Base-catalysed Alkylation of 2,7-Naphthalenediol with Glyoxal. Isolation of Structurally Intriguing Products and their Stereochemistry

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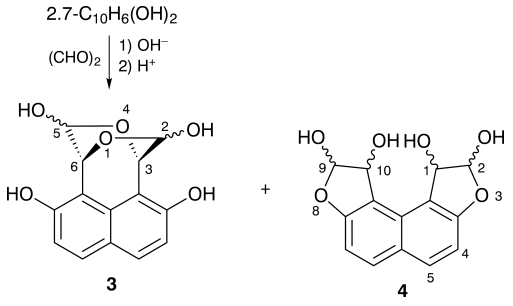
Xiaobo Fan,[a] Tomoko Yanai,[b] Makoto Yamaye,[c] Hirochi Okazaki[b] and Taketoshi Kito*[d]

[a]*Shima Tec Co., Ltd., 4-6 Yubaru-machi Yahatanishi-ku, Kitakyushu-shi 807, Japan*
[b]*Shinnikka Environmental Engineering Co., Ltd., Nakabaru, Tobata-ku, Kitakyushu-shi 804, Japan*
[c]*Faculty of Engineering, Kyushu Kyoritsu University, Jiyugaoka, Yahatanishi-ku, Kitakyushu-shi 807, Japan*
[d]*Department of Chemistry, Kyushu Institute of Technology, Sensui-cho, Tobata-ku, Kitakyushu-shi 804, Japan*

1,8-(2,5-Dihydroxy-1,4-dioxane-3,6-diyl)naphthalene-2,7-diol and 1,2,9,10-tetrahydronaphtho[2,1-*b*:7,8-*b*′]difuran-1,2,9,10-tetrol are prepared by reaction of 2,7-naphthalenediol with glyoxal, and their stereochemistry investigated mainly by NMR spectroscopy.

The base-catalysed alkylation of 2,7-naphthalenediol with glyoxal was carried out in aqueous KOH. Ether extraction of the reaction mixture gave compound 1,2,9,10-tetrahydronaphtho[2,1-*b*:7,8-*b*′]difuran-1,2,9,10-tetrol (**4**). Addition of methanesulfonic acid to the aqueous layer, followed by stirring the resultant mixture at 45 °C for 2 h, afforded 1,8-(2,5-dihydroxy-1,4-dioxane-3,6-diyl)naphthalene-2,7-diol (**3**) as a precipitate. The latter product had a 1,4-dioxane ring system fixed on the 1,8-positions of the naphthalene ring. Under acidic conditions, the tetrol readily reacted with 2-naphthol to form the corresponding furofuran derivatives or underwent dehydration to afford the corresponding dilactone. The stereochemistry of these products was investigated mainly by NMR spectroscopy with the help of MO calculation. A possible pathway for their formation was discussed.



Scheme

An inspection of the molecular model of **3** revealed that three types of stereoisomers are possible in regard to the orientation of the two hydroxy groups on the two hemiacetal carbons (C^2 and C^5), namely up-up, down-down and up-down isomers. For each of these three isomers, there are a pair of mirror images. The ^{1}H NMR study for **3** showed two groups, each of which is composed of three singlets for the two hydroxy groups on the hemiacetal carbon and the two phenolic hydroxy groups with the proton ratio of 0.74:0.74:0.52, respectively; indicating that compound **3** may consist of three stereoisomeric structural isomers. Attempted separation of these stereoisomers failed. Consequently, **3** was transformed into its tetraacetate (**3***ac*) for characterization.

In the liquid chromatogram of **3***ac*, there was a small peak with a retention time of 29 s and two large peaks with times of 43 and 48 s. Although the first component (**3***ac*$_1$) could not be isolated due to its low content, the other two compounds (**3***ac*$_2$ and **3***ac*$_3$) were successfully separated by recrystallization from benzene. The ^{1}H NMR and NOE spectra (in $CDCl_3$) of **3***ac*$_2$ and **3***ac*$_3$ were measured. Based on the results of NMR and the MO calculation, the stereochemistries of **3***ac*$_2$ and **3***ac*$_3$ are up-down and up-up isomers, respectively.

The structure of **4**, whose structure was reported in a previous paper[2] without geometry, consists of six isomers with regard to the orientation of the four hydroxy groups on C^1, C^2, C^9 and C^{10} atoms, excluding mirror images. According to the discussion of the results for ^{1}H NMR and NOE spectra of **4***ac*$_1$, **4***ac*$_2$ and **4***ac*$_3$, they were assigned to the *cis-cis-syn*, *cis-cis-anti* and *trans-trans-anti* isomers, respectively.

In the synthesis of **3** and **4**, it was found that their yields differed depending on the ether extraction times after the base-catalysed alkylation of 2,7-naphthalene with glyoxal. When the extraction times were 0, 3, 4, 5 and more, the yield of **4** was 0, 18, 27, 44 and 60%, respectively, the corresponding yield of **3** was 67, 55, 42, 29 and very little. This results suggest that isomers **3** and **4** can interconvert under base or acid conditions.

Techniques used: IR, ^{1}H and ^{13}C NMR, NOE, mass spectroscopy, elemental analysis, DSC

References: 10

Table 1: The ^{1}H NMR chemical shifts of isomers of **3***ac* in $CDCl_3$

Table 2: Heats of formation and dihedral angles of **3***ac*

Table 3: The signals in ^{1}H NMR spectra of **4***ac* isomers in $CDCl_3$

Fig. 1: Stereoisomers of **3** (R = H) and **3***ac* (R = COMe)

Scheme 1: Reaction of 2,7-dihydroxynaphthalene with glyoxal

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Reference cited in this synopsis

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*To receive any correspondence (*e-mail:* tkito@che.kyutech.ac.jp).