SYNTHESIS OF THYMOL VINYL ETHER

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Annotation
This article discusses the mechanism of the thymol vinylation reaction in the presence of acetylene in an overbasic medium. The main results were obtained on the basis of quantum chemical calculations and are consistent with the experimental results. Quantum-chemical calculations and modeling of intermediate complexes were performed using the HyperChem 8 software package based on MM+ and the Gaussian09 software using RHF/6-31-G* and MP2/6-311++G**//B3LYP. /6-31+G* combined methods.
Key words: thymol, acetylene, vinylation, superbasic medium, quantum chemistry.
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INTRODUCTION.

The use of superbasic systems in organic synthesis, in particular the reaction system consisting of potassium hydroxide-dimethyl sulfoxide, led to the discovery of new possibilities in the chemistry of acetylene. It is known that acetylene as an electrophile enters into the vinylation reaction due to nucleophilic addition to the triangle, and as a nucleophile enters into the ethynylation reaction due to the addition of acetylene to the carbonyl group. This two-way reactivity of acetylene is especially pronounced under the influence of a superbasic medium.

By using a superbasic medium, industrially important vinyl ester synthesis processes can be improved. Despite the fact that studies of acetylene reactions carried out in superbasic media have been started for several decades, the explanation of the mechanisms of these reactions and the nature of superbasic catalysis has not lost its relevance so far. The multicomponent composition of the reaction mixture, the high rate of the chemical reaction, and the multistage nature of the experimental study of reaction mechanisms in superbasic systems present a big problem. Therefore, it is important to apply high-level quantum chemical calculations in order to formulate basic ideas about the specifics of the main reactions of organic synthesis (vinylation or ethynylation), correctly direct and describe the synthesis of complex organic compounds, and also substantiate the reliability of these ideas.

RESEARCH METHODS.

When the components of the overbasic system are taken into account, the number of atoms and, accordingly, the number of basis functions also increases sharply. Therefore, when choosing a calculation method, not only the accuracy of one or another approach is important, but also the optimal consumption of computing resources. The mechanisms of thymol vinylation with acetylene were calculated by the combined calculation method (MP2/6-311++G**//B3LYP/6-31+G*) within the monosolvate model. The search for stationary points and optimization of their geometry, as well as the calculation of the frequency of normal vibrations and thermodynamic corrections, were performed using the most popular density functional method - the B3LYP method. The exchange functionals were constructed using local spin density functionals (LSDA, general state LDA), Hartree-Fock exchange functionals, and Becke functionals. The correlation functionals consist of the LYP functional and the VWN functional proposed by Li, Yang, Parr. We used basis sets (6-31+G*) filled with diffuse functions necessary to describe the geometry of various intermolecular complexes and transition states, anionic centers, and polarization functions. At the

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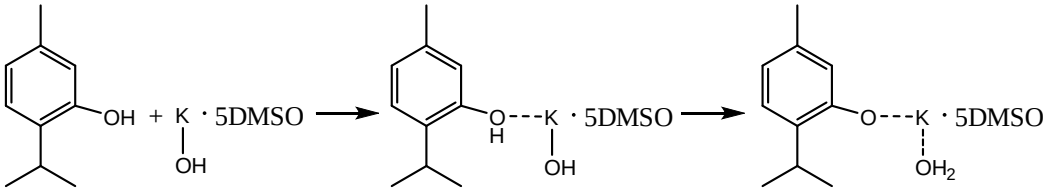
level of the second order of the Möller-Plesset excitation theory, the energies of all points of the monosolvate system were determined. To improve the accuracy of calculations, an extended trivalent exponential basis 6-311++G** was additionally used.

RESULTS AND DISCUSSION.

