under vacuum. The residue was diluted with water, acidified with ice-diluted HCl and extracted with ether. The ethereal solution was washed with aqueous $NaHCO_3$, and the aqueous layer was acidified with dilute HCl and extracted with ether. Usual workup gave pure **26a** in 75% yield: $[\alpha]^{25}_D$ −3.5° (*c* 6.4, CHCl3); IR ($CHCl_3$) 3620, 3000–2500, 1710, 1420 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (6 H, 2 d, J = 6 Hz, CH_3CH), 1.0–2.4 (12 H, m, CH_2 and CH), 3.65 (2 H, t, J = 6.4 Hz, CH_2OH), 5.0 (2 H, br s, exchanged with D_2O, COOH and OH). Anal. Calcd for $C_{11}H_{22}O_3$: C, 65.31; H, 10.96. Found: C, 65.60; H, 10.85.

A solution of **26a** (50 mg, 0.25 mmol) in dry ether (12 mL) was added dropwise to a stirred and ice-cooled suspension of $LiAlH_4$ (19 mg, 0.5 mmol) in dry ether (6 mL)). The stirring was continued for 3 h at room temperature under argon. Subsequent workup gave the crude product (42 mg), which was flash chromatographed (1:1.5 benzene–AcOEt) to obtain pure **27a** in 78% yield: $[\alpha]^{25}_D$ 0.0° (*c* 1.8, $CHCl_3$); IR ($CHCl_3$) 3620 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (6 H, d, J = 6 Hz, CH_3CH), 1.0–1.8 (14 H, m, CH_2, CH, and OH), 3.64 (4 H, t, J = 6.7 Hz, 2 CH_2OH); MS (dis), *m/e* (relative intensity) 189 (M^+ + 1, 1). Anal. Calcd for $C_{11}H_{24}O_2$: C, 70.16; H, 12.85. Found: C, 70.01; H, 12.76.

(3*S*,7*S*)-(−)-3,7-Dimethyl-1,9-nonanediol (27b). **27b** was prepared through the same pathway reported for **27a**, starting from 8 (37% overall yield). **26b**: $[\alpha]^{25}_D$ −9.3° (*c* 2.7, $CHCl_3$). **27b**: $[\alpha]^{25}_D$ −7.4° (*c* 1.7, $CHCl_3$).

Acknowledgment. We thank Dr. Diego Monti (CNR, Milano) for recording ^{13}C NMR spectra on the Bruker CXP 300 to determine diastereomeric purities. We gratefully acknowledge National Research Council (CNR), Roma, Progetto Finalizzato "Chimica Fine e Secondaria" for financial support.

Registry No. 1, 98105-56-7; **2**, 98105-60-3; **3**, 98168-99-1; **4**, 98169-00-7; **5**, 1117-61-9; **6**, 7540-51-4; **7**, 98105-57-8; **8**, 98105-61-4; **9**, 98168-98-0; **10**, 98169-01-8; **22**, 98168-95-7; **27a**, 98105-59-0; **27b**, 98169-02-9; **29**, 77878-85-4; (±)-2,6-dimethyl-8-hydroxy-2-octenal, 98168-96-8; (2*RS*,6*RS*)-2,6-dimethyl-1,8-octanediol, 98168-97-9; (2*RS*,6*SR*)-2,6-dimethyl-1,8-octanediol, 98169-03-0; (2*RS*,6*RS*)-2,6-dimethyl-8-acetoxyoctan-1-ol, 98105-58-9; (2*RS*,6*SR*)-2,6-dimethyl-8-acetoxyoctan-1-ol, 98105-62-5; geraniol, 106-24-1; **24a**, 98244-62-3; **25a**, 98267-82-4; **26a**, 98244-63-4; **26b**, 98244-64-5.

Precursors in the Alkylation of 2-Naphthol with Benzyl Alcohol in the Presence of a Base

Taketoshi Kito,* Kohji Yoshinaga, Shuji Ohkami, Kenjiro Ikeda, and Makoto Yamaye[1]

Department of Chemistry, Kyushu Institute of Technology, Sensui-cho, Tobata-ku, Kitakyushu-shi 804, Japan

Received February 28, 1985

We previously reported the reaction of potassium 2-naphthyl oxide (2-NK) with a primary alcohol at high temperatures (200 °C) followed by acidification to afford the corresponding 1-alkyl-2-naphthol in good yield.[2] Most characteristic in a series of these reactions are the following: (1) only primary alcohols are capable of performing this alkylation and (2) no isomerization of incoming *n*-alkyl groups takes place, an observation in marked contrast to typical Friedel–Crafts alkylations.

