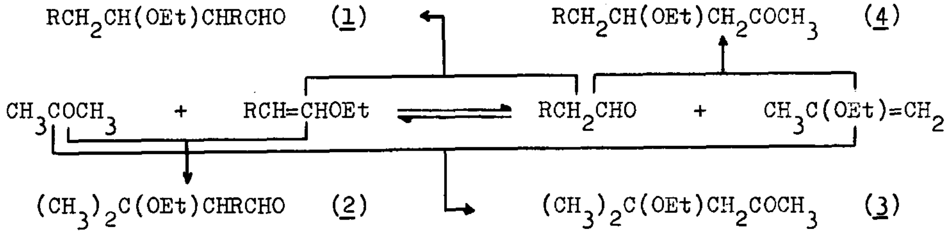
Tetrahedron Letters No. 26, pp 2221 - 2224, 1975. Pergamon Press. Printed in Great Britain.

SIDE REACTIONS PROMOTED BY TRANSENOLETHERIFICATION IN THE ACID CATALYZED CONDENSATION OF CARBONYL COMPOUNDS AND VINYL ETHERS

A. Guerrero, F. Camps[*], J. Albaigés and J. Rivera
Instituto de Química Orgánica. Patronato "Juan de la Cierva"
(C.S.I.C.), c/Jorge Girona Salgado. Barcelona-17. Spain

(Received in UK 2 May 1975; accepted for publication 15 May 1975)

Recently, we have pointed out that the complex mixtures resulting from some acid catalyzed condensations of aldehyde vinyl ethers with acetone could arise from cross reactions of the components of a transenoletherification equilibrium, established in the presence of the acid catalyst:[1,2]



In the present communication, we provide evidence of the foregoing assumption, based on the identification of some products formed in the boron trifluoride etherate catalyzed condensation of acetone with ethyl vinyl ether and ethyl 1-butenyl ether and of butyraldehyde with ethyl isopropenyl ether.

Unless otherwise stated, all reactions were carried out without solvent at room temperature with a 8:1:0.05 carbonyl compound:vinyl ether:catalyst molar ratio. The 1:1 condensation fractions were analyzed by combined glc-ms and "reaction-glc".[3] This technique furnishes structural information of the components of a mixture by matching the normal chromatogram with those obtained after insertion of columns packed with reactive phases in an appropiate point of the chromatographic system. For this aim, in the gas chromatograph injection block were inserted columns packed with 5% o-dianisidine on Chromosorb P for substraction of aldehydes and with 20% benzidine on silanized Chromosorb W for elimination of aldehydes and ketones[4]. The different structures were assigned by comparison of glc and ms data with those of authentic samples.

In the reaction of acetone and ethyl vinyl ether, after 17 hrs. under the above conditions, no aldehyde could be detected in the 1:1 condensation fractions (b.p. 45-88º/21 mm, 46% of the amount distilled from the residue after elimination of excess of acetone at normal pressure), being 4-ethoxy-4-methyl-2-pentanone (3) the major component. On the other hand, "reaction glc" of the above fractions, isolated after 1 hr., revealed the presence of nine compounds, namely three aldehydes, four ketones and two products unaffected by the foregoing reactive phases.

The aldehydes, identified as 3-ethoxybutanal (1, R=H), crotonaldehyde and 3-methyl-3-ethoxybutanal (2, R=H), were in minor amounts, whereas the ketones (3), 4-ethoxy-2-pentanone (4, R=H) and mesityl oxide were the main components of these fractions. The structure of 3-penten-2-one could be assigned to the ketone present in minor amount. One of the minor components, unchanged with the above subtractive phases, exhibited a molecular ion peak at m/e 144 ($C_8H_{16}O_2$) and the mass fragmentations of crotonaldehyde diethyl acetal.

In an independent experiment, the formation of ketone (3) by another possible pathway under the above reaction conditions, namely by ethanol addition to mesityl oxide, was ruled out.

