ISSN 1070-3632, Russian Journal of General Chemistry, 2009, Vol. 79, No. 3, pp. 513–514. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © E.V. Kluchareva, E.V. Ershova, M.Yu. Vozhdaeva, E.A. Kantor, 2009, published in Zhurnal Obshchei Khimii, 2009, Vol. 79, No. 3, pp. 523–524.

LETTERS TO THE EDITOR

Thermal Rearrangement of 1-(1-Methyl-2-Butenoxy)-4-methoxybenzene

E. V. Kluchareva, E. V. Ershova, M. Yu. Vozhdaeva, and E. A. Kantor

Ufa State Oil Technical University,
ul. Kosmonavtov 1, Ufa, 450062 Russia
e-mail: e.kluchareva@mail.ru

Received March 27, 2008

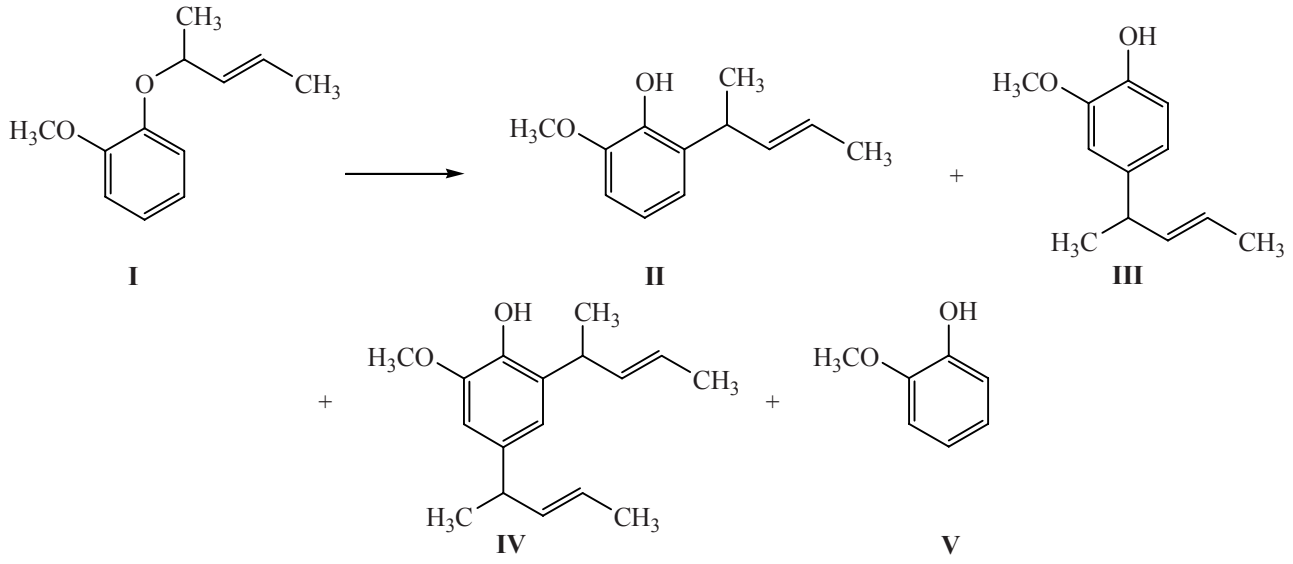
DOI: 10.1134/S107036320903030X

Thermal rearrangement of allyl ethers of phenols is the classical example of intramolecular Claisen rearrangement (3,3-sigmatropic shift) [1]. As known, the position of methoxy group in the aromatic ring affects the reaction mechanism. 1-(1-Metyl-2-butenoxy)-4-methoxybenzene undergoes the intramolecular rearrangement while 1-(1-methyl-2-butenoxy)-3-methoxybenzene takes part not only in the intramolecular process, but also in the intermolecular reaction proceeding with the preliminary cleavage of O–C bond [2]. Rearranement of 1-(1-methyl-2-butenoxy)-2-meth-oxybenzene **I** was not described before.

We have carried out rearranement of the ether **I** at heating (200°C, dodecane, 1 h, argon). 2-Methoxy-6-(1-methyl-2-butenyl)phenol **II** and 2-methoxy-4-(1-methyl-2-butenyl)phenol **III** in the 4:1 ratio and insignificant amounts of 2-methoxy-4,6-di-(1-methyl-2-butenylphenol **IV** and 2-methoxyphenol **V** were found in the reaction products. Presence of dialkylphenol **IV** and phenol **V** may be regarded as the evidence of the intermolecular transfer of alkenyl fragment of molecules **I, II** or **III** to the molecules **II** or **III** (Scheme 1).

Reaction mixture was analyzed by chromatomass-spectrometry (Agilent, HP-SMS 30×0.25×0.25 column; column temperature 30–250°C, heating rate 20°C/min in the range 30–60°C and 6°C/min in the range 60–250°C; injection temperature 250°C, ion source temperature 230°C; quadrupole analyzer temperature 150°C, ionization energy 70 eV). Mass spectra, *m/e*

Scheme 1.



(I_{rel}, %): **I**: 8.971 min, 124(100), 109(49), 69(28), 41 (19), 81(8); **II:** 9.981 min, 192(100), 145(75), 177(42), 117(38), 163(20); **III:** 10.148 min, 192(100), 145(77), 177(45), 117(40), 163(17); **IV:** 12.750 min, 69(100), 260(68), 245(25), 191(19), 159(19); **V:** 5.83 min, 109 (100), 124(91), 81(60), 53(13), 39(7).

Identification of isomers was based on the calculated activation energy data. More probable formation of isomer corresponds to the larger area of the chromatographic peak. Besides, the phase used provides the order of elution of analytes corresponding to their boiling points. Combination of these two factors permits a conclusion that the presented identification of isomers is quite reliable.

REFERENCES

1. Aleksandrovam E.K., Bunina-Krivorukovam L.I., Moshinskayam A.V., and Bal'yan, Kh.V., *Zh. Org. Khim*., 1974, vol. 10, no. 5, p. 1039.
2. Shornik, N.A., Aleksandrova, E.K., and Bunina-Krivorukova, L.I., *Zh. Org. Khim*., 1984, vol. 10, no. 10, p. 2245.