

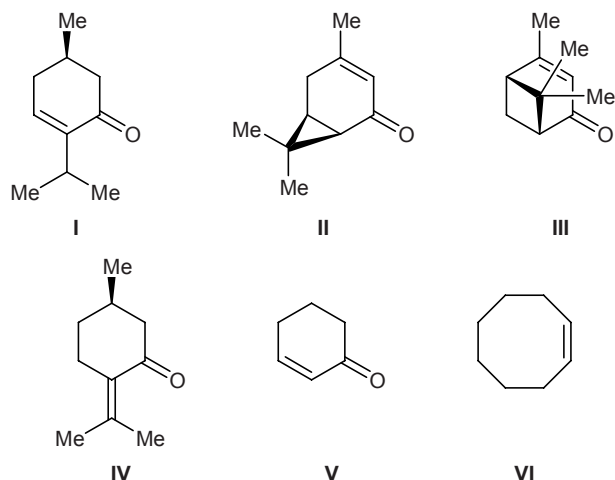
SHORT
COMMUNICATIONSComparative Ozonolysis of Cyclic α,β -Unsaturated EnonesG. Yu. Ishmuratov^a, E. R. Latypova^b, A. V. Bannova^b, R. Ya. Kharisov^a,
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Ozonolysis of cyclic olefins has been well documented; this reaction provides preparation of various α,ω -functionalized oxygen-containing compounds in good yields [1]. However, ozonolysis of cyclic olefins with electron-deficient double bonds involves some difficulties related to the substrate nature [2, 3]. In keeping with scarce published data available on the ozonolysis of α,β -unsaturated cyclic ketones, the reaction takes anomalous pathways and is often accompanied by decomposition of the carbon skeleton [2, 4]. Conjugated carbonyl compounds are considerably less reactive toward ozone than common olefins [5, 6].

We previously reported [7] on enhanced reactivity of (*R*)-4-menthenone (**I**) in the ozonolysis process, which was interpreted [8] in terms of both unusual polarization of the double bond in the enone system



and steric hindrances created by the isopropyl group in the α -position.

In the present work we compared the reactivities of some α,β -unsaturated cyclic ketones **I–IV**, conjugated cyclohexenone **V**, and cyclooctene (**VI**) in the oxidation with ozone. For this purpose, a solution of 0.096 g (1.0 mmol) of cyclohex-2-en-1-one (**V**) and 1.0 mmol of enone **I–IV** or cyclooctene **VI** in a mixture of 2 ml of anhydrous methylene chloride and 2 ml of anhydrous methanol was subjected to ozonation at 0°C until 1.0 mmol of ozone was absorbed (ozonator capacity 1.5 mmol/h). Dimethyl sulfide, 0.5 ml (5.0 mmol), was then added to the reaction mixture, and the mixture was kept for 2 h at room temperature until peroxy compounds disappeared (test with an acidified aqueous solution of potassium iodide). The mixture was analyzed by gas–liquid chromatography on a Shimadzu GC-9A instrument equipped with a 15-m DB-225 MS quartz capillary column (oven temperature 80–230°C, carrier gas helium) to determine the concentration of unreacted enone **I–V** or cyclooctene **VI** using cyclohexanone as internal standard. The consumption of ozone for each enone **I–V** or cyclooctene **VI** corresponded to the difference between their concentrations in the initial mixture and reaction products. According to the ozone consumption, the following relative reactivity values were obtained with respect to cyclohexenone **V**: **I**, 1.38; **II**, 0.52; **III**, 0.54; **IV**, 3.17; **VI**, 5.25. Thus the examined olefins rank as follows with respect to their reactivity in the ozonolysis: **II** \approx **III** < **V** < **I** < **IV** < **VI**.

The results obtained in the present work confirmed that conjugated cyclic enones **I–V** are less reactive toward ozone than cyclooctene **VI** having no functional substituents. We also demonstrated enhanced reactivity of (*R*)-4-menthenone (**I**) in this reaction, which is likely to result from more pronounced +*I* effect of alkyl group in the α -position. (*R*)-Pulegone (**IV**) exhibited even higher reactivity, presumably due to joint +*I* effects of two methyl groups and lesser steric hindrances as compared to menthenone **I**. Steric hindrances are also responsible for the reduced reactivity of carenone **II** and verbenone **III** relative to cyclohexenone **V**.

(*R*)-4-Menthenone (**I**) was synthesized according to the procedure described in [9, 10]; compounds **II–VI** were commercial products (Lancaster). All substrates had a purity of no less than 97%.

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