

## Section 1. Chemistry

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### INFLUENCE OF A NANOSTRUCTURAL CATALYST IN THE ALLYLATION REACTIONS OF ANISOLE AND NEROLIN

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#### Abstract

The allylation reactions of anisole and nerolin with allyl alcohol were studied in nanostructured  $\text{FeCl}_3/\text{TiO}_2 \cdot \text{SiO}_2$  catalyst systems and the optimal conditions for obtaining the product with a yield of 70, 75% were determined. The influence of the solvent, the amount of catalyst and the duration of the reaction on the yield of the reaction was studied.

**Keywords:** *Methoxybenzene (anisole), methoxynaphthalene (nerolin), allylation, nanostructured  $\text{FeCl}_3/\text{TiO}_2 \cdot \text{SiO}_2$  catalyst, thin layer chromatography, heterogen catalyst*

#### Introduction

Allylphenols and allylnaphthols are prepared by the allylation of phenols and naphthols with allylating agents. Friedel–Crafts alkylation is among the most fundamental and convenient processes for construction of fine chemicals, pharmaceuticals, and agrochemicals containing functionalized arenes and heteroaromatic substructures. Allylation of aromatic compounds and their products are notable for its physiological activity and usefulness (Masanari Kimura, a Miki Fukasaka, a Yoshinao Tamaru, 2006. 3611–3612). Various sources contain data on the allylation of substituted phenols and naphthols with allyl alcohols (Masanari Kimura, a Miki Fukasaka, a Yoshinao Tamaru, 2006. 3611–3612; Jimmy A. van Rijn, Martin Lutz, Lars S. von Chr-

zanowski, Anthony L. Spek, Elisabeth Bouwman and Eite Drenta, 2009. 1637–1647; Jimmy A. van Rijn, Angela den Dunnen, Elisabeth Bouwman, Eite Drent, 2010. 96–102; Das B., Veeranjanyulu B., Krishnaiah M., Balasubramanyam P., 2009. 1929–1935), allyl halides (Zadmard R., Aghapoor K., Bolorutchian M. & Saidi M. R., 2013. 4495–4498; Thierry Ollevier, Topwe M. Mwene-Mbeja, 2006. 4051–4055), allyl acesates (Halligudi S. B., Sajjanikumari C. S., Kala Raj N. K., Deshpande S. S., Degaonkar M. P., 2001. 161–167; Amit Saha, John Leazer, Rajender S. Varma, 2012. 67–71, allyl tosylates (Naofumi Tsukada, Yasushige Yagura, Tetsuo Sato, Yoshio Inoue. 2003. 1431–1434), and allyl ethers (Christopher A. D., Graves Alexander G., Deardorf Donald R., 2016. 1–34) in

the presence of various catalysts. As a catalyst for the allylation of phenol and naphthol with various allylating agents,  $[\text{Rh}(\text{nbd})(\text{CH}_3\text{CN})_2]\text{PF}_6$ ,  $[\text{Rh}(\text{nbd})\text{Cl}]_2$ ;  $[\text{Rh}(\text{nbd})_2]\text{BF}_4$ ,  $\text{RhCl}(\text{PPh}_3)_3$ ,  $[\text{Ir}(\text{cod})\text{CH}_3\text{CN}_2]\text{PF}_6$ ,  $\text{Pd}(\text{OAc})_2/\text{MS } 4\text{\AA}$ ,  $[\text{Fe}_3\text{O}_4\text{-Dopamine-P}_d]$ ,  $\text{P}_d \cdot \text{Et}_3\text{B}$ ,  $\text{H}\beta$  zeolite.

The fact that each allylating agent reacts differently with phenols and naphthols, depending on the reaction conditions, the influence of solvent and catalyst, is reflected in modern scientific work. Allylation of naphthol-1 and naphthol-2 with allyl alcohol were carried out in the  $\text{P}_d \cdot \text{Et}_3\text{B}$  catalyst system and selective methods for the synthesis of C-allyl product were developed (Masanari Kimura, a Miki Fukasaka, a Yoshinao Tamaru. 2006. 3611–3612).

In order to synthesize biologically active allyl derivatives of naphthols, Indian scientists used the widely used catalyst Amberlyst-15 (Das B., Veeranjanyulu B., Krishnaiah M., Balasubramanyam P., 2009. 1929–1935). When using the Amberlyst-15, only C-allylation products-2-allyl-naphthol-1 and 1-allyl-naphthol-2- are mainly formed, the formation of O-allyl products under these conditions was not observed.

