# Chemistry

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## Abstract

## Full Text

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# ALKYLATION OF $\alpha$- AND $\beta$-NAPHTHOLS WITH ACETYLENE

*(Presented by Academician A. V. Topchiev, 15 III 1957)*

Alkylation was carried out in a reactor into which were placed a solution of naphthol in 50 ml of ethyl or butyl alcohol and the catalyst $H_3PO_4 \cdot BF_3$ + 1 g of mercuric oxide. Acetylene was supplied from a cylinder at a regulated rate. The reactor was heated with a water bath. After completion of the reaction, the resulting mass was filtered with suction on a Büchner funnel, and the alkylate crystals were washed with butyl alcohol. The results of the experiments are presented in Table 1.

Experiments Nos. 1, 2, 17, in which the alkylate yields were, respectively, 41, 42, and 42%, as well as Nos. 4 and 8 and Nos. 5 and 9, carried out under identical conditions of temperature, catalyst concentration, etc., show their reproducibility, irrespective of whether they were conducted in ethyl or butyl alcohol solution.

Data on the yield of alkylate as a function of catalyst concentration, other conditions being equal, are given in Fig. 1. The optimum alkylate yield proved to be 68% at a catalyst concentration of 18% in the reaction mixture at a temperature of 65-70°. Data on the yield of alkylate as a function of temperature, other conditions being equal, are given in Fig. 2. The optimum temperature proved to be 75-80° at a catalyst concentration of 14%.

Increasing the rate of passage of acetylene from 2 l/hr to 4 l/hr decreases the alkylate yield by only 16%.

The alkylate obtained is sparingly soluble in benzene, readily soluble in acetone, acetic acid, ether, and chloroform; in carbon tetrachloride–

### Table 1

### Alkylation of $\beta$-naphthol

| Experiment No. | Naphthol, mmol | Catalyst, ml | Catalyst, wt. % in reaction mixture | Temperature, °C | Rate of acetylene passage, l/hr | Reaction time, hr | Alkylate yield, g | Alkylate yield, % of theory (based on naphthol taken) |
|---|---|---|---|---|---|---|---|---|
| 1 | 20 | 5 | 14 | 65–70 | 2 | 3 | 8.5 | 41 |
| 2 | 20 | 5 | 14 | 65–70 | 2 | 3 | 8.7 | 42 |
| 3 | 20 | 5 | 14 | 75–80 | 2 | 1.5 | 9.5 | 46 |
| 4 | 20 | 5 | 14 | 65–70 | 2 | 1.5 | 6.5 | 32 |
| 5 | 20 | 5 | 14 | 21–25 | 2 | 1.5 | 2 | 10 |
| 6 | 20 | 5 | 14 | 105–110 | 2 | 1.5 | 8 | 39 |
| 7 | 20 | 5 | 14 | 75–80 | 2 | 1.5 | 9.5 | 44 |
| 8 | 20 | 5 | 14 | 65–70 | 2 | 1.5 | 7 | 34 |
| 9 | 20 | 5 | 14 | 21–25 | 2 | 3 | 3 | 15 |
| 10 | 20 | 2.5 | 7 | 65–70 | 2 | 3 | 4 | 20 |
| 11 | 20 | 1.25 | 4 | 65–70 | 2 | 3 | 1 | 5 |
| 12 | 20 | 10 | 24 | 65–70 | 2 | 3 | 9.5 | 46 |
| 13 | 20 | 10 | 24 | 65–70 | 2 | 3 | 6 | 30 |
| 14 | 15 | 5 | 15 | 65–70 | 2 | 3 | 6 | 39 |
| 15 | 10 | 5 | 16 | 65–70 | 2 | 3 | 7 | 68 |
| 16 | 5 | 5 | 18 | 65–70 | 2 | 3 | 2.8 | 55 |
| 17 | 20 | 5 | 14 | 65–70 | 2 | 3 | 8.6 | 42 |
| 18 | 32 | – | – | 65–70 | 2 | 3 | 13.5 | 41 |
| 19 | 39 | – | – | 65–70 | 2 | 3 | 9.5 | 24 |
| 20 | 50 | – | – | 65–70 | 2 | 3 | 10 | 20 |

**Notes.** 1. In experiments Nos. 5, 6, 7, 8, *n*-butyl alcohol was used as the solvent; in all the others, ethyl alcohol. 2. In experiments Nos. 18, 19, 20, 21, 20 g of naphthol and a mother liquor containing catalyst and unconsumed naphthol remaining from the preceding experiment were placed in the reactor.

in carbon tetrachloride and in *n*-heptane it dissolves on heating; it does not dissolve in alkali, nor in dilute sulfuric acid. M.p. 173°C.

