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UNUSUAL DISPROPORTIONATION ENCOUNTERED IN THE ALUMINA-CATALYZED DEHYDRATION OF 4-(α-HYDROXYETHYL)PHENOLS

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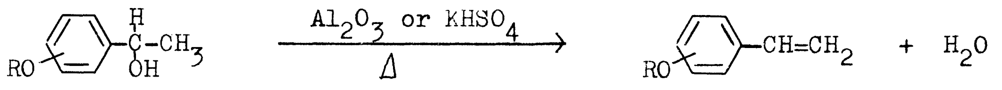
Alumina-catalyzed dehydrations of 4-(α-hydroxyethyl)phenols provided unusual disproportionation products: 4-ethylphenols and 4-acetylphenols and their tautomers.

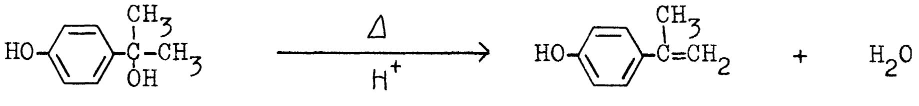
It is well known that the α-hydroxyethyl group neighboring to an aromatic ring usually undergoes dehydration with acidic catalysts such as $KHSO_4$ and alumina to afford the vinyl group.1) Thus, α-hydroxyethylphenols with R = Me2) and Ac3) (1) provide vinyl compounds 2 as in eq. 1.



1 2

(1)

Compound 3 was also found to afford normal dehydration product 4 (eq. 2).4)



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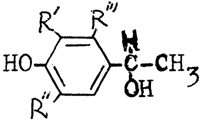
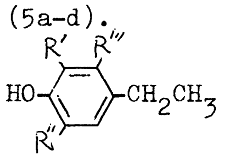
(2)

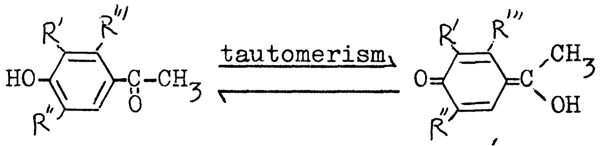
In this communication, we wish to report on the unusual behavior encountered in an attempt to get vinyl compounds by the alumina-catalyzed dehydration of 4-(α-hydroxyethyl)phenols (5a-d).



5a-d



6a-d



7a-d 7'a-d

Compound			R'	R''	R'''
5a,	6a,	7a (7'a)	H	H	H
5b,	6b,	7b (7'b)	Me	Me	H
5c,	6c,	7c (7'c)	t-Bu	t-Bu	H
5d,	6d,	7d (7'd)	Me	Me	Me

A 50 ml flask containing alumina (Woelm, neutral, 20g) and 5a-d (5g), prepared from the corresponding phenols via p-hydroxyacetophenones and subsequent $NaBH_4$-reduction, was heated in an oil bath under 5 mmHg. The temperature of the bath was raised gradually up to 300 °C and the resulting distillate was collected and subjected to alumina column chromatography to separate each component. Identifications of the components separated were made by IR, ^1H-NMR, mass, and elemental analyses with satisfactory purities.

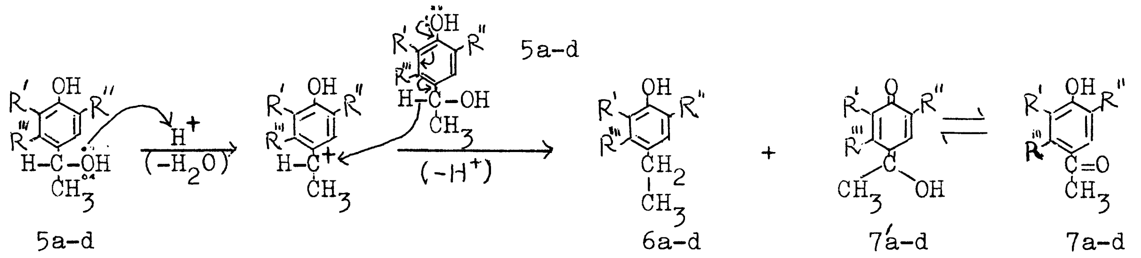
It is recognized from Table 1 that vinyl compounds are hardly present in the distillates, whereas 4-ethylphenols (6a-d) and 4-acetylphenols (7a-d) and their tautomers (7'a-d), which are the disproportionation products of 5a-d, are clearly recognized, although apparent yields are not high except in the cases of 5b and 5d. The reason why yields of 7a-d (7'a-d), oxidation products, as indicated in Table 1, are lower than those of 6a-d, except in the case of 5b, is that 7a-d (7'a-d) either remained in the distillation flask[7c (7'c)] or were only partially isolated from distillates because of wide distributions in chromatography eluates [7a (7'a) and 7d (7'd)] .

Table 1. Yields of products in Al_2O_3-catalyzed dehydration of 5a-d

Starting compd	Yield$^{a)}$ of distillation product based on initial 5a-d used								
	6a	6b	6c	6d	7a(7'a)	7b(7'b)	7c(7'c)	7d(7'd)	Normal vinyl compd
5a	16	-	-	-	2	-	-	-	none
5b	-	36	-	-	-	42	-	-	none
5c	-	-	29	-	-	-	small amt	-	trace
5d	-	-	-	37	-	-	-	b)	none

a) Figures indicate mole % of purified products. b) % Undetermined.

These results suggest that the Al_2O_3-catalyzed dehydration of 4-(α-hydroxyethyl) phenols of the 5a-d type takes place generally as in eq. 3 without providing the corresponding normal vinyl compounds, the extent of the reaction being dependent upon the kind of ring substituent (R', R'', R''').



(3)

The mechanism postulating the presence of an intermediate carbocation followed by the transfer of a hydride anion from another 5a-d to this cation may be supported by the fact that compound 3 with no α-hydrogen affords usual dehydration product (eq. 2). The formation of 7'a-d from 5a-d requires the presence of phenolic hydrogen, which explains the usual progress of reaction in the case of compound 1 with no phenolic hydrogen (eq. 1).

References

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