The allylation of phenol with allyl acetate catalyzed by  $\text{H}\beta$ -30 gave mainly C-allylated phenols (o-allyl phenol and p-allyl phenol), allyl phenyl ether, 1,3-bis-(2-hydroxy phenyl)-propane and an unidentified polymeric product (Halligudi S. B., Sajani-kumari C. S., Kala Raj N. K., Deshpande S. S., Degaonkar M. P., 2001. 161–167).

As part of alternative, sustainable technologies of green chemistry, in the method of allylation of phenols using magnetically extractable catalysts. Allylic ethers were synthesized in water using magnetically recoverable heterogeneous  $[\text{Fe}_3\text{O}_4\text{-Dopamine-P}_d]$  catalyst via O-allylation of phenols with allylic acetates under ambient conditions. The aqueous reaction medium, easy recovery of the catalyst using an external magnet, efficient recycling, and the high stability of the catalyst renders the protocol economic and sustainable (Amit Saha, John Leazer, Rajender S. Varma, 2012. 67–71).

Chemists of Japanese conducted an allylation reaction of electron-donating arenes with allyl tosylate at  $0^\circ\text{C}$  in the pres-

ence of  $[\text{Rh}(\text{nbd})(\text{CH}_3\text{CN})_2]\text{PF}_6$ ,  $[\text{Rh}(\text{nbd})\text{Cl}]_2$ ;  $[\text{Rh}(\text{nbd})_2]\text{BF}_4$ ,  $\text{RhCl}(\text{PPh}_3)_3$ ,  $[\text{Ir}(\text{cod})\text{CH}_3\text{CN}_2]\text{PF}_6$ . Various methoxybenzene were allylated with high couple-selectivity in almost all cases. In the allylation of naphthols using the following catalysts  $[\text{Rh}(\text{nbd})(\text{CH}_3\text{CN})_2]\text{PF}_6$ ,  $[\text{Rh}(\text{nbd})\text{Cl}]_2$ ;  $[\text{Rh}(\text{nbd})_2]\text{BF}_4$ ,  $\text{RhCl}(\text{PPh}_3)_3$ ,  $[\text{Ir}(\text{cod})\text{CH}_3\text{CN}_2]\text{PF}_6$ , the disadvantage is the low reaction yields (up to 33%). In the reaction of allylation of  $\beta$ -naphthol with allyl tosylate in the presence of the catalyst  $[\text{Rh}(\text{nbd})(\text{CH}_3\text{CN})_2]\text{PF}_6$ , produces 1-allyl-2-naphthol and methyldihydronaphthofuran in 38% and 32% yield (Naofumi Tsukada, Yasushige Yagura, Tetsuo Sato, Yoshio Inoue, 2003. 1431–1434).

### Experimental part

A thin layer chromatography plate (TLC) DC-Fertigfolien ALUGRAM ® Xtra SIL G/UV254 (Germany) was used, the appearance of spots was determined under the influence of a UV lamp on the plate. The reaction products were identified by IR analysis (Perkin Elmer Spectrum IR, Version 10.06.1) and NMR  $\text{H}^1$  and  $\text{C}^{13}$  (Unity 400 plus ICPSASR Uz).

### Preparation of catalysts from nanoporous metal oxides and iron (III) chloride $\text{FeCl}_3/\text{TiO}_2\text{-SiO}_2$

The catalytic system  $\text{FeCl}_3/\text{TiO}_2 \cdot \text{SiO}_2$  was prepared as follows  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and  $\text{TiO}_2 \cdot \text{SiO}_2$  (Khusniddin Musaev, Dilorom Mirkhamitova, Abdurasul Yarbekov, Khamdam Akbarov, Suvonkul Nurmanov, Olim Ruzimuradov, 2019) were weighed on an analytical balance in an amount of  $2 \cdot 10\text{--}4$  grams. In powder form, both substances were melted and mixed in a mortar. It was dried in the oven at  $50\text{--}60^\circ\text{C}$  for 1 hour, then at  $100\text{--}120^\circ\text{C}$  also for 1 hour.

