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THE THERMAL CYCLIZATION OF ALKENYLPHENOLS AND ALKENYLANILINES

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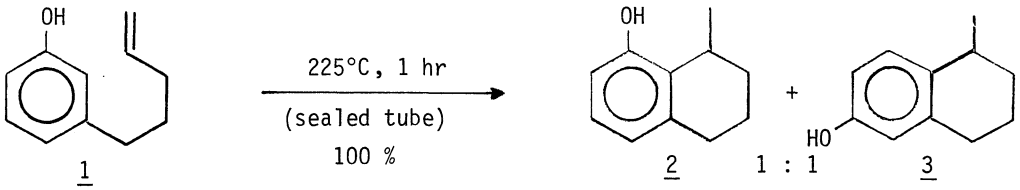
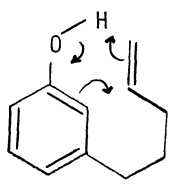
In the present paper we report the thermal cyclization of various alkenylphenols in order to investigate the scope and limitations of this reaction. Different experimental conditions were used to elucidate the mechanism.

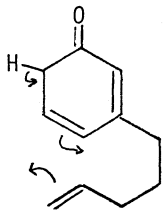
By heating 3-(4-Pentenyl)phenol 1 in a sealed tube (liquid phase) it was established [1] that 1 was converted quantitatively into a mixture of 2 and 3, in the approximatively 1 : 1 ratio.

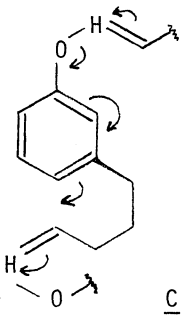


It was suggested [1] that formation of 2 could follow an intramolecular ene reaction in which the hydrogen shift occurred via a six-membered cyclic transition state A, as in the thermally induced cyclization of unsaturated ketones via their enols forms (see for a review [2]). Furthermore, it was postulated that 3 was obtained by such a reaction in which the migrating hydrogen was coming from a CH_2 group as in B.

Recently we have observed that upon heating 1 in the gas phase (350°C, 3 hrs), a unique cyclization product 2 (100 % yield) is formed, which indicates that for the formation of 3 in sealed tube an intermolecular migration of the phenolic hydrogen (Route C) involves instead of route B.


A


B


C

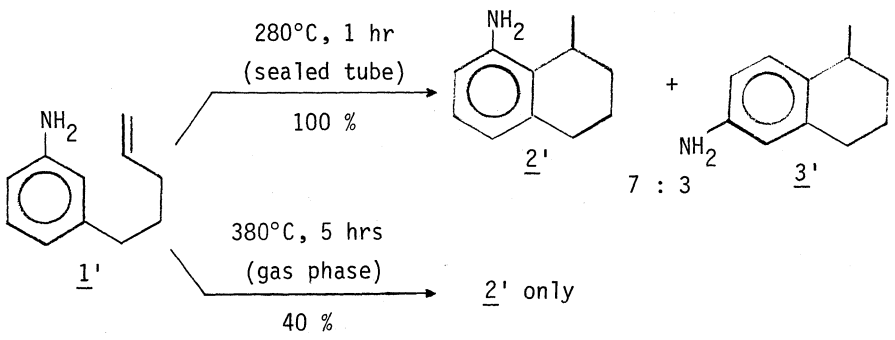
In view of these results further work was extended to other alkenylphenols.

Phenol 4 does not cyclize even at 450°C in the gas phase. However 4 in the liquid phase gives 5 exclusively under mild conditions (225°C, 1 hr). Moreover isomers ortho 6 and para 7 are recovered unchanged by heating in a sealed tube or in the gas phase (see table).

Other experiments are in full agreement with the intra- or inter- molecular processes proposed and show that the mechanism does not follow a Friedel-Crafts type reaction, involving a carbonium ion intermediate : the methyl ether of alkenylphenol 1 remains unchanged even at 350°C, this compound being either in the pure state or mixed with an équimolecular quantity of phenol. The nature of the glass used in the experiments had no influence whatsoever on the thermal behaviour of 1

But, on the other hand, refluxing phenols 4, 6 or 7 with benzene in the presence of a catalytic amount of p-toluenesulfonic acid or boron trifluoride etherate [3] leads respectively to the cyclization isomers 5, 8 or 9. A similar treatment carried out on 1 also gives a 7 : 3 mixture of 2 and 3, the ratio being different when reaction proceeds thermally.

