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Modification of the nitrofunction in the Michael adduct of α -bromolevoglucosenone and 2,2-dimethyl-1,3-dinitropropane

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Abstract

Nitro compounds are widely used in organic synthesis due to the possibility of their transformation into carbonyl derivatives by the Neff reaction, into amines, nitriles, oximes, hydroxylamines, and imines by reduction of the nitro group. (-)-(1S,2R,3S,8R)-4,4-Dimethyl-3-nitro-9,11-dioxatricyclo-[6.2.1.02,6]-undec-5-en-7-one (**1**) is promising compound for the synthesis of cyclopentanoids. Its structural similarity with iridoids, protoylludane sesquiterpenoids, stimulated us to study the possibilities of this compound in this direction. Various methods are known for the transformation of nitro derivatives by the Neff reaction: (1) treatment of nitronates with acid, (2) oxidation of nitronates, and (3) reduction of nitroalkenes. Attempts to modify the nitro group in adduct **1** led to unexpected results. Thus, efforts to convert the nitro group to the carbonyl group under the standard Neff reaction conditions did not lead to the desired result – the starting compound turned out to be inert. Treatment of adduct **1** with a 15% aqueous solution of $TiCl_3$ led to the hydroxylation of the enone system by Michael heteroreaction to obtain tricycle alcohols in good yield in a ratio of 1:6 (α : β). It was found that the removal of conjugation by blocking the ketofunction with a dioxolane protecting group or by hydrogenation or epoxidation of the double bond allows the Neff reaction to be realized by the cleavage of the *aci*-nitroform with ozone or oxone (potassium monosulfate hydroperoxide) in the presence of Na_2HPO_4 - $NaOH$. Methods have been developed for the modification of the nitro group in (-)-(1S,2R,3S,8R)-4,4-dimethyl-3-nitro-9,11-dioxatricyclo[6.2.1.02,6]undec-5-en-7-one **1**, allowing its transformation into alcohols, oximes and amines. The reduction of the nitro group was carried out with in situ nickel borohydride and Ni/Ra. Hydrostannylation of the dioxolane derivative by the action of Bu_3SnH -AIBN in boiling toluene gave the oxime (-)-(1S,2R,8R)-4,4-dimethyl-7,7-ethylenedioxy-9,11-dioxatricyclo[6.2.1.02,6]undec-5-en-3-one.

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References

- [1] I.P. Tsypysheva, L.Kh. Kalimullina, M.G. Safarov, F.A. Valeev. Cyclopentaannulation of α -bromo- and -iodo derivatives of levoglucosenone with 2,2-dimethyl-1,3-dinitropropane. *Journal of Organic Chemistry*. **2003**. Vol.39. No.7. P.1119-1120. (Russian)
- [2] L.Kh. Faizullina, M.G. Safarov, Yu.S. Kondrova, V.S. Kolosnitsyn, L.V. Spirikhin, F.A. Valeev. Interaction of nitro compounds with levoglucosene and its α -halogen derivatives. Cyclopentaannulation of α -halogen cyclenones. *Journal of Organic Chemistry*. **2010**. Vol.46. P.897-902. (Russian)
- [3] V.A. Mnatsakanyan Iridoid glycosides. *Yerevan*. **1986**. 187p.
- [4] K. Shimoda, Y. Yamaoka, D. Yoo, K. Yamada, H. Takikawa, K. Takasu. Total syntheses of allelopathic 4-oxypseudoilludanes, melleolides, and echinocidins. *J. Org. Chem*. **2019**. Vol.84. P.11014-11024.
- [5] L.Kh. Faizullina, M.G. Safarov, I.A. Zagreeva, L.V. Spirikhin, F.A. Valeev. Some transformations of the cyclopentaannulation product of levoglucosenone. *Butlerov Communications*. **2009**. Vol.13. No.3. P.1-6. ROI-jbc-01/09-13-3-1 (Russian)
- [6] J.E. McMurry, J. Melton. Mild procedure for transforming nitro groups into carbonyls. Application to the synthesis of cis-jasmone. *J. Am. Chem. Soc.* **1971**. Vol.93. P.5309-5311.
- [7] D. Kalita, A.T. Khan, A.K. Saikia, G. Bez, N.C. Barua. A short synthesis of optically active corey lactone by means of the dirhodium(II)-catalyzed intramolecular C-H insertion reaction of an α -diazo ketone. *Synthesis*. **1998**. P.975.
- [8] J.F. McMurry, J. Melton, H. Padgett. New method for converting nitro compounds into carbonyls. Oxonolysis of nitronates. *J. Org. Chem*. **1974**. Vol.39. P.259-260.
- [9] P.A. Grieco, R.P. Nargund. Synthesis studies on diterpenes from a termite soldier. Total synthesis of (\pm)-biflora-4,10(19),15-triene. *Tetrahedron Lett*. **1986**. Vol.27. No.40. P.4813-4816.
- [10] S.J. Hecker, C.H. Heathcock. Total synthesis of (+)-dihydromevinolin. *J. Am. Chem. Soc.* **1986**. Vol.108. No.15. P.4586-4594.
- [11] H.J. Wu, C.C. Lin. First exclusive regioselective fragmentation of primary ozonides controlled by remote carbonyl groups and a new method for determining the regiochemistry of carbonyl oxide formation. *J. Org. Chem*. **1996**. Vol.61. No.11. P.3820-3828.
- [12] Liliya Kh. Faizullina, Minnigul M. Kanchurina, Farid A. Valeev. Modification of the nitrofunction in the Michael adduct of α -bromolevogluosenone and 2,2-dimethyl-1,3-dinitropropane. *Butlerov Communications*. **2021**. Vol.68. No.10. P.78-88. DOI: 10.37952/ROI-jbc-01/21-68-10-78 (Russian)