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STEREOCHEMISTRY OF THE EPOXIDATION OF BICYCLO[2.2.1]HEPT-2-ENE AND ITS 7-SYN-SUBSTITUTED DERIVATIVES. A DFT STUDY

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Abstract

The stereochemical aspects of epoxidation of norbornene and its 7-*syn*-substituted derivatives by performic acid were investigated. Geometry and thermodynamic parameters of transition states and prereactive complexes were computed at the UBHandHLYP/6-31G(d) level of theory. It is shown that the transition states have a pronounced biradical character and a nearly coplanar orientation of the C=C bond and the molecule of performic acid. Transition state analysis revealed that, in the case of the *syn*-7-hydroxy derivative, the preference for the *exo*-approach of the oxidant can be explained by the stabilization of transition state with hydrogen bonding. In contrast, a chlorine atom or a methyl group at the 7-*syn* position facilitated the formation of *endo*-epoxides due to steric repulsion between the substituent and the oxidant.

Keywords: alkene epoxidation mechanism, peroxy acid, diradical transition state, density functional theory.

СТЕРЕОХІМІЯ ЕПОКСИДУВАННЯ БІЦИКЛО[2.2.1]ГЕПТ-2-ЕНІВ ТА ЇХ 7-SYN-ЗАМІЩЕНИХ ПОХІДНИХ. ДОСЛІДЖЕННЯ МЕТОДОМ DFT

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Вивчено стереохімічні аспекти епоксидування норборнену та його 7-*syn*-заміщених похідних пероксимурашиною кислотою. Геометричні та термодинамічні параметри перехідних станів та передреакційних комплексів розраховано у наближенні UBHandHLYP/6-31G(d). Показано, що перехідні стани мають бірадикальний характер та близьку до копланарності орієнтацію зв'язку C=C та молекули пероксикислоти. Аналіз перехідних станів свідчить, що у випадку *syn*-7-гідрокси похідного, переважна екзо-атака окиснювача пов'язана зі стабілізацією перехідного стану за рахунок водневих зв'язків. Наявність у 7-*syn* положенні атома хлору або метильної групи, навпаки, призводить до утворення ендо-епоксиду внаслідок стеричного відштовхування між замісником та окиснювачем.

Ключові слова: механізм епоксидування алкена, пероксикислота, бірадикальний перехідний стан, теорія функціоналу густини.

СТЕРЕОХИМИЯ ЭПОКСИДИРОВАНИЯ БИЦИКЛО[2.2.1]ГЕПТ-2-ЕНОВ И ИХ 7-SYN-ЗАМЕЩЕННЫХ ПРОИЗВОДНЫХ. ИССЛЕДОВАНИЕ МЕТОДОМ DFT

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Изучены стереохимические аспекты эпоксидирования норборнена и его 7-*syn*-замещенных производных пероксимуравьиной кислотой. Геометрические и термодинамические параметры переходных состояний и предреакционных комплексов рассчитаны в приближении UBHandHLYP/6-31G(d). Показано, что переходное состояние имеет бирадикальный характер и близкую к копланарности ориентацию связи C=C и молекулы пероксикислоты. Анализ переходных состояний свидетельствует, что в случае *syn*-7-гидрокси производного, преимущественная экзо-атака окислителя связана со стабилизацией переходного состояния за счет водородных связей. Наличие в 7-*syn* положении атома хлора или метильной группы, напротив, приводит к образованию ендо-эпоксида вследствие стерического отталкивания между заместителем и окислителем.

Ключевые слова: механизм эпоксидирования алкена, пероксикислота, бирадикальное переходное состояние, теория функционала плотности.

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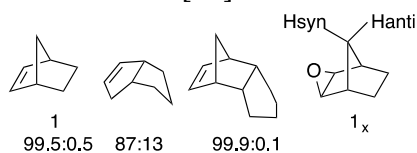
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Introduction

Norbornene (bicyclo[2.2.1]hept-2-ene, **1**) is a unique representative of cyclic olefins. Its high activity in electrophilic additions, *exo*-stereospecificity in cycloaddition reactions, and facile rearranging under various conditions manifested norbornene as an invaluable object of investigation in organic and physical chemistry [1–15].

Epoxidation of norbornene and its derivatives attracted significant attention, since it allows to investigate the influence of strain and steric factors upon reactivity [9; 11; 15], regio- and stereoselectivity [10; 16; 17]. Stereochemistry of the epoxidation was studied by conversion of the resulting epoxides into known norbornanols. Epoxynorbornane was shown to contain 94% [18] or 99.5% [19] of the *exo*-isomer (**1_x**). Brown explained this *exo*-selectivity by steric hindrance of the concave (*endo*-) face of the substrate. Using *cis*-bicyclo[3.3.0]octene and *endo*-tricyclo[5.2.1.0^{2,6}]deca-3-ene as the model substrates, he observed preferential formation of the *exo*-product with the increase in steric bulk [19].