By applying milder reaction conditions for the alkylation, we were able to isolate three precursors and confirmed that the actual reaction involved the benzaldehyde produced from benzyl alcohol. We here report characterization of these precursors, i.e., 1-(α-hydroxybenzyl)-2-naphthol (**1**), benzylidene-1,1′-bis(2-naphthol) (**2**), and 1-[α-(benzyloxy)benzyl]-2-naphthol (**3**), and discuss their transformation to the final product, 1-benzyl-2-naphthol (**4**).

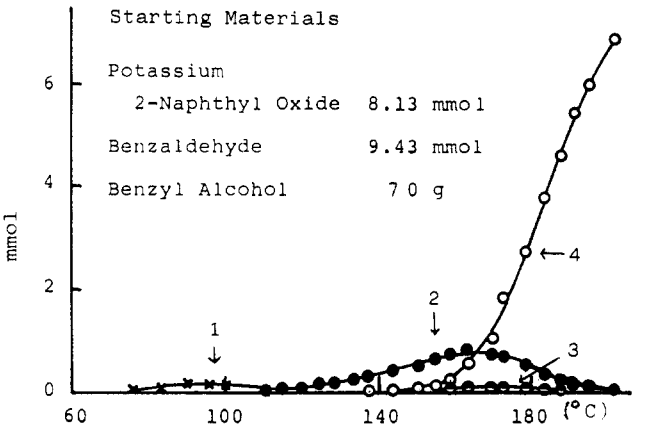


Figure 1. Temperature dependence of formation of 1, 2, 3, and 4. Rate of increasing temperature, 0.5 °C/min. Benzaldehyde was added at 68 °C.

Results and Discussion

As reported previously, 1-alkyl-2-naphthol was obtained in good yield when the mixture of 2-NK and a primary alcohol was heated at temperatures higher than 200 °C in an autoclave.[2] However, the alkylation occurred even at 170 °C under an atmospheric pressure if benzyl alcohol, relatively reactive alcohol, was employed. Therefore, we examined the alkylation pathway by use of this alcohol. Another advantage of using benzyl alcohol is that the Guerbet-type dimerization of the alcohol does not take place. Formation of such dimeric alcohols is inevitable in this series of reactions and makes it difficult to study the reaction pathway.

The final product **4** did not form in an atmosphere of oxygen-free nitrogen. The alkylation, however, did occur when either a small amount of benzaldehyde or air was present in the mixture of 2-NK and benzyl alcohol (see Experimental Section). On the other hand, the formation ratio of the precursors **1**, **2**, and **3** and the final product **4** was varied in a stirred mixture of 2-NK, benzyl alcohol, and benzaldehyde depending on the reaction temperature. Results are shown in Figure 1.

Precursors **1**, **2**, and related compounds have been synthesized by a variety of methods different from ours. An organometallic reagent and an aldehyde are generally employed to synthesize **1** and related compounds. For example, **1** was prepared from 2-hydroxy-1-naphthylaldehyde and phenylmagnesium bromide.[3] Pope and Howard prepared 2,4-dihydroxybenzhydrol from resorcinol and benzaldehyde in an aqueous alkaline solution.[4] Bennett and his co-workers prepared derivatives of **2**, such as *p*-methoxybenzylidene-1,1′-bis(2-naphthol), in the presence of hydrochloric acid.[5] Although Allan and his co-workers investigated the reaction of 2-naphthol with acetaldehyde in the presence of hydrochloric acid, they did not isolate such products as Bennett did.[6]

From Figure 1, the reaction pathway may be outlined as follows:

(a) Precursor **1** firstly forms.

(b) Precursor **1** changes into precursor **2**.