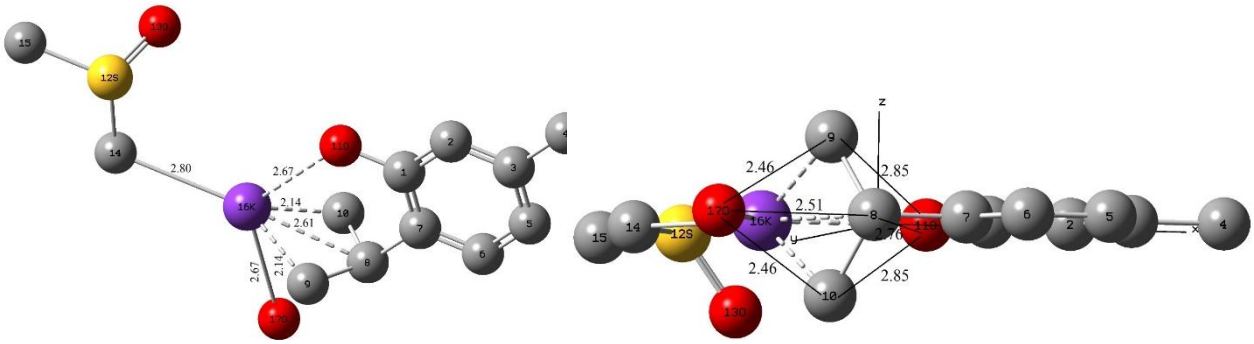
*The formation of thymolate ion.*At the initial stage of the reaction, the thymol molecule coordinates with potassium hydroxide, forming complex 1, which, as a result of proton transfer, turns into potassium thymolate 2.



1 **1a**

In this case, the weakly bound intermediate complex 1 is formed due to the coordination of the thymol molecule with the superbasic system. This complex is formed by the interaction of the proton of the hydroxyl group of thymol with the superbasic complex KOH·5DMSO, the H–O interatomic distance is 2.255 Å (Fig. 1).

It is known that the thymol hydroxyl proton has a greater mobility than all the protons of complex 1. Therefore, this proton interacts with the hydroxyl group in potassium hydroxide and leaves the complex. In addition to the oxygen atom (11) with the thymolate-ionic potassium cation in the resulting complex 2, it coordinates simultaneously with the 8th, 9th, and 10th carbon atoms (Fig. 1):



а) **б)**

Rice. 1. Structure of potassium thymolate complex 2.

This property of the thymolate ion is explained by the distribution of negative charges in the atoms. According to the calculation results obtained by the RHF/6-31-G* method, the charge of the oxygen atom (11) is -0.75 at. units, carbon atom (8) -0.37, carbon atoms (9, 10) respectively -0.540250 and -0.540248 atomic unit.

*Intermediate complexes.*The addition of acetylene to the potassium thymolate complex 2 leads to the formation of an intermediate vinylation complex 3:

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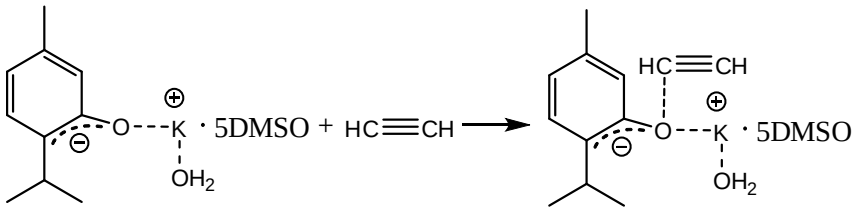
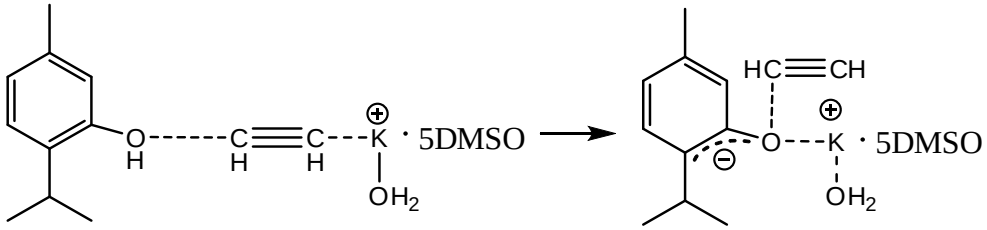


2 **3**

As a result of this change, the change in the enthalpy of the system is ΔH=-100.12 kcal/mol. In the intermediate complex 3, the acetylene molecule is coordinated with the oxygen (11) of the thymolate ion.

The environment of the solvent is also important for the stability of this intermediate complex, and acetylene is affected by protons in the methyl group of the DMSO molecule. As a result, acetylene is in a partially polarized state.

The formation of intermediate complex 3 as a result of thymol deprotonation and coordination of acetylene to form a thymolate complex is certainly not the only mechanism of the vinylation reaction. As a result of the direct action of acetylene on the superbasic complex KOH·5DMSO, the molecule is partially polarized and complex 2a is formed, and under its influence thymol is deprotonated and converted into intermediate complex 3.