Formation of *endo*-epoxides can be preferred when the *exo*-face of norbornene is shielded by bulky groups. Brown quantified the influence of methyl substituents in various positions on the stereochemistry of epoxidation with *meta*-chloroperbenzoic acid (*m*CPBA) [20]. Table 1 shows that only 7-*syn*-substituents inhibited the *exo*-attack. This data agrees with the earlier results for the epoxidation of bornylene [21].

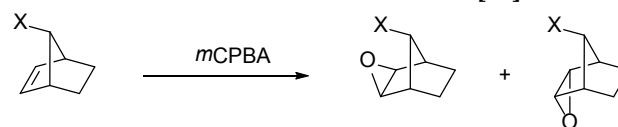
Table 1

Influence of the position of a methyl group on epoxidation of substituted norbornenes [17; 20; 21]		
Starting material	Total yield, %	% of the <i>exo</i> -isomer
	87	99.5
	87	10.0
	88	99.0
	100	99.5
	100	10.0

Later, epoxidation of 7-*syn*-substituted norbornenes with *m*CPBA was used to quantify the steric bulk of various groups [22; 23], as shown in Table 2. The observed *exo/endo* ratios are in line with the amount of the «open space» between the double bond and the substituent, as calculated by Davis and co-workers [23] using Wilcox's approach [24]. Polarity factors did not influence the reaction, as shown by the comparison between the outcomes for epoxidation and hydroboration.

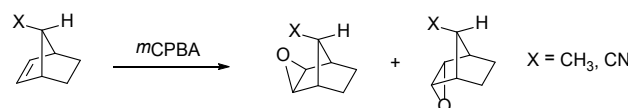
Table 2

Substituent influence on the stereochemistry of epoxidation of substituted norbornenes [23]



X =	H	Cl	Me ₃ Sn	Br	Me	t-Bu
<i>exo</i> -epoxide, %	99–99.5	62.0	55.0	45.0	6–14	0.0
<i>exo/endo</i> ratio	100	1.6	1.2	0.8	0.1	0.0

The influence of methyl and nitrile groups on the epoxidation of bicyclo[2.2.1]hept-2-en-*anti*-7-ols was studied by Gassman [25]:

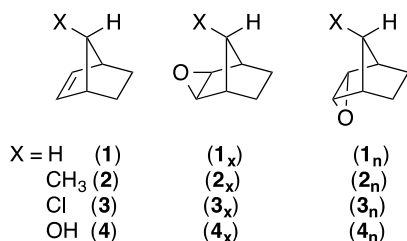


For X = CH₃, the ratio of *exo*- to *endo*-isomers was 78:22, while for X = CN this ratio was 55:45. This was interpreted as evidence of the lesser steric bulk from the nitrile group. Epoxidation of *syn*-7-bromomethyl-*anti*-7-bromonorbornene gave approximately equal amounts of the two epoxide isomers [26].

Several cases are known when the bridge-substituted norbornenes undergo preferential *exo*-attack. It is possible when the polar factor outweighs the steric one. A hydroxyl group is one of such substituents [27; 28].

Despite the significant interest to the epoxidation of substituted norbornenes, the stereochemistry of this process has been computationally studied only by closed-shell PES scanning for the reactions of *unsubstituted* norbornene, using either a PM3 approach [11] or a spin-restricted variant of B3LYP/6-31G(d) [9; 10]. No quantum-chemical investigation has been published so far that would deal with the substituent effects, steric and electronic factors. Therefore, we studied PES's for the reactions of norbornene (**1**), and its *syn*-7-substituted derivatives (**2–4**), with performic acid. Importantly, an earlier investigations of PES's for the epoxidation of ethylene and cyclopropene by peroxyformic acid at the CASSCF(10,10)/6-31G(d) and UQCISD/6-31G(d) levels

of theory yielded highly unsymmetrical biradical transition states for the rate-limiting stage [29; 30]. Thus, spin unrestricted variant of DFT theory at the UBHandHLYP/6-31G(d) level has been applied in the current study.



Results and discussion

First-order saddle points, which represented the transition states (TS's) for the formation of *syn*-7-substituted epoxynorbornanes (Fig. 1), as well as the corresponding reactive complexes were located on the calculated PES's.

