

Selective Allylation of Sodium Naphtholate

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Synopsis. The reaction of 1- or 2-naphthol with allylic halides (1-chloro-3-methyl-2-butene, 1-chloro-3,7-dimethyl-2,6-octadiene, *trans*-1-chloro-2-butene and *trans*-1-chloro-2-hexene) in the presence of metallic sodium gave naphthols having the corresponding allylic group selectively.

1,4-Naphthoquinones and 1,4-naphthalenediols which have polyprenyl units as side chains are widely distributed from bacteria to higher plants and animals, and many of these compounds are known as biological active compounds.¹⁾

In previous papers,^{2–4)} we described that the reaction of phenols with allylic halides in the presence of alkali metals gave ortho-allylated phenols in high yields. This procedure was considered to be applicable to the synthesis of the naturally occurring compounds. Therefore, we now wish to report the allylation of 1- or 2-naphtholate which gives 2- or

1-allylic naphthol selectively.

In regard to C-allylation of naphthols, Sharma et al.⁵⁾ have reported that the naphthols were treated with isoprene and iodotrimethylsilane in acetonitrile to give C-allylated naphthols. Whiting et al.⁶⁾ also have reported that 1-(3-methyl-2-butenyl)-2-naphthol was prepared from the (phenylthio)naphtho[2,1-*b*]pyran derivative. However, the yields of allylic naphthols in each cases were quite poor.

By contrast, when this reaction actually was attempted with our method, C-allylated compounds were obtained in good yields. In the reaction of 1-(**1**) or 2-naphthol (**2**) with 1-chloro-3-methyl-2-butene in the presence of metallic sodium, 2-(3-methyl-2-butenyl)-1-naphthol (**3**) or 1-(3-methyl-2-butenyl)-2-naphthol (**4**) was obtained in a yield of 82% or 86%, respectively. As the minor products, 1-naphthyl 3-methyl-2-butenyl ether (**5**), 2,2-dimethyl-3,4-dihydro-2*H*-naphtho[1,2-*b*]pyran (**6**), 2-naphthyl 3-methyl-2-butenyl ether (**7**) and 3,3-dimethyl-1,2-dihydro-3*H*-naphtho[2,1-*b*]pyran (**8**) were found in very poor yields, respectively.

The effect of the alkali metals in this reaction is shown in Table 1.⁷⁾ From this result, it was found that the metallic sodium was useful for obtaining selectively naphthols having 3-methyl-2-butenyl group.

In a same manner as above, the reaction of

Table 1. The Effects of Alkali Metals

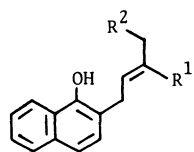
Metals	Conv. %	Product/%			Unknown
		3	5	6	
Li	73	63	12	4	21
Na	96	82	3	2	13
K	88	77	6	4	13

Table 2. Spectral and Analytical Data for Compounds

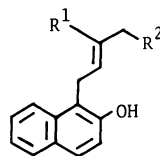
Compd	IR (cm ⁻¹)	¹ H NMR (δ, CCl ₄)	Formula	Found (%) (Required)	
				C	H
3	3450, 1210, 845, 810, 750	1.70(s, 6), 3.30(d, 2), 5.15(s, 1), 5.18(t, 1), 6.85–8.10(m, 6)	C ₁₅ H ₁₆ O	85.08 (84.87)	6.46 (6.71)
4	3450, 1200, 810, 795, 750	1.53(s, 3), 1.68(s, 3), 3.53(d, 2), 6.05(t, 1), 5.55(s, 1), 6.65–7.80(m, 6)	C ₁₅ H ₁₆ O	84.62 (84.87)	6.91 (6.71)
9	3470, 1660, 1200, 870, 810, 745	1.32(s, 3), 1.42(s, 3), 1.48(s, 3), 1.65–1.95(m, 4), 3.09(d, 2), 4.68(s, 1), 4.98(t, 2), 6.65–7.70(m, 6)	C ₂₀ H ₂₄ O	85.48 (85.66)	8.85 (8.63)
10	3450, 1660, 1200, 860, 810, 745	1.42(s, 6), 1.55(s, 3), 1.80–2.05(m, 4), 3.55(d, 2), 4.80(s, 1), 5.05(t, 2), 6.55–7.65(m, 6)	C ₂₀ H ₂₄ O	85.89 (85.66)	8.35 (8.63)
11	3500, 1660, 1210, 980, 810, 750	1.62(d, 3), 3.30–3.50(m, 2), 4.10(s, 1), 5.25–5.65(m, 2), 6.90–8.20(m, 6)	C ₁₄ H ₁₄ O	84.59 (84.81)	7.43 (7.12)
12	3300, 1660, 1220, 975, 815, 750	1.50(d, 3), 3.55–3.80(m, 2), 4.10(s, 1), 5.35–5.55(m, 2), 6.70–7.65(m, 6)	C ₁₄ H ₁₄ O	85.02 (84.81)	7.05 (7.12)
13	3500, 1680, 1210, 980, 810, 750	0.88(t, 3), 1.33(sext, 2), 1.96(q, 2), 3.28–3.50(m, 2), 5.40–5.80(m, 3), 6.90–8.20(m, 6)	C ₁₆ H ₁₈ O	84.87 (84.91)	8.45 (8.02)
14	3300, 1660, 1205, 975, 810, 745	0.80(t, 3), 1.25(sext, 2), 1.85(q, 2), 3.50–3.80(m, 2), 6.75–7.90(m, 6)	C ₁₆ H ₁₈ O	84.96 (84.91)	8.25 (8.02)

