Synthesis of 2-Naphthyl Vinyl Ethers

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Published methods for the preparation of vinyl ethers[1,2,3] failed in attempts to synthesize the vinyl ethers of 2-naphthol[2] (with the exception of the unsubstituted 2-vinyloxynaphthalene[3]). We have found, however, that these compounds are accessible by a synthesis originally developed by Hoch[4] for the preparation of enamines. Hereby the diethyl acetal of an appropriate phenyl ketone **(2)** is subjected to reaction with the 2-naphthol **(1)**. Also, ethyl enol ethers **(3)** can be used instead of diethyl acetals (see Table).

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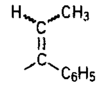
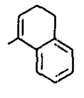
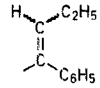
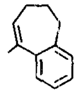
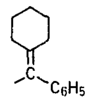
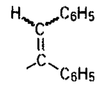
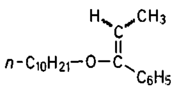
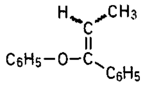
Table. Vinyl Ethers (R—O—R′) from 2-Naphthol (**1**), *n*-Decanol, or Phenol and Diethyl Acetals (**2**) or Ethyl Enol Ethers (**3**)

Product R	R′	Yield [%]	m.p. [°C][a] or b.p. [°C][a]/torr	Molecular formula[b]	U.V. (hexane)[c] λ_{max} [nm] (log ε)	¹H-N.M.R. (CDCl₃/TMS)[d] δ [ppm]
2-naphthyl		40	88°, 185°/0.2	$C_{19}H_{16}O$ (260.3)	328 (3.27); 312 (3.04); 314 (3.12); 282 sh; 250 sh	1.8 (d, 3H); 5.9 (q, 1H); 7.0–8.0 (m, 12H)
2-naphthyl		34[e]	45°, 222°/0.2	$C_{20}H_{16}O$ (272.3)	329 (3.09); 320 (3.03); 314 (3.08); 297 sh; 271 (4.08); 263 (4.09)	2.3 (m, 2H); 2.8 (m, 2H); 5.3 (t, 1H); 6.9–7.8 (m, 11H)
2-naphthyl		39	38°, 178°/0.2	$C_{20}H_{18}O$ (274.3)	328 (3.29); 321 (3.07); 314 (3.15); 284 sh, 252 sh	1.0 (t, 3H); 2.1 (m, 2H); 5.8 (t, 1H); 6.9–7.8 (m, 12H)
2-naphthyl		31[e]	—, 225°/0.2	$C_{21}H_{18}O$ (286.4)	329 (3.23); 320 (3.11); 314 (3.16); 292 sh, 280 sh	2.1 (m, 4H); 2.9 (m, 2H); 5.8 (t, 1H); 6.9–7.8 (m, 11H)
2-naphthyl		33	, 187°/0.2	$C_{23}H_{22}O$ (314.4)	329 (3.46); 321 (3.27); 3.14 (3.34); 301 (3.15); 272 sh, 260 sh	1.6 (br s, 6H); 2.4 (br s, 4H); 6.9–7.8 (m, 12H)
2-naphthyl		38	127°, 240°/0.2	$C_{24}H_{18}O$ (322.4)	2.90 (4.51)	8.8 (s, 1H); 7.0–8.0 (m, 17H)
		68	—, 135°/0.2	$C_{19}H_{30}O$ (274.4)	250 (4.01)	0.9 (t, 3H); 1.2 (br s, 16H); 1.8 (d, 3H); 3.5 (t, 2H); 5.3 (q, 1H); 7.0–7.5 (m, 5H)
		40	44°, 105°/0.2	$C_{15}H_{14}O$ (210.3)	290 sh; 276 sh; 250 (4.12)	1.7 (d, 3H); 5.8 (q, 1H); 6.6–7.5 (m, 10H)

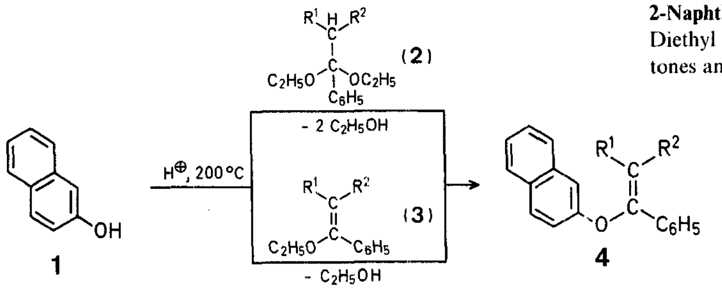
[a] Not corrected.

[b] The microanalyses, performed by Pascher Mikroanalytisches Laboratorium, Bonn, were in satisfactory agreement with the calculated values (C ±0.37, H ±0.11, O ±0.37).

[c] Recorded with a Beckman Acta M VII spectrophotometer.

[d] Recorded with a Varian A 360 spectrometer at 60 MHz.

[e] Ethyl enol ether **3** used as starting material.



As can be seen in the Table, the method is applicable to the acetals of cyclic and acyclic ketones. Also, vinyl ethers of other aromatic alcohols as well as of aliphatic alcohols can be prepared; two examples are listed in the Table. However, an attempt to prepare the 2-naphthyl vinyl ether of 1-indanone failed, indicating that the method may be incapable to yield products with ring constraint. Also, the method was unsuccessful when acetals of aliphatic ketones were used; in these cases aldol-condensation products were formed.

2-Naphthyl vinyl ethers (**4**) may be used as educts for a photocyclization yielding compounds containing dihydrofuran ring systems. This photocyclization has been shown to be a useful method for synthesizing morphine analogous compounds[5].

2-Naphthyl Vinyl Ethers 4; General Procedure:

Diethyl acetals (**2**) or ethyl enol ethers (**3**) are prepared from ketones and orthoformic acid triethyl ester[6].

2-Naphthol (**1**; 28.83 g, 0.2 mol) and the diethyl acetal (**2**) or ethyl enol ether (**3**; 0.2 mol) are heated in the presence of *p*-toluenesulfonic acid (0.5 g) at 190–200 °C in a distillation apparatus until the formation of ethanol, which is distilled from the reaction mixture, ceases. The residue is dissolved in benzene (150 ml) and washed with 1 normal sodium hydroxide solution (2 × 50 ml) and with water (50 ml). The organic solution is dried with magnesium sulfate, benzene is evaporated, and the crude product fractionated in vacuum. Solid products are recrystallized from petroleum ether (b.p. 35–38 °C).

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[1] H. Meerwein in Houben-Weyl, *Methoden der Organischen Chemie*, 4th Edn., E. Müller, Ed., Vol. VI/3, Georg Thieme Verlag, Stuttgart, 1965, pp. 90–254, and references cited therein.

[2] G. Dittus in Houben-Weyl, *Methoden der Organischen Chemie*, 4th Edn., E. Müller, Ed., Vol. VI/3, Georg Thieme Verlag, Stuttgart 1965, p. 485, and references cited therein.

[3] H. Christol, H.-J. Christen, M. Soleiman, *Synthesis* **1975**, 737.

[4] J. Hoch, *C. R. Acad. Sci. (Paris)* **200**, 938 (1935).

[5] A. G. Schultz et al., *J. Am. Chem. Soc.* **100**, 2150 (1978).

[6] *Organikum*, VEB Deutscher Verlag der Wissenschaften, 7th Edn., Berlin, 1967, p. 377.

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