According to the calculations, the activation

energy for the formation of *exo*-epoxynorbornane (**1_x**) is 13.13 kJ/mol higher than for the corresponding *endo*-isomer (**1_n**). Steric repulsion between the performic acid and the norbornene core in all transition states leads to the essentially coplanar alignment of the oxidant and the C=C bond (H-O¹-C²-C³ (α) dihedral angle, Fig. 1). The major destabilizing factor in the TS1_n when compared to TS1_x is a higher deformation energy, arising from the deformation of the rigid molecular framework. Among the noteworthy structural alterations in the TS1_n are the change in the H-C²-C³-C⁴ dihedral angle and the more planar arrangement of the six-membered ring, quantified by the β parameter – an angle between the planes C¹C²C³ and C²C⁶C⁵ (Fig. 1, Table 3). The β value for norbornene itself is 111.9° and for TS1_n – 116.5°. In contrast to TS1_x and norbornene, the double bond fragment in TS1_n is *exo*-bent, and thus the C¹-H and C²-H bonds are more eclipsed, leading to the significant torsional strain.

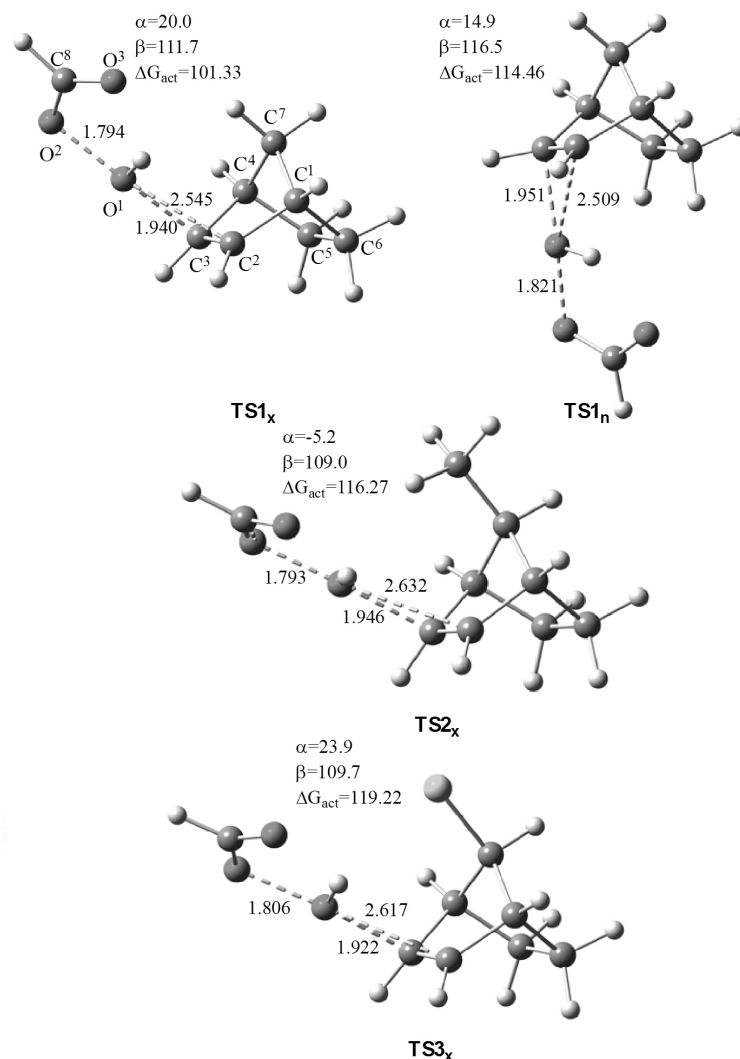


Fig. 1. Structure, bond lengths (Å), α and β angles ($^\circ$) of the transition states for epoxidation of compounds (1-4) and the corresponding activation energies (kJ/mol)