2a **3**

But if we pay attention to the calculation results, it becomes clear that the value of the relative enthalpy of complex 2a (352.41 kcal/mol) is significantly higher than that of complex 2 (52.85 kcal/mol). It goes without saying that the stability of the system at such high energies is much less, and therefore complex 2a passes into a more stable state of complex 2.

Thus, during the acetylenic vinylation of thymol in an overbasic medium, a potassium dimesyl intermediate complex is initially formed, which acts as a solvent and catalyst. As a result of the binding of thymol molecules with it, 2 intermediate complexes are formed. As a result of adding acetylene to the reaction mixture, complex 3 is formed from the addition of acetylene to complex 2, resulting in the formation of the thymol vinyl ester product.

Literature

1. B.A. Trofimov, E.Yu. Schmidt, E.V. Skital'tseva, et al. //Base-Catalyzed Vinylation of Tertiary Propargylic Alcohols with Acetylene: a First Examples / Mendeleev Commun. – 2012. – V. 22, No. 2. – P. 62–63.
2. 2. N.M. Vitkovskaya, E.Yu. Larionova, A.D. Skitnevskaya et al. // Quantum-chemical model of the reaction of nucleophilic addition of methanol and methanethiol to acetylene in the superbasic KOH–DMSO system / Izv. AN. Ser. Khim., 2013, No. 1. – P. 27–34.
3. 3. Theoretical evaluation of some interactions in the acetylene–alkali metal hydroxide–DMSO system / N.M. Vitkovskaya, V.B. Kobychev, E.Yu. Larionova and others // Zhurn. structures. Chemistry.– 2009.– V. 50, No. 1.– S. 24–32.
4. B.A. Trofimov, E.Yu. Schmidt. Reactions of acetylenes in superbasic media -

eISSN 1303-5150

results of recent years // Russ. Chem. Rev. -2014, -vol. 83 No. 7. S. 600-619.

5. Ziyadullev O.E., Nurmonov S.E., Sirliboev T.S. Factors influencing the process of synthesis of new vinyl derivatives based on aromatic acetylene alcohols // Chemical technology. -2008, № 4; 18-22 b.
6. C.S. Jones, M.J. O' Connor, M.M. Haley. In acetylene chemistry // Wiley-VCH, Weinheim, 2005. p. 303-318.
7. Y. Chen, F. Lie, Z. Li. White biotechnology for sustainable chemistry // Adv. Synth. Catal., -2009, -vol. 351, p. 2107-2125.
8. Trofimov B. A., Oparina L. A., Kolyvanov N. A., Vysotskaya O. V., Gusarova N. K. Nucleophilic addition to acetylenes in superbasic catalytic systems: XVII. Vinylation of phenols and naphthols with acetylene // Zh. organic chemistry. 2015. V. 51, No. 2. pp. 200-206.
9. Ivanov A. V., Barnakova V. S., Mikhaleva A. I., Trofimov B. A. One-pot synthesis of 4,5-dihydrobenzo[g]indole and its 1-vinyl derivative from 1-tetralone, hydroxylamine and dichloroethane in the system KOH–DMSO // Izv. Ak. Sciences. Series Chemical. 2013. Vol. 11, pp. 2557-2558.
10. M.I.Soliev, A.K.Okhundadaev. Theoretical calculations of the electronic structure of the menthol and thymol molecules // Journal of Science and Education. No. 8 (20), 2018. Russia. Journal website: https://scientificpublication.ru.
11. Nurmanov S.E., Soliev M.I., Mirkhamitova D.Kh. Electronic structure of aromatic acetylene alcohols and modeling of their vinylation // Modern scientific research and innovations. 2015. No. 3. Part 1 [Electronic resource]. URL: https://web.snauka.ru/issues/2015/03/43329 (date of access: 09/13/2022).
12. Soliev M.I., Abdilalimov O., Nurmonov S.E. The reaction for obtaining 3-vinyloxymethyl-chamazulene // Universum: chemistry and biology: electron. scientific magazine 2020.1(79). URL: https://7universum.com/en/nature/archive/item/11051(date of access: 09/26/2022).
13. Soliev M.I., Abdilalimov O., Nurmonov S.E. Technology for the production of vinyl esters of menthol and thymol // Universum: technical sciences: electron. scientific magazine 2021.9(90). URL: https://7universum.com/ru/tech/archive/item/12254(accessed 26.09.2022).