., *J. Chem. Thermodyn.*, 1973, **5**, 715; Packer, J., Vaughan, J., and Wong, E., *J. Am. Chem. Soc.*, 1958, **80**, 905.

strain is the dominant, but not the only, factor controlling the position of protonation in these systems.



Scheme 1. Percentage of ions formed in fluorosulfonic acid at -50° : for R = H, (A)/(B) 20 : 80, (C)/(D) 52 : 48; for R = Me, (A)/(B) 94 : 6, (C)/(D) 100 : 0.

Experimental

^1H n.m.r. spectra were obtained at -50° on a Varian T-60 spectrometer fitted with a variable temperature probe. Chemical shifts in fluorosulfonic acid solutions were measured relative to $\text{Me}_4\text{N}^+ \text{BF}_4^-$ as standard reference and converted into $\delta(\text{Me}_4\text{Si}) - 3 \cdot 20$ for the reference ion. Before use, fluorosulfonic acid was distilled over sodium fluoride (1 g/100 ml) under dry nitrogen. The fluorosulfonic acid solutions (7% w/v) were prepared at -78° ; the solutions were then warmed to -50° before their ^1H spectra were recorded.

The phenols either were available commercially or were prepared by established routes.

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