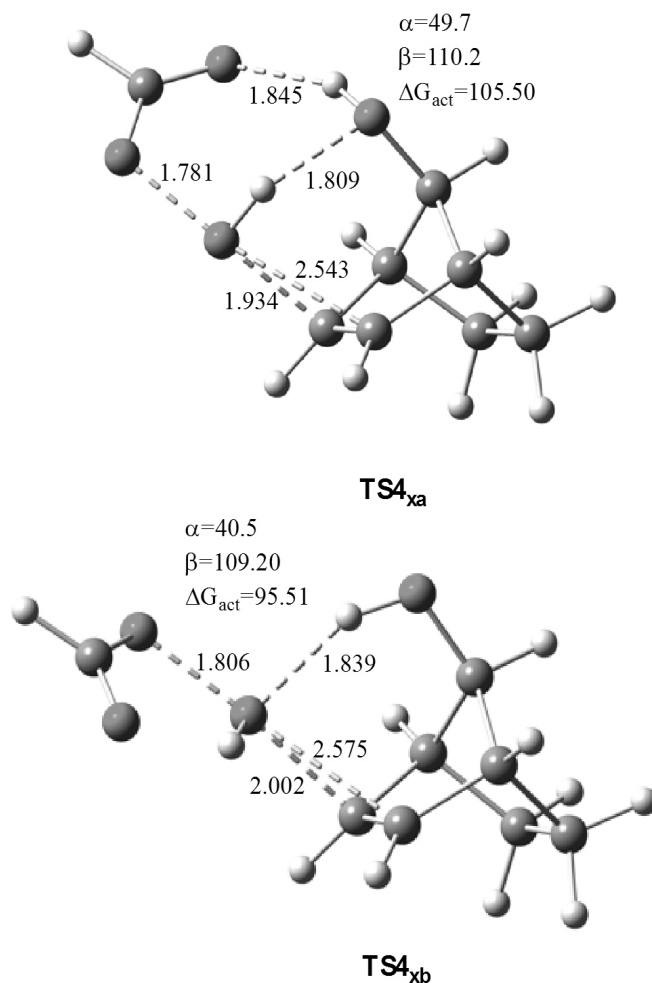


Fig. 1 (continued)

Attachment of a chlorine atom or a methyl group to the C⁷ leads to a significant increase in the energy of activation of *exo*-epoxidation compared to *unsubstituted* norbornene. This manifests itself in the reversal of stereochemistry of epoxidation and the predominant formation of *syn*-7-methyl- and *syn*-7-chloro-*endo*-epoxynorbornanes (2_n, 3_n). The observed selectivity can be explained by the steric (van der Waals) repulsion between the substituent and the hydrogen atom of the peracid.

Further analysis of the computational data showed that the *syn*-7-hydroxyl group in TS4_{xa} and TS4_{xb} participates in the hydrogen bonding with the attacking peracid during *exo*-addition. When the peracid is *syn*-oriented (TS4_{xa}), two hydrogen bonds are formed, and the molecule of performic acid becomes non-planar (the H-O¹-O²-C⁸ angle is 63.8°). TS4_{xb} is characterized by a single hydrogen bond and planar oxidant structure (Fig. 1).

Table 3

Bond angles and dihedral angles (°) in compounds 1-4 and the corresponding transition states (UBHandH-LYP/6-31G(d))

Structure	C ² -C ¹ -C ⁷	C ² -C ¹ -C ⁶	H-C ² -C ³ -C ⁴	H-C ² -C ¹ -H	C ¹ -C ² -C ³ -C ⁴	C ¹ -C ⁶ -C ⁵ -C ⁴
1	100.1	106.3	173.3	25.6	0.0	0.0
TS1_x	100.7	105.7	156.5	43.2	2.7	1.0
TS1_n	99.9	108.9	-160.1	-21.6	3.3	3.2
2	101.1	105.9	173.6	25.3	0.0	0.0
TS2_x	102.9	104.3	150.8	47.8	0.6	0.1
3	101.1	106.2	174.4	25.7	0.1	0.0
TS3_x	102.9	104.8	149.1	50.1	0.6	0.3
4	100.2	106.5	173.9	26.0	0.0	0.0
TS4_{xa}	101.3	106.1	155.6	44.6	2.0	0.3
TS4_{xb}	101.7	105.2	157.5	42.5	2.2	1.0

Due to the significant stabilizing effect of the hydrogen bonding in transition states $TS4_{xa}/TS4_{xb}$, the *exo*-approach of the peracid is much more favored over the *endo*-attack.

Wavefunction analysis for the located TS's indicates the biradical nature of all of these species (Table 4). Interestingly, spin densities on the atoms C^2 and C^3 in the *exo*-transition states are sybatic with the calculated activation energies of the corresponding reactions.