The validity of our mechanism was supported by the thermal behaviour of the corresponding aniline 1'. 3-(4-Pentenyl)aniline 1' was cyclized in the sealed tube into a 7 : 3 mixture of two amines 2' and 3', suggesting an analogous migration of one of the NH_2 hydrogens. In the gas state, however, only 2' was formed.



Observation of the thermal behaviour of other 3-alkenylphenols which differ by the type of substitution on the double bond or by its position, not only confirm the interest of such rearrangements but let know how the polarity of the C=C double bond may be involved in the cyclization mechanism.

Though phenol 10 led the two normally expected gem-dimethyltetrahydronaphtol 11 and 12, (sealed tube), phenol 13 was converted into two hydroxy-benzocycloheptanes 14 and 15 (1 : 1 mixture). Friedel-Crafts reaction (BF_3 Et_2O) gives 11 + 12 and 14 + 15 in a 1 : 9 mixture respectively. It is noteworthy with 13 that no isopropyltetrahydronaphtols could be detected.

3-(3-Butenyl)phenol 16 is stable upon heating but is readily transformed in the presence of $AlCl_3$ into 17, as the sole product.

This thermal cyclization of alkenylphenols and alkenylanilines which requires milder conditions than unsaturated ketones must be compared with the recently reported ortho alkylation of phenols by olefins[4]. The steric constraint by aromatic ring which places the two ends of the molecule (OH and C=C) in a very suitable steric relationship, is in favour of an H transfer, as it has been observed for the smooth ring closure of 1-8 or 1-7 dienes where a benzo substitution is a part of the system[5].

This constraint would overcome the lack of aromaticity which is unfavourable in cases involved herein, which are quite uncommon.

Table : Cyclizations of alkenylphenols

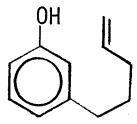
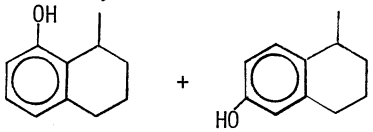
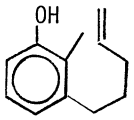
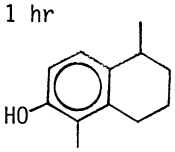
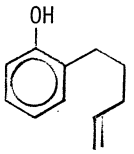
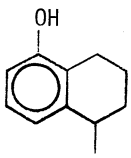
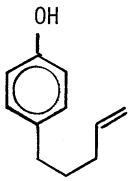
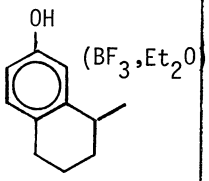
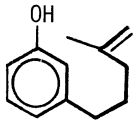
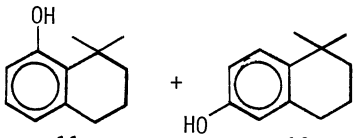
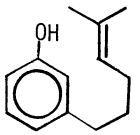
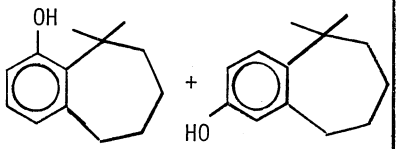
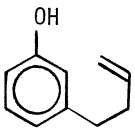
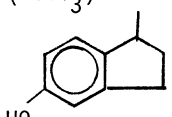
Starting phenol	In the sealed tube	Gas phase	Friedel-Crafts
 1	225°C, 1 hr  2 1 : 1 3	350°C, 3 hrs 2 (only)	2 + 3 (TsOH) 7 : 3
 4	340°C, 1 hr  5 (only)	450°C unchanged	5 (BF_3, Et_2O)
 6	unchanged	unchanged	 (BF_3, Et_2O) 8

Table (continued)

Starting phenol	In the sealed tube	Gas phase	Friedel-Crafts
 7	unchanged	unchanged	 9
 10	225°C, 1 hr  11 + 12 1 : 1	11	11 + 12 (1 : 9) (BF_3, Et_2O)
 13	225°C, 1 hr  14 + 15 1 : 1	unchanged	14 + 15 (1 : 9) (BF_3, Et_2O)
 16	unchanged	unchanged	($AlCl_3$)  17

Note : Most of the compounds obtained and described in this paper were identified by their IR and NMR spectra and by microanalyses. Some other ones were synthesized unambiguously. Preparation of starting phenols will be reported in a full paper.[6]

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