**Synthesis of 2-allylanisole.** Anisole (0.05 mol, 5.42 ml), allyl alcohol (0.05 mol, 3.4 ml) and  $\text{FeCl}_3/\text{TiO}_2 \cdot \text{SiO}_2$  catalyst ( $2.4 \cdot 10^{-4}$  mol, 0.084 g), hydroquinone (0.0005 mol, 0.55 g) are poured into a three-necked round bottom flask connected to a stirrer, thermometer, a reflux condenser and, with a working stirrer. The reaction mixture is heated six hours at a temperature of  $100\text{--}120^\circ\text{C}$ . After cooling the reaction mixture, distillation was carried out by fractional distillation under vacuum. The 1-fraction

15–80 °C (20mm, remaining allyl alcohol and anisole), 2-fraction 70–90 °C (22 mm.) 3-fraction 98 °C (22 mm, 2-allylanisole). Yield 70%. **IR (KBr,  $\text{cm}^{-1}$ )** 751, 1172 1496, 1587, 2945, 1599. **NMR  $\text{H}^1$**  (Unity 400 plus ICPS AS RUz, referce HMDSO, Solvent CD3OD, chemical shift of protons,  $\delta$ , ppm) 3.24 m (2H,  $\text{CH}_2$ ), 3.81 s (3H,  $\text{OCH}_3$ ), 4.838, 5.00–5.20 d (2H,  $-\text{CH} = \text{CH}_2$ ), 5.884 m (1H,  $-\text{CH} = \text{CH}_2$ ), 6.803, 6.82, 7.14, 7.17 t (4H, ArH).  **$\text{C}^{13}$  spectrum** 100 MHz,  $\text{CDCl}_3$  d = 49, 55.442, 63.913, 114.795, 121.511, 129.271, 130.352, 138.827, 161.004

**Synthesis of 1-allyl-2-naphthylmethylether.** 2-naphthylmethylether (0.01mol, 1.58g), allyl alcohol (0.01mol, 1.45ml) and  $\text{FeCl}_3/\text{TiO}_2 \cdot \text{SiO}_2$  catalyst ( $2.4 \cdot 10^{-4}$  mol, 0.098g), hydroquinone (0.0005 mol, 0.55g) are poured into a three-necked round bottom flask connected to a stirrer, thermometer, a reflux condenser and, with a working stirrer. The reaction mixture is heated 5 hours at a temperature of 100–120 °C. After cooling the reaction mixture, the precipitate was filtered. Unreacted 2-naphthylmethyl ether and the obtained product-1-allyl-2-naphthylmethyl ether are washed and separated in hexane. Yield 75% (1.485g). Melting point 31–33 °C. **NMR  $\text{H}^1$**  (Unity 400 plus ICPS AS RUz, referce HMDSO, Solvent CD3OD, chemical shift of protons,  $\delta$ , ppm) 3.55 m (2H,  $\text{CH}_2$ ), 3.81 s (3H,  $\text{OCH}_3$ ), 4.838 d (2H,  $-\text{CH} = \text{CH}_2$ ), 5.884 m (1H,  $-\text{CH} = \text{CH}_2$ ), 6.803, 6.82, 7.24, 7.81t (6H, ArH).  **$\text{C}^{13}$  spectrum** 100 MHz,  $\text{CDCl}_3$  d = 31.4, 56.1, 109.0, 115.9, 118.4, 123.4, 124.3, 126.3, 128.0, 128.3, 129.2, 133.6, 153.2.

### Results and discussion

The formation of mainly para-allyl phenols in the allylation of phenols and naph-

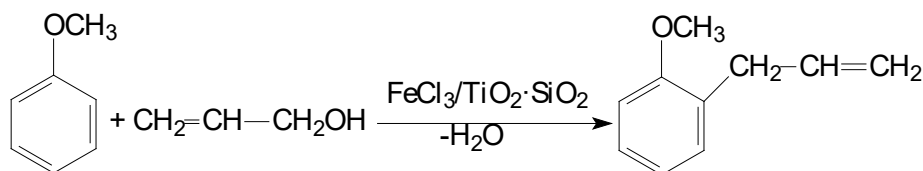
thols in the presence of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  by the Friedel-Crafts method was proved by gas-liquid chromatography (Azimova G. Z., Tajimuhamedov H. S., Yuldasheva M. R., 2019. 39–42). The formation of mainly ortho-allylphenols in the isomerization reactions of allylphenyl ethers using a new type nanostructured catalyst  $\text{FeCl}_3/\text{TiO}_2 \cdot \text{SiO}_2$  was confirmed by chromatography-mass spectrometry (Khusniddin Musaev, Azimova Gulmira, Yuldasheva Mukhabbat, Tadjimuhamedov Khabibullo, Khamdam Akbarov, Olim Ruzimuradov, 2019. 40–45). Allylation reaction of 2-naphthol under catalytic conditions  $\text{FeCl}_3/\text{TiO}_2 \cdot \text{SiO}_2$  with allyl alcohol and allyl acetate have also been studied. It was observed that iron (III) chloride with a nanostructured catalyst has a higher selectivity for the production of mono- and ortho- products, according to the ratio of iron (III) chloride itself is used as a catalyst. This can be explained by the fact that iron (III) chloride is adsorbed on the surface of the nanocatalyst and forms unstable complexes with allylating agent and this reduce the polyallylating ability of the reagent (Azimova Gulmira, Yuldasheva Mukhabbat, Tadjimuhamedov Khabibullo, 2020).