Table 4

**Spin density in transition states TS1-TS4
(BHandHLYP/6-31G(d))**

TS	C^2	C^3	O^1	O^2
$TS1_x$	0.1919	-0.5067	-0.1995	0.4922
$TS1_n$	0.1869	-0.5182	-0.1945	0.5098
$TS2_x$	0.2156	-0.5301	-0.2171	0.5106
$TS3_x$	0.2555	-0.5694	-0.2777	0.5676
$TS4_{xa}$	0.2041	-0.5270	-0.1740	0.4747
$TS4_{xb}$	0.1588	-0.4790	-0.2327	0.5271

Conclusions

In this work, we have investigated the potential energy surfaces that correspond to the biradical mechanism of the interaction of norbornene, and its 7-*syn*-substituted derivatives, with performic acid. All of the located transition states are characterized by the nearly coplanar alignment of the oxidant and the C=C bond. Stereochemistry of the epoxidation is determined by the balance of steric and electronic factors. Thus, a chlorine atom or a methyl group at the 7-*syn* position facilitate formation of *endo*-epoxides while *syn*-7-hydroxyl group significantly stabilizes *exo*-transition state due to formation of hydrogen bonds.

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Bibliography

- Erol S. *exo*-Selective inverse-electron-demand hetero Diels-Alder reactions of norbornene with 5-benzylidene-2-arylimino-3-aryl-thiazolidine-4-thiones at room temperature / S. Erol, I. Dogan // *Tetrahedron*. – 2013. – Vol. 69, N 4. – P. 1337–1344.
- Lopez S. A. Alkene Distortion Energies and Torsional Effects Control Reactivities, and Stereoselectivities of Azide Cycloadditions to Norbornene and Substituted Norbornenes / S. A. Lopez, K. N. Houk // *J. Org. Chem.* – 2013. – Vol. 78, N 5. – P. 1778–1783.
- De Jong S. Methods for direct alkene diamination, new & old / S. De Jong, D. G. Nosal, D. J. Wardrop // *Tetrahedron*. – 2012. – Vol. 68, N 22. – P. 4067–4105.
- Dang T. T. Hidden Brønsted Acid Catalysis: Pathways of Accidental or Deliberate Generation of Triflic Acid from Metal Triflates // T. T. Dang, F. Boeck, L. Hintermann // *J. Org. Chem.* – 2011. – Vol. 76, N 22. – P. 9353–9361.
- Epoxidation of N-(10-camphorsulfonyl)-endo-5-(aminomethyl)-bicyclo[2.2.1] hept-2-ene / L. I. Kas'yan, S. A. Prid'ma, A. V. Turov, A.O. Kas'yan // *Russ. J. Org. Chem.* – 2008. – Vol. 44, N 3. – P. 467–469.
- Gucma M. NMR Studies on 1,3-Dipolar Cycloaddition of Nitrile Oxides to Norbornenes / M. Gućma, W. M. Gołębiewski, M. Krawczyk // *J. Braz. Chem. Soc.* – 2013. – Vol. 24, N 5. – P. 805–813.
- Khusnutdinov R. I. Stereoselective *exo*-Addition to Norbornenes of Acetic Acid Generated from Vinyl Acetate in the Presence of Rhodium Complexes / R. I. Khusnutdinov, N. A. Shchadneva, L. F. Mukhametshina // *Russ. J. Org. Chem.* – 2010. – Vol. 46, N 1. – P. 54–58.
- Hydroacetoxylation of Olefins with Acetic Acid Generated in situ from Vinyl Acetate in the Presence of Ruthenium Complexes / R. I. Khusnutdinov, N. A. Shchadneva, L. F. Khisamova, U. M. Dzhemilev // *Russ. J. Org. Chem.* – 2011. – Vol. 47, N 2. – P. 155–160.
- Relative Reactivity of Peracids versus Dioxiranes (DMDO and TFDO) in the Epoxidation of Alkenes. A Combined Experimental and Theoretical Analysis / R. B. Bach, O. Dmitrenko, W. Adam, S. Schambony // *J. Am. Chem. Soc.* – 2003. – Vol. 125, N 4. – P. 924–934.
- Planar transition structures in the epoxidation of alkenes. A DFT study on the reaction of peroxyformic acid with norbornene derivatives / M. Freccero, R. Gandolfi, M. Sarzi-Amade, A. Rastelli // *J. Org. Chem.* – 2002. – Vol. 67, N 24. – P. 8519–8527.
- Okovytyy S. I. Theoretical investigation of the strain and reactivity of alicyclic olefins / S. I. Okovytyy // *Visn. Dnipropetr. Univ.: Khim.* – 1998. – Vol. 8, N 3. – P. 99–104.
- Shackelford S. A. A Novel Reaction of Xenon Trioxide: organic π -Bond Epoxidation. II. Concerning the Mechanism / S. A. Shackelford, G. H. Yuen // *J. Org. Chem.* – 1975. – Vol. 40, N 13. – P. 1869–1875.
- Awasthy A. K. The Nature of the Transition State in the Oxidation of Olefins by Chromium(VI) / A. K. Awasthy, J. Rocek // *J. Am. Chem. Soc.* – 1969. – Vol. 91, N 4. – P. 991–996.
- Jefford C. W. The reaction of singlet oxygen with Norbornene / C. W. Jefford, A. F. Boschung // *Helv. Chim. Acta.* – 1974. – Vol. 57, N 7. – P. 2257–2261.
- Epoxidation of stereoisomeric substituted norbornenes. Kinetic and theoretical investigation / L. I. Kas'yan, S. I. Okovityi, M. F. Bomushkar', V. G. Dri