Thus, in this case, the presence in the reaction mixture of ketones

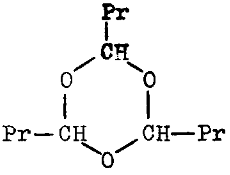
(3) and (4) (R=H), formed respectively by condensation of acetone and acetaldehyde with ethyl isopropenyl ether, and of aldehyde (1) (R=H), formed by condensation of acetaldehyde with ethyl vinyl ether, supports the occurrence of the aforementioned transenoletherification.

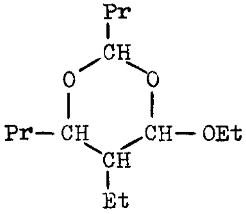
Satsumabayashi et al.[5] reported in a recent study of the acid catalyzed reactions of several β-substituted vinyl alkyl ethers with different aldehydes and ketones that the boron trifluoride etherate catalyzed condensation of acetone and ethyl 1-butenyl ether afforded 2-ethyl-3-methyl-2-butenal in moderate yield (28%). However, no account of other products formed in this reaction was given by these authors.

We have restudied this condensation on the ground of the preceding considerations. After 17 hrs. of reaction, glc analyses of the 1:1 condensation fractions (b.p. 66-96º/26 mm, 44% of the amount distilled from the residue after elimination of excess of acetone) showed the presence of eleven compounds, being ketone (3), 4-ethoxy-2-heptanone (4, R=Et), mesityl oxide and 3-hepten-2-one the major components. Although no other **unequivocal structural** assignments could be made, the identification of ketones (3) and (4) (R=Et), formed respectively by reaction of acetone and butyraldehyde with ethyl isopropenyl ether supports also in this case the foregoing assumption.

Finally, we studied the condensation of butyraldehyde and ethyl isopropenyl ether. If the transenoletherification would also prevail in this case, formation of the same products identified in the preceding condensation should be expected. However, after 16 hrs. of reaction, ketone (3) was not found among the components of the 1:1 condensation fractions (b.p. 36-63º/19 mm, 4,6% of the amount distilled). "Reaction glc" of this fraction revealed the presence of seven main components, namely two aldehydes, two ketones and three acetals. The ketones were identified as 4-ethoxy-2-heptanone (4, R=Et) and 3-hepten-2-one, and the acetals as butyraldehyde diethyl acetal, 2,4,6-

tripropyl-1,3,5-trioxane (5) and 2,6-dipropyl-4-ethoxy-5-ethyl-1,3-dioxane (6). The two last products were also present in the higher boiling fraction (b.p. 90-135º/19 mm) amounting trioxane (5), formed by trimerization of excess of butyraldehyde under the reaction conditions, to 90% of the distilled products.


(5)


(6)

To circumvent this autocondensation, the reaction was repeated using a 2:1 butyraldehyde:ethyl isopropenyl ether molar ratio. Under these conditions, trioxane (5) was not found among the compounds of the main distillation fraction (b.p. 100-125º/19 mm, 45% of the distilled products), being dioxane (6) the major component. As it was independently proved, this dioxane is formed under the reaction conditions by condensation of butyraldehyde and ethyl 1-butenyl ether, a transenoletherification product.

The above mentioned side reactions, so far unreported by previous authors,[5,6] can lower the yields obtained in the acid catalyzed condensations of carbonyl compounds and vinyl ethers, rendering this synthetic procedure worthless in some cases.

References

1. J. Albaigés, F. Camps, J. Castells, J. Fernández and A. Guerrero, Synthesis, 378 (1972)
2. F. Camps, J. Castells and A. Guerrero, Anales Quim., 70, 254 (1974)
3. F. Drawert, R. Felgenhauer and G. Kupfer, Angew. Chem., 72, 555 (1960)
4. B.A. Bierl, M. Beroza and W. T. Ashton, Mikrochim. Acta, 637 (1969)
5. S. Satsumabayashi, N. Kiyoshi, R. Soneda and Sh. Motoki, Bull. Chem. Soc. Japan, 43, 1586 (1970)
6. R. I. Hoaglin, D. G. Kubler and R. E. Leech, J. Amer. Chem. Soc., 80, 3069 (1958)