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Alkylation of Naphthalene, β-Methylnaphthalene, and Tetralin with Acetylene

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Reilly and Newland (1) studied the alkylation of naphthalene with acetylene. Using sulfuric acid and mercury oxide as the catalyst, they showed that naphthalene and other polynuclear hydrocarbons, such as diphenyl, diphenylmethane, dibenzyl, and triphenylmethane, are not alkylated. Reilly and Newland attempted to explain the fact that naphthalene is not alkylated under the above conditions by saying that the naphthalene molecule is similar to a benzene derivative with an unsaturated radical in the side chain.

Other investigators (2) likewise regard the naphthalene molecule as consisting of two rings: one aromatic and the other alicyclic.

In our opinion, naphthalene is not alkylated with acetylene under these conditions because the naphthalene molecule, consisting of two aromatic nuclei, is a stable molecule. According to Fries' rule, the most stable form of polynuclear compounds is that form which has the greatest number of nuclei with the normal structure of the benzene ring (i.e., with three double bonds, and not with two, as in the quinoid form).

It may also be assumed that the solvent has a predominant significance in the alkylation reaction. Proceeding from this, we attempted to alkylate naphthalene in an alcoholic solution with the catalyst $H_3PO_4 \cdot BF_3$, assuming that the alkylation would proceed similarly to the alkylation of β-naphthol (3). The results, however, were negative: after passing acetylene for three hours through a solution of naphthalene at various temperatures, and after the corresponding treatment of the crude alkylate obtained, only pure naphthalene was distilled off.

Subsequently we turned to other solvents: chloroform and carbon tetrachloride. Under these conditions, alkylation of naphthalene takes place.

Alkylation of Naphthalene

Into a reactor equipped with a mechanical stirrer we poured a solution of naphthalene, the catalyst $H_3PO_4 \cdot BF_3$, and 1–2 g of mercury oxide. The experiments were carried out at a temperature of 50–55°. Acetylene was supplied from a cylinder at a rate of 3 l/hr. The crude alkylate obtained was dissolved in sulfuric ether; the ether extract was neutralized with soda and water and dried over calcium chloride. After removal of the ether, the residue was distilled under vacuum. The principal product was obtained at a temperature of 243–245° at 5 mm Hg, or at 236–238° and 3 mm Hg.

The results of the experiments are given in Table 1.

The optimum reaction conditions are: temperature 50–55°, catalyst concentration in the mixture 16%, and molar ratio naphthalene—acetylene ~ 1.0.

The alkylate is, at room temperature, a solidified transparent mass of slightly yellow color; it dissolves in benzene, chloroform, and ether.

Table 1

Experiment no.	Naphthalene, g	Solvent*, ml	Catalyst, ml	Catalyst, % in reaction mixture	Acetylene, g	Molar ratio naphthalene/acetylene	Alkylate, g	Alkylate, % of theory
1	40	25	20	33	8.7	0.9	16	36
2	40	40	20	28	10.4	0.8	17	39
3	40	40	10	16	10.4	0.8	17	39
4	40	40	5	9	10.4	0.8	15	34
5	120	120	30	16	32	0.8	53	40

* In experiment no. 1 chloroform; in experiments nos. 2–5 CCl_4.

M found 279; 287; calculated for ethylidenedinaphthyl $C_{22}H_{18}$, 282. The reaction proceeds according to the equation

$$\mathrm{CH{\equiv}CH + 2\,C_{10}H_8 \longrightarrow CH_3{-}CH(C_{10}H_7)_2}$$

We determined the molecular refraction of this compound by dissolving it in benzene. MR found 91.5; calculated for $C_{22}H_{18}$, 90.3.

Attempts to oxidize the alkylate for purposes of identification did not give the required results: the oxidation products obtained were aromatic acids that were difficult to separate. Confirmation of the structural formula $C_{22}H_{18}$ was obtained by cracking this product. A solution of $C_{22}H_{18}$ in benzene was passed through a layer of aluminosilicate catalyst at a temperature of 550° in the presence of a diluent—steam. From the cracking products β-vinylnaphthalene was isolated—white crystals in the form of leaflets, mp 65–65.5° (literature data 66° (4)); α-vinylnaphthalene was not detected in the cracking products.

In accordance with our investigations (5, 6), on the basis of the cracking products it is also possible to identify $C_{22}H_{18}$ as ethylidene-di-β-naphthyl.

Alkylation of β-methylnaphthalene. β-Methylnaphthalene (mp 31.5°) was subjected to alkylation with acetylene, just like naphthalene, at a temperature of 50-55°; the solvent was chloroform or carbon tetrachloride.

The results of the experiments are given in Table 2.

Table 2

Experiment no.	Methylnaphthalene, g	Solvent*, ml	Catalyst, ml	Catalyst, % in reaction mixture	Acetylene, g	Molar ratio naphthalene/acetylene	Alkylate, g	Alkylate, % of theory
1	30	20	20	39	10.4	0.5	7	21
2	40	40	20	28	7	1.0	9	21
3	40	40	10	16	7	1.0	14	33
4	40	40	5	9	7	1.0	7	17

* In experiment no. 1 chloroform; in experiments nos. 2-4 CCl_4.

The optimum reaction conditions are the same as in the alkylation of naphthalene.

The alkylate obtained, after treatment, was distilled under vacuum. The main product distilled at 262—265° and 5 mm Hg.
M found 308; 308; calculated for $C_{24}H_{22}$ 310.

The hydrocarbon obtained, ethylidene-di-β-methylnaphthalene, is formed according to the reaction

$$\mathrm{CH{\equiv}CH} + 2\,(\beta\text{-methylnaphthalene}) \longrightarrow \text{ethylidene-di-}\beta\text{-methylnaphthalene}$$

It is a thick viscous liquid of greenish color; soluble in benzene, chloroform, carbon tetrachloride, and n-heptane; insoluble in alcohol.

Alkylation of tetralin. Tetralin, b.p. 72—74°/4 mm, was subjected to alkylation. The results of experiments carried out at 60—65° in carbon tetrachloride solution are given in Table 3.

Table 3

Experiment No.	Tetralin, g	Solvent, ml	Catalyst, ml	Catalyst, % in mixture	Acetylene, g	Molar ratio tetralin/acetylene	Alkylate, g	Alkylate, % of theory
1	40	20	10	21	10.4	0.8	18	41
2	40	20	5	12	10.4	0.8	14	32

The optimum conditions and the yield of alkylate in this reaction are approximately the same as in the alkylation reaction of naphthalene.

The alkylate obtained has b.p. 214—216°/5 mm.
M found 288; 288; calculated for ethylidene-di-tetralin $C_{22}H_{26}$ 290.

Ethylidene-di-tetralin is formed according to the reaction

$$\mathrm{CH{\equiv}CH} + 2\,(\text{tetralin}) \longrightarrow \text{ethylidene-di-tetralin}$$

It is a thick viscous liquid of pale-yellow color; soluble in benzene, chloroform, *n*-heptane; insoluble in alcohol.

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