- uk // Russ. J. Org. Chem. – 2000. – Vol. 36, N 2. – P. 195–202.
16. Kasyan L.I. Epoxidation of substituted norbornenes. stereochemical aspects accompanying intramolecular transformations / L. I. Kasyan // Usp. Khim. – 1998. – Vol. 67, N 4. – P. 299–316.
 17. Zefirov, N. S. Synthesis of norbornene endo-epoxide (3-oxatricyclo [3.2.1.0^{2,4}]octane) / N. S. Zefirov, L. I. Kasyan, L. Yu. Gnedenkov et al. // Tetrahedron Lett. – 1979. – Vol. 20, N 11. – P. 949–950.
 18. Kasjan L. I. Synthesis of cyclic diepoxides / L. I. Kasjan // Ukr. Khim. Zh. – 1978. – T. 44. – N 9. – P. 956–959.
 19. Brown H. C. Exo-endo Relative Reactivities in three Representative U-Shaped Systems. The exo-endo Rate Ratio in Solvolysis as a Steric Phenomenon / H. C. Brown, J. Hammar, J. H. Kawakami et al. // J. Am. Chem. Soc. – 1967. – Vol. 89, N 24. – P. 6381–6382.
 20. Brown H. C. Stereochemistry of Additions to Norbornene and 7,7-Dimethylnorbornene. A New Interpretation of the Steric Influence of 7,7-Dimethyl Substituents on Reactions of the Norbornyl System / H. C. Brown, Liu K.-T. // J. Am. Chem. Soc. – 1971. – Vol. 92, N 1. – P. 201–202.
 21. Yang X.-Q. Synthesis and Characterization of Epoxides from Bornylene / X.-Q. Yang, T. Zeng, L.-J. Du, J. Zhu, X. Zhu // Chemistry and Industry of Forest Products. – 2012. – Vol. 32, N 1. – P. 71–74.
 22. Davis D. D. Synthesis of some trimethyltinorbornanols / D. D. Davis, H. T. Johnson // J. Organomet. Chem. – 1975. – Vol. 86, N 1. – P. 75–87.
 23. Davis D. D. An estimate of the steric bulk of the trimethyltin group / D. D. Davis, A. J. Surmatis, G. L. Robertson // J. Organomet. Chem. – 1972. – Vol. 46, N 1. – P. 9–12.
 24. Wilcox C. F. A systemized Method of Calculating Dipole Moments and Internuclear Distances in Bicyclic Molecules / C. F. Wilcox // J. Am. Chem. Soc. – 1960. – Vol. 82, N 2. – P. 414–417.
 25. Gassman P. G. Neighboring Group Participation by the Carbon-Carbon Bond of an Epoxide synthesis and Solvolysis of Derivatives of 3-oxa-endo-tricyclo[3.2.1.0^{2,4}]octan-anti-8-ol / P. G. Gassman, J. G. Schaffhausen, P.W. Reynolds // J. Am. Chem. Soc. – 1982. – Vol. 104, N 23. – P. 6408–6411.
 26. Hoffmann R. W. Bicyclofulvenes. 9. Stereoelectronic Effects In Additions To 8-Methylenetricyclo[3.2.1.0^{2,4}]Octane Derivatives / R.W. Hoffmann, N. Huel, B. Landmann // Chem. Ber. – 1983. – Vol. 116, N 1. – P. 389–403.
 27. Epoxidation of allylic alcohols with hydrogen peroxide catalyzed by $[PMO_{12}O_{40}]^{3-}[C_5H_5N^+(CH_2)_{15}CH_3]_{3,13}$ / Y. Matoba, H. Inoue, J. Akagi et al. // Synth. Commun. – 1984. – Vol. 14, N 9. – P. 865–873.
 28. Richey H. G., Stereochemistry of titanium-assisted additions of organoaluminum compounds to hydroxybicyclo[2.2.1]hept-2-enes / H. G. Richey, L. M. Moses, J. J. Hangeland // Organometallics – 1983. – Vol. 2, N 11. – P. 1545–1549.
 29. Okovytyy S., A reinvestigation of the mechanism of epoxidation of alkenes by peroxy acids. A CASSCF and UQCISD study / S. Okovytyy, L. Gorb, J. Leszczynski // Tetrahedron Lett. – 2002. – Vol. 43, N 23. – P. 4215–4219.
 30. Okovytyy S., Is 2-oxabicyclobutane formed during the reaction of peroxyacids with cyclopropene. A high-level ab initio study / S. Okovytyy, L. Gorb, J. Leszczynski // Tetrahedron. – 2002. – Vol. 58, N 43. – P. 8751–8758.