(1) Faculty of Engineering, Kyushu Kyoritsu University.
(2) Kito, T.; Ota, K. *J. Org. Chem.* **1977**, *42*, 2020.
(3) Becker, H. D.; Bremholt, T. *Tetrahedron Lett.* **1973**, 197.
(4) Pope, F. G.; Howard, H. *J. Chem. Soc.* **1910**, *97*, 79.
(5) Bennett, D. J.; Dean, F. M.; Herbin, G. A.; Matkin, D. A.; Price, A. W.; Robinson, M. L. *J. Chem. Soc., Perkin Trans. 1* **1980**, 1978.
(6) Van Allan, J. A.; Giannini, D. D.; Whitesides, T. H. *J. Org. Chem.* **1982**, *47*, 820.

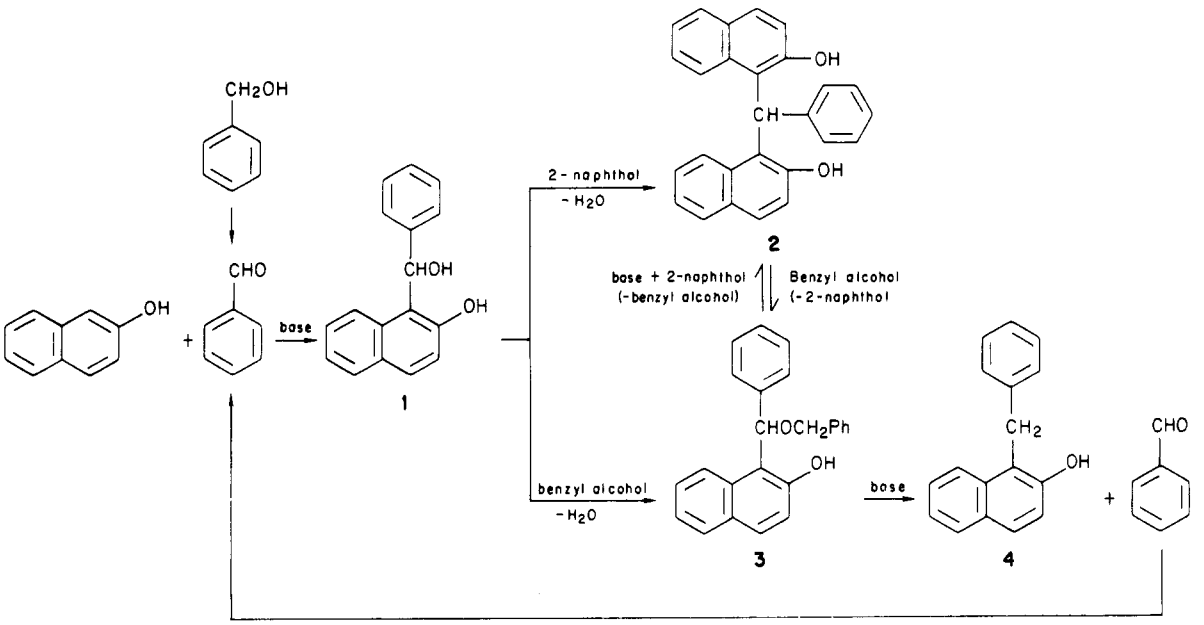
0022-3263/85/1950-4628$01.50/0

Table I. Reactions of Precursors[a]

ex. no.	temp, °C	time,[b] min	concn (mmol) 2-naph	1	2	3	4	mat. bal.[c]
		materials: 1, 0.80 mmol; balc, 50 g						
1	140	120	0.02	0.00	0.00	0.74	0.00	0.95
		materials: 1, 0.40 mmol; 2-naph, 5.49 mmol; balc, 30 g						
2	120	0	5.45	0.11	0.01	0.24	0.00	0.99
		materials: 2, 0.80 mmol; balc, 51 g						
3	170	60	0.60	0.00	0.09	0.67	0.05	0.94
		materials: 2, 0.82 mmol; balc, 50 g; PBO, 1.64 mmol						
4	120	0	0.00	0.00	0.70	0.16	0.00	0.95
		150	0.45	0.00	0.39	0.26	0.16	1.01
	170[d]	60	0.71	0.00	0.01	0.01	0.80	0.94
		materials: 3, 0.88 mmol; balc, 40 g						
5	170	180	0.09	0.00	0.00	0.76	0.05	1.02
		200[e]	0.09	0.00	0.01	0.26	0.51	0.98
		materials: 3, 0.44 mmol; 2-naph, 1.74 mmol; balc, 30 g						
6	140	120	1.70	0.00	0.00	0.45	0.00	0.99
		materials: 3, 0.88 mmol; 2-naph, 0.90 mmol; PBO, 0.88 mmol; balc, 32 g						
7	100	180	0.50	0.00	0.42	0.46	0.00	1.01

