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The ozonolitic method for direct conversion of Δ^3 -carene and (+)-(α)-pinene to the dysemicarbazones

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Abstract

The reactivity of semicarbazide in the conversions of ozonolysis peroxide products of monoterpenes was investigated. Previously, treatment of peroxides obtained by ozonolysis of Δ^3 -carene and (+)- α -pinene in methanol with the semicarbazide hydrochloride corresponding ketoesters were obtained in high yields. Condensation products with semicarbazide were not observed either in the keto- or aldehyde group, which was probably due to the presence of HCl in the molecule, which, as is known, can itself participate in the decomposition of peroxides. In this paper, the use of semicarbazide for the reduction of ozonolysis peroxide products of trisubstituted bicyclic monoterpenes Δ^3 -carene and (+)- α -pinene is shown. When studying the transformations of the products of ozonolysis of these substrates under the action of semicarbazide, prepared according to a known method, it was found that they are converted into the corresponding disemicarbazones with the anti-configuration of the C=N bond. An alternative method of obtaining the desired disemicarbazones by treatment with semicarbazide formed in situ from its hydrochloride upon neutralization with sodium acetate is proposed. The ozonation products were treated with a 1:1 mixture of NH₂C(O)NHNH₂·HCl and AcONa, and the reaction time was significantly reduced. Thus, an effective one-pot method for the conversion of Δ^3 -carene and (+)- α -pinene into disemicarbazones is proposed, it is based on the reduction of the peroxide products of ozonolysis by semicarbazide. The advantage of the proposed method is that it is not necessary to isolate the carbonyl compound, while the standard ozonolitic method for the preparation of molecules with a hydrazone group from alkenes involves the reduction of peroxides with reducing agents such as Me₂S, PPh₃, etc., the formation of the resulting aldehyde or ketone and their subsequent condensation with derivatives of hydrazine.

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