Found (in %): C 89.3; $H_2$ 5.5; $O_2$ 5.2
For $C_{22}H_{16}O$ calculated (in %): C 89.2; $H_2$ 5.4; $O_2$ 5.4

Molecular weight 296—301. For $C_{22}H_{16}O$, calculated molecular weight 296. Determination by the Tseretvinov method revealed the absence of hydroxyl groups.

Fig. 1. Dependence of the yield of the β-naphthol alkylate on temperature.

Figure 1: Fig. 1. Dependence of the yield of the β-naphthol alkylate on temperature.

Fig. 2. Dependence of the yield of the β-naphthol alkylate on catalyst concentration.

Figure 2: Fig. 2. Dependence of the yield of the β-naphthol alkylate on catalyst concentration.

**Fig. 1**

**Fig. 2**

**Fig. 1.** Dependence of the yield of the β-naphthol alkylate on temperature
**Fig. 2.** Dependence of the yield of the β-naphthol alkylate on catalyst concentration

Taking into account the results of our experiments on the alkylation of phenol ([1,2]) and cresols ([3]) under analogous conditions, we can identify the alkylate as ethylidene-di-β-naphthol oxide, formed according to the following scheme:

$$1 \qquad \beta\text{-naphthol} + \mathrm{CH} \equiv \mathrm{CH} \longrightarrow \text{vinylnaphthol}$$

$$2 \qquad \text{vinylnaphthol} + \beta\text{-naphthol} \xrightarrow[-\mathrm{H_2O}]{} \text{ethylidene-di-}\beta\text{-naphthol oxide}$$

This heterocyclic compound may be regarded as a xanthene derivative, 9-methyl-1,2,7,8-dibenzoxanthene,

9-methyl-1,2,7,8-dibenzoxanthene

or as a pyran derivative, 4-methyl-[di-naphtho$\{2''1'' : 2, 3;\ 1'2' : 5, 6\}$]-pyran.

4-methyl-[di-naphtho$\{2''1'' : 2, 3;\ 1'2' : 5, 6\}$]-pyran

Such a compound with m.p. 173° was obtained by Claisen ([4]), by condensation of β-naphthol and paraldehyde in the presence of HCl.

On oxidation of the alkylate with chromic anhydride, crystals with m.p. 194° were obtained. The oxidation reaction proceeds in such a way that the radical is oxidized to a carbonyl group and the corresponding ketone is formed:

[structural formula]
$C_{21}H_{12}O_2$ —dinaphtho-γ-pyrone,
mol. wt. 296

The catalytic condensation of acetylene with naphthol was carried out by Wenzke and Nieuwland ($^5$). The reaction was conducted in a 95% alcoholic solution in the presence of concentrated sulfuric acid and mercury salts. However, attempts to isolate any crystals from the resulting solution ended in failure. With $\alpha$- and $\beta$-naphthols the reaction was carried out by the authors mentioned for 10 days; a certain amount of crystals with m.p. 173° was obtained. According to the authors, when $\beta$-naphthol is used acetaldehyde is obtained, and from $\alpha$-naphthol, ethylidenedinaphthol oxide. Unfortunately, the authors did not provide sufficient grounds for such an assertion.

The alkylation of $\alpha$-naphthol was carried out by us under the same conditions as that of $\beta$-naphthol. But the alkylate obtained dissolves neither in benzene nor in camphor, which makes it difficult to determine the molecular weight.

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## CITED LITERATURE

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*Note: Figure translations are in progress. See original paper for figures.*

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