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

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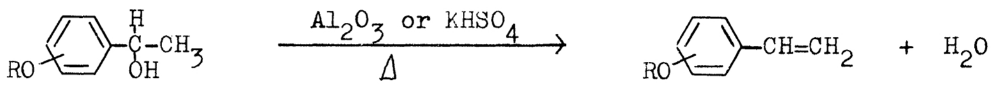
Alumina-catalyzed dehydrations of 4-(α-hydroxyethyl)phenols provided unusual disproportionation products: 4-ethylphenols and 4-acetylphenols and their tautomers.

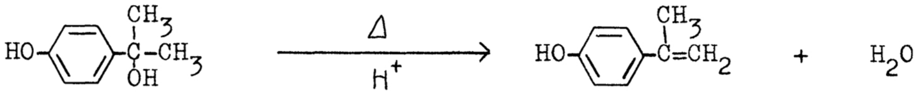
It is well known that the α-hydroxyethyl group neighboring to an aromatic ring usually undergoes dehydration with acidic catalysts such as $KHSO_4$ and alumina to afford the vinyl group.[1] Thus, α-hydroxyethylphenols with R = Me[2] and Ac[3] (1) provide vinyl compounds 2 as in eq. 1.



(1)

1 2

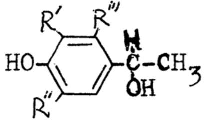
Compound 3 was also found to afford normal dehydration product 4 (eq. 2).[4]



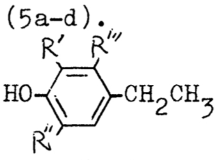
(2)

3 4

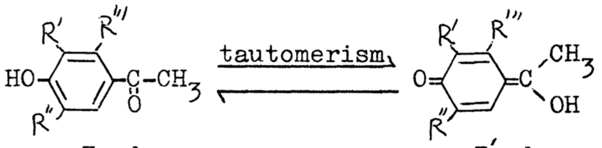
In this communication, we wish to report on the unusual behavior encountered in an attempt to get vinyl compounds by the alumina-catalyzed dehydration of 4-(α-hydroxyethyl)phenols (5a-d).



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.

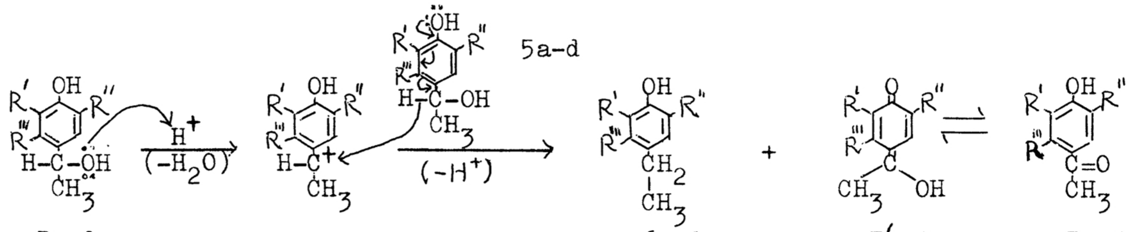
It is recognized from Table 1 that vinyl compounds are hardly present in the distillates, whereas 4-ethylphenols (6a-d) and 4-acetylphenols (7a-d) and their tautomers (7'a-d), which are the disproportionation products of 5a-d, are clearly recognized, although apparent yields are not high except in the 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								
	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''').



5a-d 6a-d 7'a-d 7a-d (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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