[a] balc, benzyl alcohol; 2-naph, 2-naphthol; PBO, potassium benzyl oxide; mat. bal., material balance. [b] Each listed figure is residence time held at a given temperature. [c] Material balances were calculated on the base of the number of naphthalene rings because precursor 2 has two naphthalene rings. [d] It took 30 min to raise the temperature from 120 °C to 170 °C. [e] PBO (0.88 mmol) was added after a 180-min heating.

Scheme I



(c) At temperatures higher than 170 °C, alkylated product 4 is formed from precursor 2.

Three precursors were separately heated under various conditions to examine the above pathway. The results are summarized in Table I, indicating the following pathway. (Numbers in parentheses are experimental numbers in Table I.)

(d) Presursor 1 is formed from 2-NK and benzaldehyde (Figure 1).

(e) Precursor 1 reacts with benzyl alcohol to give precursor 3 (no. 1) or reacts with 2-naphthol to give precursor 2 (see Experimental Section), which in turn reacts with benzyl alcohol to give precursor 3 (no. 2 and no. 3). A base is not required for these transformations.

(f) Precursor 3 reacts with 2-naphthol to give precursor 2 in the presence of a base at low temperatures (compare no. 7 with no. 6).

(g) Precursor 3 is transformed into product 4 in the presence of a base at higher temperatures (compare no. 5 with no. 7) to liberate an equivalent mole of benzaldehyde. Results shown in no. 4 in Table I are consistent with the conclusions d–g.

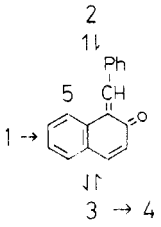
On the basis of the observations d–g, the interconversions among 1, 2, 3, and 4 may be correlated as in Scheme I. As shown in Scheme I, benzaldehyde is regenerated at the final step for recycling. Accordingly, a catalytic amount of benzaldehyde generated by the oxidation of benzyl alcohol would be enough to carry out the alkylation.

Cornforth and his co-workers obtained 1-methyl-2-naphthol (MN) by heating 2-naphthol in the mixture of sodium and methanol at 200 °C.[7] They proposed a mechanism that 2-naphthol is attacked by formaldehyde generated by decomposition of the methoxide ion. They also prepared MN by heating bis(2-hydroxy-1-naphthyl)methane in the methanol solution of sodium methoxide at 210 to 220 °C for 7 h. In both reactions, they did not isolate the products corresponding to 1 and 3.

For a straightforward interpretation of the pathway, a possible mechanism involves a quinone methide intermediate as in the base-catalyzed reactions of a variety of phenols. For example, a quinone methide was proposed

(7) Cornforth, J. W.; Cornforth, R. H.; Robinson, R. *J. Chem. Soc.* 1942, 682.

Scheme II



in the base-catalyzed condensation of hydroxybenzyl alcohol.[8] If such a product as **5** is present, the pathway could be depicted as in Scheme II. We are now making our effort to trap **5** or to seek unambiguous evidence supporting the intervention of **5**.

Experimental Section

Proton and ^{13}C NMR spectra were recorded on a JEOL JNM-FX-60 (Me_4Si as internal standard) spectrometer and IR spectra on a Shimadzu IR-408 spectrometer. MS spectra were obtained on a JEOL JMS-DX300 (70 eV) spectrometer. Gas and liquid chromatographies were performed with Yanagimoto G-180 and Toyo Soda HLC-802UR spectrometers, respectively. Melting points were determined and uncorrected on a Meihoh MP-2 spectrometer.