In this study, the allylation of electron-rich arenes, namely methoxybenzene (anisole) and methoxynaphthalene (2-naphthylmethyl ether, nerolin) in the presence of a catalyst containing  $\text{FeCl}_3/\text{TiO}_2 \cdot \text{SiO}_2$  impregnated with nanostructured metal oxides, was studied.

The allylation of anisole with allyl alcohol in the presence of  $\text{FeCl}_3/\text{TiO}_2 \cdot \text{SiO}_2$  was carried out under solvent-free conditions in a magnetic stirrer at 100–120 °C. The reaction showed that 2-allylanisole was formed.

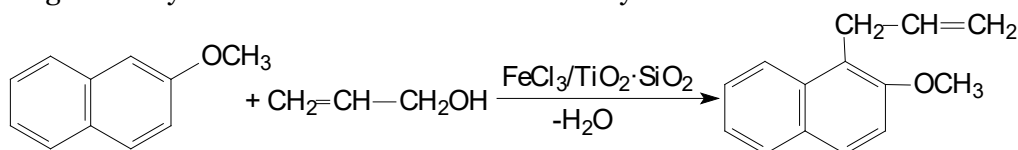
**Table 1.** Reaction conditions of anisole with allyl alcohol and the results obtained

The molar ratio of anisole: allyl alcohol: catalyst	Conditions of reaction, °C	Reaction duration, hours	Products	Yield, %	$R_t$ , system= hexane: ethylacetate = 5 : 1
1:1:10 <sup>-4</sup>	100–120	3		10%	0.45
1:1:10 <sup>-4</sup>	100–120	6	2-allyl-anisole	22%	0.45
1:1:2,4*10 <sup>-4</sup>	100–120	3		62%	0.45
1:1:2,4*10 <sup>-4</sup>	100–120	6		70%	0.45



Allylation reactions anisole: allyl alcohol: catalyst = 1: 1:  $2.4 \cdot 10^{-4}$  in a benzene solvent at 76–80 °C for 6 hours, the reaction yield was low (53%), the reaction time was increased to 8 hours profitability (55%) has not changed significantly.

The reaction of 2-naphthylmethyl ether with allyl alcohol on a  $\text{FeCl}_3/\text{TiO}_2 \cdot \text{SiO}_2$  catalyst was carried out in a reagent ratio of 1: 1:  $2.4 \cdot 10^{-4}$ , when it was carried out in a benzene solvent in a magnetic stirrer for 5 hours with a yield of 75%.



**Table 2.** Reaction conditions of 2-naphthylmethyl ether with allyl alcohol and the results obtained

The molar ratio of 2-naphthylmethyl ether: allyl alcohol: catalyst	Conditions of reaction, °C	Reaction duration	Products	Yield, %	$R_f$ system= hexane: ethylacetate = 5 : 1
1:1:10 <sup>-4</sup>	76–80	3		45%	0.93
1:1:10 <sup>-4</sup>	76–80	4	1-allyl-2-naphthyl-	63%	0.93
1:1:2,4*10 <sup>-4</sup>	76–80	5	methyl ether	75%	0.93
1:1:2,4*10 <sup>-4</sup>	76–80	6		75%	0.93

The resin was observed when the allylation reactions of naphthyl methyl ether were carried out in the absence of a solvent.

### Conclusions

Based on the results obtained, it can be concluded that allylation of anisole with allyl alcohol leads to a selective reaction with a high yield when carried out in a solvent-free state and 2-naphthylmethyl ether in good yield for 1-allyl-2-naphthylmethyl ether in good yield at using a benzene solvent achieved. The use of a nanostructured catalytic system –  $\text{FeCl}_3/\text{TiO}_2 \cdot \text{SiO}_2$  at allylation reactions made it possible to carry out them selectively with respect to ortho-allylation and with increased product yield than at using Lewis acids, and

the reaction of 2-naphthylmethyl ether with allyl alcohol proceeds with the participation of the C1 carbon atom at using nanostructured catalyst  $\text{FeCl}_3/\text{TiO}_2 \cdot \text{SiO}_2$ . In the anisole allylation reactions, it was found that anisole also acts as a solvent in the reaction process and that 2-naphthylmethylether is a crystalline substance that can complicate the reaction without a solvent.