naphthols (**1**, **2**) with 1-chloro-3,7-dimethyl-2,6-octadiene, *trans*-1-chloro-2-butene and *trans*-1-chloro-2-hexene gave good yields of (3,7-dimethyl-2,6-

octadienyl)naphthols (**9**, **10**), (*trans*-2-butenyl)naphthols (**11**, **12**) and (*trans*-2-hexenyl)naphthols (**13**, **14**), respectively.⁸⁾



			Yield/% (convn. %)
3	R ¹ =CH ₃ , R ² =H	82	(96)
9	R ¹ =CH ₃ , R ² =C ₅ H ₉	80	(91)
11	R ¹ =R ² =H	75	(90)
13	R ¹ =H, R ² =C ₂ H ₅	73	(84)



			Yield/% (convn. %)
4	R ¹ =CH ₃ , R ² =H	86	(95)
10	R ¹ =CH ₃ , R ² =C ₅ H ₉	82	(90)
12	R ¹ =R ² =H	80	(88)
14	R ¹ =H, R ² =C ₂ H ₅	79	(78)

Experimental

The following procedure is the typical experimental conditions used in the reaction of naphthols with allylic halides in the presence of metallic sodium.

The reaction of 1-naphthol with 1-chloro-3-methyl-2-butene. To an ethereal solution (15 ml) of 1-naphthol (2.88 g, 0.02 mol), metallic sodium (0.46 g, 0.02 g atom) was added. After the mixture was stirred for 1 h, 1-chloro-3-methyl-2-butene (2.09 g, 0.02 mol) was added slowly and the mixture was refluxed for 30 min. Then, the solution was acidified with 0.1 mol dm⁻³ aq HCl and extracted with ether. The ethereal solution was treated with 10% aq NaOH to remove the unreacted naphthol, and washed with Claisen's alkali. The Claisen's alkali phase was acidified with 1 mol dm⁻³ aq HCl and extracted with ether, and the ether layer was washed with water and dried over anhydrous sodium sulfate. After the removal of the solvent by distillation under reduced pressure, 2-(3-methyl-2-butenyl)-1-naphthol (**3**) was obtained in the yield of 82%. In order to identify the minor products, the ether layer, which was washed with Claisen's alkali as described above, was chromatographed over alumina. The alumina column was eluted with hexane and 1-naphthyl 3-methyl-2-butenyl ether (**5**) and 2,2-dimethyl-3,4-dihydro-2*H*-naphtho[1,2-*b*]pyran (**6**) were obtained in 3 and 2% yields, respectively. The structures of these products were identified by means of the IR, ¹H NMR and elemental analysis (Table 2).

References

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- 7) The reaction was carried out under conditions described below: (**1**) (0.02 mol), 1-chloro-3-methyl-2-butene (0.02 mol), alkali metal (0.02 g atom), ether (15 ml), reflux, reaction time 30 min.
- 8) It was found that these compounds (**9**–**13**) are composed of approximately 90–93% of E-type configuration by means of HPLC. HPLC was performed with a JASCO BIP-I instrument equipped with a UV detector (250 nm) using a Finepak SIL reversed-phase column (4.6 mm×25 cm) and methanol/H₂O (17/4) as an eluent at a flow speed of 1.0 ml min⁻¹.