Alkylation of 2-NK with Benzyl Alcohol at 180 °C (Effect of Added Benzaldehyde). In a flask equipped with a thermometer, a mechanical stirrer, and a reflux condenser whose top was connected to a 100-mL Erlenmeyer flask containing liquid paraffin were placed 2-NK (5.49 g, 0.0302 mol) and phenyl ether (30.2 g). The mixture was stirred at 180 °C for 2 h in a stream of oxygen-free nitrogen through a column packed with oxygen absorber (OXISORB L). In this mixture benzyl alcohol (5.23 g, 0.0484 mol) was added through a dropping funnel, and the whole mixture was kept at this temperature for additional 3 h, but no reaction occurred (this was confirmed by gas chromatography). Then, the addition of benzaldehyde (0.99 g, 0.0093 mol) caused the formation of **4** (0.0179 mol/4 h) and the consumption of benzyl alcohol (0.0115 mol/4 h).

Temperature Dependence of the Formation of 1, 2, 3, and 4. A mixture of 2-NK (1.48 g, 8.13 mmol), benzyl alcohol (70 g), and phenyl ether (0.96 g, as an internal standard) was heated at a rate of 0.5 °C/min in a nitrogen stream. At 68 °C, benzaldehyde (1.00 g, 9.43 mmol) was added, and occasional sampling was made to determine the amounts of **1**, **2**, **3**, and **4** by liquid chromatography. The results are shown in Figure 1.

Preparation of 1-(α-Hydroxybenzyl)-2-naphthol (1). A mixture of 2-NK (30.2 g, 0.166 mol) and benzaldehyde (53.8 g, 0.508 mol) was stirred for 5 h at room temperature. Precipitates were collected, washed with aqueous HCl and water, and recrystallized from benzene to give **1**, 24.0 g, (58%): mp 114 °C; MS (70 eV), *m/e* (relative intensity) 250 (M^+, 14), 231 (base peak, 100), 202 (12), 78 (11); ^1H NMR (δ value, in acetone-d_6) 6.34 (s, 1 H, C-OH), 6.86–7.98 (m, 12 H, Ar H + methyne proton), 9.88 (s, 1 H, Ar OH) [signals at 6.34 and 9.88 disappeared by addition of D_2O]; ^{13}C NMR (ppm, in acetone-d_6) 72.6 (methyne carbon, off-resonance method; 70.7 and 74.1), 119.7–129.7 (aromatic carbons); IR (cm^{-1}) 3400 (s), 830, 815 (m), 755 (s, with a shoulder), 710 (s, with a shoulder).

Anal. Calcd for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64. Found: C, 81.77; H, 5.71.

Preparation of Benzylidene-1,1′-bis(2-naphthol) (2). A mixture of 2-NK (20.3 g, 0.112 mol) and benzaldehyde (35.9 g, 0.339 mol) was stirred at 100 °C for 9 h. After usual workup, precipitates were recrystallized from ether/cyclohexane (1:2) to afford **2**, 11.3 g (54%): mp 187 °C; MS, (*m/e*) 376 (M^+, 9), 234 (13), 233 (38), 232 (50), 231 (base peak, 100), 202 (15), 144 (30), 115 (12), 44 (29); ^1H NMR (in Me_2SO-d_6) 7.07–8.22 (m, 18 H, Ar H + methyne proton), 9.70 (s, 2 H, OH); ^{13}C NMR (in Me_2SO-d_6) 41.5 (methyne carbon; off-resonance method; 40.1 and 42.8), 117.1–152.7 (aromatic carbons); IR (cm^{-1}) 3200 (br, OH), 810 (s, with a shoulder), 743 (s, with two shoulders), 705 (m).

Anal. Calcd for $C_{27}H_{20}O_2$: C, 86.14; H, 5.36. Found: C, 85.94; H, 5.39.

Alternative Synthesis of 2. Heating a mixture of **1** (2.00 g, 0.0080 mol) and 2-naphthol (10.0 g, 0.0694 mol) at 130 °C for 3 h gave **2**, 2.64 g (88%).