References

1. Erol, S. Dogan, I. exo-Selective inverse-electron-demand hetero Diels-Alder reactions of norbornene with 5-benzylidene-2-arylimino-3-aryl-thiazolidine-4-thiones at room temperature. Tetrahedron, 2013, vol. 69, no 4, p. 1337–1344.
2. Lopez, S. A., Houk, K. N. Alkene Distortion Energies and Torsional Effects Control Reactivities, and Stereoselectivities of Azide Cycloadditions to Norbornene and Substituted Norbornenes. J. Org. Chem., 2013, vol. 78, no 5, p. 1778–1783.
3. De Jong, S., Wardrop, D. G., Nosal, D. J. Methods for direct alkene diamination, new & old. Tetrahedron, 2012, vol. 68, no 22, p. 4067–4105.
4. Dang, T. T., Boeck, F., Hintermann, L. Hidden Bronsted Acid Catalysis: Pathways of Accidental or Deliberate Generation of Triflic Acid from Metal Triflates. J. Org. Chem., 2011, vol. 76, no 22, p. 9353–9361.
5. Kas'yan, L. I. Prid'ma, S. A., Turov, A. V., Kas'yan, A. O. Epoxidation of N-(10-camphorsulfonyl)-endo-5-(aminomethyl)-bicyclo[2.2.1] hept-2-ene. Russ. J. Org. Chem., 2008, vol. 44, no 3, p. 467–469.
6. Gućma, M. Gołębiewski, W. M., Krawczyk, M. NMR Studies on 1,3-Dipolar Cycloaddition of Nitrile Oxides to Norbornenes. J. Braz. Chem. Soc., 2013, vol. 24, no 5, p. 805–813.
7. Khusnutdinov, R. I. Shchadneva, N. A., Mukhametshina, L. F. Stereoselective exo-Addition to Norbornenes of Acetic Acid Generated from Vinyl Acetate in the Presence of Rhodium Complexes. Russ. J. Org. Chem., 2010, vol. 46, no 1, p. 54–58.
8. Khusnutdinov, R. I., Shchadneva, N. A., Khisamova, L. F., Dzhemilev, U. M. Hydroacetoxylation of Olefins with Acetic Acid Genetated in situ from Vinyl Acetate in the Presence of Ruthenium Complexes. Russ. J. Org. Chem., 2011, vol. 47, no 2, p. 155–160.
9. Bach, R.B., Dmitrenko, O., Adam, W., Schambony, S. Relative Reactivity of Peracids versus Dioxiranes (DMDO and TFDO) in the Epoxidation of Alkenes. A Combined Experimental and Theoretical Analysis. J. Am. Chem. Soc., 2003, vol. 125, no 4, p. 924–934.
10. Freccero, M., Gandolfi, R., Sarzi-Amade, Rastelli, M. A. Planar transition structures in the epoxidation of alkenes. A DFT study on the reaction of peroxyformic acid with norbornene derivatives. J. Org. Chem., 2002, vol. 67, no 24, p. 8519–8527.
11. Okovytyy, S. I. Theoretical investigation of the strain and reactivity of alicyclic olefins. Visn. Dnipropetr. Univ.: Khim., 1998, vol. 8, no 3, p. 99–104.
12. Shackelford, S. A., Yuen, G. H. A Novel Reaction of Xe-

