

The Action of Heat on 2-(3-Methylbut-2-enyloxy)naphthalene: a Novel Rearrangement

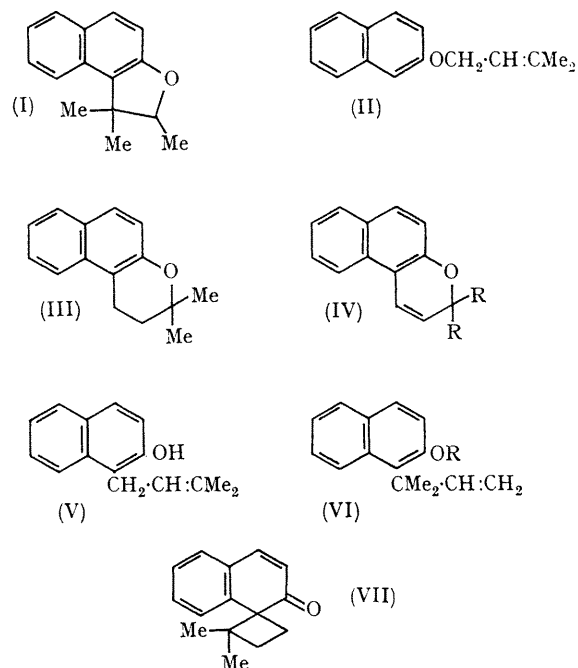
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Summary 2-(3-Methylbut-2-enyloxy)naphthalene on heating affords 1,2-dihydro-3,3-dimethyl-3*H*-naphtho[2,1-*b*]pyran.

An attempt to prepare the naphthofuran (I) by heating 2-(3-methylbut-2-enyloxy)naphthalene (II) at 200° *in vacuo* gave instead 1,2-dihydro-3,3-dimethyl-3*H*-naphtho[2,1-*b*]pyran¹ (III)† in 74% yield. The product (III) was also obtained by heating the ether (II) in various solvents, at different temperatures, and in the presence of radical scavengers. In quinoline, however, the dehydro-compound¹ (IV; R = Me) was isolated, which on treatment with hydrogen in the presence of palladium on charcoal gave a product identical in all respects with the naphthopyran (III). The position of the double bond follows from the near identity of the u.v. spectrum with that of the naphthopyran (IV; R = H).² Furthermore, the mass spectrum of the saturated compound (III) is identical in all respects with that of 1-(3-methylbut-2-enyl)-2-naphthol (V) which was obtained together with the ether (II) by the reaction of sodium 2-naphthoxide and 3-methylbut-2-enyl bromide in *NN*-dimethylformamide.³ The structure of (III) was finally proved by its formation on heating the naphthol (V).

A clue to the mechanism of formation of the naphthopyran (III) is given by the observation that heating the ether (II) in a mixture of acetic anhydride and quinoline yielded 2-acetoxy-1-(1,1-dimethylprop-2-enyl)naphthalene (VI; R = Ac). It is suggested that the initial product in the formation of (III) is the naphthol (VI; R = H) formed by Claisen rearrangement. The large steric interaction between the *gem*-dimethyl group and the *peri*-hydrogen atom prevents attack by the oxygen atom on the double bond. Instead, a novel isomerization of the allylic side-



chain occurs by way of the postulated spirocyclobutane intermediate (VII) to give the naphthol (V) in which steric interaction between the methylenic hydrogen atoms and the *peri*-hydrogen is insufficient to prevent cyclization to the naphthopyran (III). An alternative mechanism, which would involve a thermal 1,3-sigmatropic shift in the ether (II), is forbidden by the Woodward-Hoffman rules.⁴

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† The structures of all compounds have been confirmed by chemical and spectroscopic analysis. Other physical constants agree with literature values.

¹ R. Livingstone, D. Miller, and R. B. Watson, *J. Chem. Soc.*, 1958, 2422; R. Livingstone, D. Miller and S. Morris, *ibid.*, 1960, 2422.

² I. Iwai and J. Ide, *Chem. and Pharm. Bull. (Japan)*, 1962, 10, 926.

³ Cf. D. R. Buckle and E. S. Waight, *Org. Mass Spectrometry*, 1969, 2, 367.

⁴ R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, 1965, 87, 2511.