Preparation of 1-[α-(Benzyloxy)benzyl]-2-naphthol (3). A mixture of **1** (2.00 g, 0.0080 mol) and benzyl alcohol (10.0 g, 0.0926 mol) was heated at 115 °C for 3 h. After usual workup, **3** was obtained in a yield of 2.02 g (74%): mp 119 °C; MS, (*m/e*) 340 (M^+, 26), 234 (54), 233.1 (41), 233.0 (42), 232 (base peak, 100), 231 (85), 203 (65), 202 (67), 116 (44), 108 (49), 107 (53), 101 (52); ^1H NMR (in acetone-d_6) 4.62 (s, 2 H, methylene H), 6.69–8.16 (m, 17 H, Ar H + methyne H), 9.19 (s, 1 H, OH); ^{13}C NMR (in acetone-d_6) 71.3 (methylene carbon, off-resonance method; 68.0, 71.0, and 73.9), 77.7 (methyne carbon, off-resonance method; 75.7 and 79.0), 116.1–153.7 (aromatic carbons).

Anal. Calcd for $C_{24}H_{20}O_2$: C, 84.68; H, 5.92. Found: C, 84.46; H, 6.01.

Conversion of Precursors under Various Conditions. A representative example (ex. no. 4 in Table I) is described. A mixture of **2** (0.31 g, 0.82 mmol), potassium benzyl oxide (1.64 mmol, as a solution (2.05 g) of benzyl alcohol), benzyl alcohol (50.0 g), and phenyl ether (0.16 g, as an internal standard) was placed in a flask. After displacement of the atmosphere with nitrogen, the mixture was heated at 120 °C for 150 min and then at 170 °C for 60 min. During the reaction, occasional samplings were made for the reaction mixture by means of a syringe. Quantitative analyses of **1**, **2**, **3**, **4**, and 2-naphthol were performed by liquid chromatography. The results are listed in Table I.

Registry No. **1**, 40473-53-8; **2**, 29114-24-7; **3**, 98577-46-9; **4**, 36441-31-3; 2-NK, 36294-21-0; benzyl alcohol, 100-51-6; benzaldehyde, 100-52-7; 2-naphthol, 135-19-3; potassium benzyl oxide, 22379-62-0.

(8) Merijan, A.; Gardner, P. D. *J. Org. Chem.* **1965**, *30*, 3965.

The Stereoisomers of Perhydrophenanthrene

Helmut Hönig

Institut für Organische Chemie, Technische Universität in Graz, A-8010 Graz, Austria

Norman L. Allinger*

Department of Chemistry, University of Georgia, Athens, Georgia 30602

Received January 29, 1985

There are six stereoisomers possible for perhydrophenanthrene (excluding enantiomers), four of which have been described in the literature.[1] Because this series contains one isomer with the central cyclohexane ring in a boat conformation and another with a syn-diaxial interaction, and because of the widespread occurrence of the perhydrophenanthrene skeleton in nature, the relative stabilities of the possible stereoisomers are of interest. The conformational analysis of these compounds was carried out at an early date,[1-9] and the pertinent conformations are shown in Figure 1.

(1) Allinger, N. L.; Gorden, B. J.; Tyminski, I. J.; Wuesthoff, M. T. *J. Org. Chem.* **1971**, *36*, 739.
(2) Johnson, W. S. *J. Am. Chem. Soc.* **1953**, *75*, 1498.
(3) Dauben, W. G.; Pitzer, K. S. In "Steric Effects in Organic Chemistry"; Newman, M. S., Ed.; Wiley: New York, 1956; p 33f.
(4) Dalling, D. K.; Grant, D.M. *J. Am. Chem. Soc.* **1974**, *96*, 1827.
(5) Cambron-Bruderlein, H.; Sandorfy, C. *Theor. Chim. Acta.* **1966**, *4*, 244.
(6) Arev'ev, O. A.; Vorob'eva, N. S.; Petrov, A. A. *Khim. Tverd. Topl. (Moscow)* **1972**, 119.
(7) Kogan, D.; Mazur, Y. *Tetrahedron Lett.* **1971**, 2401.
(8) Vanek, J.; Podrouzkova, B.; Landa, S. *J. Chromatogr.* **1970**, *52*, 77.
(9) Allinger, N. L.; Wuesthoff, M. T. *J. Org. Chem.* **1971**, *36*, 2051.
(10) Eliel, E. L.; Allinger, N. L.; Angyal, S. J.; Morrison, G. A. "Conformational Analysis"; Wiley: New York, 1965; p 24f.

0022-3263/85/1950-4630$01.50/0