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### References

- Masanari Kimura, a Miki Fukasaka, a Yoshinao Tamaru. (2006). Palladium-Catalyzed, Triethylborane-Promoted C-Allylation of Naphthols and Benzene Polyols by Direct Use of Allyl Alcohols. SYNTHESIS DOI: 10.1055/s-2006-950220;

- Jimmy A. van Rijn, Martin Lutz, Lars S. von Chrzanowski, Anthony L. Spek, Elisabeth Bouwman and Eite Drenta. (2009) Cationic Ruthenium-Cyclopentadienyl-Diphosphine Complexes as Catalysts for the Allylation of Phenols with Allyl Alcohol; Relation between Structure and Catalytic Performance in *O*- vs. *C*-Allylation. *Adv. Synth. Catal.*, – 351. – P. 1637–1647. URL: <http://dx.doi.org/10.1002/adsc.200900085>.
- Jimmy A. van Rijn, Angela den Dunnen, Elisabeth Bouwman, Eite Drent. (2010) Palladium–diphosphine complexes as catalysts for allylations with allyl alcohol. *Journal of Molecular Catalysis A: Chemical* – 329. – P. 96–102. Doi: 10.1016/j.molcata.2010.06.023.
- Das B., Veeranjanyulu B., Krishnaiah M., Balasubramanyam P. (2009). Benzoylation and Allylation of Naphthols Using Amberlyst-15. *Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry*. P. 1929–1935
- Zadmard R., Aghapoor K., Bolourchian M. & Saidi M. R. (2013). Solid Composite Copper-Copper Chloride Assisted Alkylation of Naphthols Promoted by Microwave Irradiation, *Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry*. – 28/24. – P. 4495–4499. DOI: 10.1080/00397919808004511
- Thierry Ollevier, Topwe M. Mwene-Mbeja. (2006). Bismuth triflate catalyzed Claisen rearrangement of allyl naphthyl ethers. *Tetrahedron Letters* – 47. – P. 4051–4055. Doi: 10.1016/j.tetlet.2006.03.193
- Halligudi S. B., Sajanikumari C. S., Kala Raj N. K., Deshpande S. S., Degaonkar M. P. (2001). Liquid phase allylation of phenol using H $\beta$  zeolite. *Journal of Molecular Catalysis A: Chemical* – 175. – P. 161–167.
- Amit Saha, John Leazer, Rajender S. Varma. (2012). *O*-Allylation of phenols with allylic acetates in aqueous medium using a magnetically separable catalytic system. *Green Chem.* – 14. – P. 67–71. DOI: 10.1039/c1gc16174a
- Naofumi Tsukada, Yasushige Yagura, Tetsuo Sato, Yoshio Inoue. (2003). Rhodium- and Iridium-Catalyzed Allylation of Electron-Rich Arenes with Allyl Tosylate. *Synlett No.* – 10. – P. 1431–1434.
- Christopher A. D., Graves Alexandr G., Deardorf Donald R. (2016). Regio and stereospecific *C*- and *O*-allylation of phenols via  $\pi$ -allyl Pd complexes derived from allylic estercarbonates. *The Journal of Organic chemistry*. P. 1–34. DOI:10.1021/acs.joc.6b02608
- Khusniddin Musaev, Dilorom Mirkhamitova, Abdurasul Yarbekov, Khamdam Akbarov, Suvonkul Nurmanov, Olim Ruzimuradov. (2019). Facile synthesis of PEG-templated SiO<sub>2</sub>-TiO<sub>2</sub> nanocomposite photocatalyst for degradation of phenolic water pollutants. *SN Applied Sciences*, Springer, – 1: 1164. – P. 1–10.
- Azimova G. Z., Tajimuhamedov H. S., Yuldasheva M. R. (2019). Allylation of phenol and naphthol with allyl acetate in the presence of small amounts of aqueous ferric chloride. *Universum: Chemistry and Biology* – No. 1 (55). – P. 39–42
- Khusniddin Musaev, Azimova Gulmira, Yuldasheva Mukhabbat, Tadjimuhamedov Khabibullo, Khamdam Akbarov, Olim Ruzimuradov. (2019). Influence of nanostructural catalyst in the synthesis of allylphenyl ether and of its isomerization products. *Journal of Chemistry and chemical technology* – No. 4. – P. 40–45
- Azimova Gulmira, Yuldasheva Mukhabbat, Tadjimuhamedov Khabibullo (2020). Influence of a nanostructural catalyst in the synthesis of allylnaphthols. “Austrian Journal of Technical and Natural Sciences”. No. 5–6.

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