- non Trioxide: organic π -Bond Epoxidation. II. Concerning the Mechanism. *J. Org. Chem.*, 1975, vol. 40, no 13, p. 1869–1875.
13. Awasthy, A. K., Rocek, J. The Nature of the Transition State in the Oxidation of Olefins by Chromium(VI). *J. Am. Chem. Soc.*, 1969, vol. 91, no 4, p. 991–996.
 14. Jefford, C. W., Boschung, A. F. The reaction of singlet oxygen with Norbornene. *Helv. Chim. Acta.*, 1974, vol. 57, no 7, p. 2257–2261.
 15. Kas'yan, L. I., Okovityi, S. I., Bomushkar', M. F., Driuk, V. G. Epoxidation of stereoisomeric substituted norbornenes. Kinetic and theoretical investigation. *Russ. J. Org. Chem.*, 2000, vol. 36, no 2, p. 195–202.
 16. Kasyan, L.I. Epoxidation of substituted norbornenes. stereochemical aspects accompanying intramolecular transformations. *Usp. Khim.*, 1998, vol. 67, no 4, p. 299–316.
 17. Zefirov, N. S., Kasyan, L. I., Gnedenkov, L. Yu. Shashkov, A. S., Cherepanova, E. G. Synthesis of norbornene endo-epoxide (3-oxatricyclo [3.2.1.0^{2,4}]octane). *Tetrahedron Lett.*, 1979, vol. 20, no 11, p. 949–950
 18. Kasjan, L. I. Synthesis of cyclic diepoxides. *Ukr. Khim. Zh.*, 1978, vol. 44, no 9, p. 956–959.
 19. Brown, H.C., Hammar, J., Kawakami, J.H., Rothberg, I., Jagt, D. L. V. Exo-endo Relative Reactivities in three Representative U-Shaped Systems. The exo-endo Rate Ratio in Solvolysis as a Steric Phenomenon. *J. Am. Chem. Soc.*, 1967, vol. 89, no 24, p. 6381–6382.
 20. Brown, H. C. Liu, K.-T. . Stereochemistry of Additions to Norbornene and 7,7-Dimethylnorbornene. A New Interpretation of the Steric Influence of 7,7-Dimethyl Substituents on Reactions of the Norbornyl System *J. Am. Chem. Soc.*, 1971, vol. 92, no 1, p. 201–202.
 21. Yang, X.-Q. Zeng, T., Du, L.-J., Zhu, J., Zhu, X. Synthesis and Characterization of Epoxides from Bornylene. *Chemistry and Industry of Forest Products*, 2012, vol. 32, no 1, p. 71–74.
 22. Davis, D. D., Johnson, H.T. Synthesis of some trimethyltinorbornanols. *J. Organomet. Chem.*, 1975, vol. 86, no 1, p. 75–87.
 23. Davis, D. D. Surmatis, A. J., Robertson, G.L. An estimate of the steric bulk of the trimethyltin group. *J. Organomet. Chem.*, 1972. vol. 46, no 1, p. 9–12.
 24. Wilcox, C. F. A systemized Method of Calculating Dipole Moments and Inter-nuclear Distances in Bicyclic Molecules. *J. Am. Chem. Soc.*, 1960, vol. 82, no 2, p. 414–417.
 25. Gassman, P. G., Schaffhausen, J. G., Reynolds, P.W. Neighboring Group Participation by the Carbon-Carbon Bond of an Epoxide synthesis and Solvolysis of Derivatives of 3-oxa-endo-tricyclo[3.2.1.0^{2,4}]octan-anti-8-ol. *J. Am. Chem. Soc.*, 1982, vol. 104, no 23, p. 6408–6411.
 26. Hoffmann, R. W., Huel, N., Landmann, B. Bicycliculvenes. 9. Stereoelectronic Effects In Additions To 8-Methylenetricyclo[3.2.1.0^{2,4}]Octane Derivatives. *Chem. Ber.*, 1983, vol. 116, no 1, p. 389–403.
 27. Matoba, Y., Inoue, H., Akagi, J., Okabayashi, T., Ishii, Y., Ogawa, M. Epoxidation of allylic alcohols with hydrogenperoxide catalyzed by $\text{PMo}_{12}\text{O}_{40}$ // $\text{C}_2\text{H}_5\text{N}^+(\text{CH}_2)_{15}\text{CH}_3)_3$. *Synth. Commun.*, 1984, vol. 14, no 9, p. 865–873.
 28. Richey, H. G., Moses, L. M., Hangeland, J. J. Stereochemistry of titanium-assisted additions of organoaluminum compounds to hydroxybicyclo[2.2.1]hept-2-enes. *Organometallics*, 1983, vol. 2, no 11, p. 1545–1549.
 29. Okovytyy, S., Gorb, L., Leszczynski, J. A reinvestigation of the mechanism of epoxidation of alkenes by peroxy acids. A CASSCF and UQCISD study. *Tetrahedron Lett.*, 2002, vol. 43, no 23, p. 4215–4219.
 30. Okovytyy, S., Gorb, L., Leszczynski, J. Is 2-oxabicyclobutane formed during the reaction of peroxyacids with cyclopropene? A high-level ab initio study. *Tetrahedron*, 2002, vol. 58, no 43, p. 8751–8758.
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