September, 1986] © *1986 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn.*, *59, 2901—2902 (1986)* 2901

Selective Allylation of Sodium Naphtholate

Shigetoshi YAMADA,* Toru TAKESHITA,† and Juntaro TANAKA
Department of Industrial Chemistry, Junior College of Technology, Shizuoka University,
Hamamatsu 432
†Teijin Institute for Biomedical Reserch, Hino, Tokyo 191

(Received March 19, 1986)

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.

Table 1. The Effects of Alkali Metals

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

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.

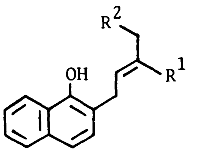
The effect of the alkali metals in this reaction is shown in Table 1.7) From this result, it was found that the metallic sodium was useful for obtaining selectively naphthols having 3-methyl-2-butenyl group.

In a same manner as above, the reaction of

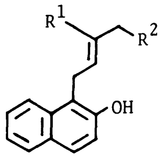
Table 2. Spectral and Analytical Data for Compounds

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), 655—765(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	$R^1=CH_3$,	$R^2=C_5H_9$	80	(91)
11	$R^1=R^2=H$		75	(90)
13	$R^1=H$,	$R^2=C_2H_5$	73	(84)



			Yield/%	(convn. %)
4	$R^1=CH_3$,	$R^2=H$	86	(95)
10	$R^1=CH_3$,	$R^2=C_5H_9$	82	(90)
12	$R^1=R^2=H$		80	(88)
14	$R^1=H$,	$R^2=C_2H_5$	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

1) G. D. Manners and L. Jurd, *J. Chem. Soc., Perkin Trans. 1*, **1977**, 405.; T. Kusumi, M. Ishitsuka, T. Kinoshita, and H. Kakisawa, *Chem. Lett.*, **1979**, 277; M. Ochi, H. Kotsuki, and A. Inoue, *ibid.*, **1979**, 831; B. H. Howard, K. Clarkson, and R. L. Berstein, *Tetrahedron Lett.*, **1979**, 4449.

2) S. Yamada, F. Ono, T. Katagiri, and J. Tanaka, *Synth. Commun.*, **5**, 181 (1975).

3) S. Yamada, F. Ono, T. Katagiri, and J. Tanaka, *Nippon Kagaku Kaishi*, **1980**, 733.

4) S. Yamada, F. Ono, T. Katagiri, and J. Tanaka, *Nippon Kagaku Kaishi*, **1981**, 1192.

5) P. Barua, N. C. Barua, and R. P. Sharma, *Tetrahedron Lett.*, **24**, 5801 (1983).

6) S. E. N. Mohamed, P. Thomas, and D. A. Whiting, *J. Chem. Soc., Chem. Commun.*, **1983**, 738.

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/H_2O (17/4) as an eluent at a flow speed of 1.0 ml min^{-1}.