# CYCLOADDITION REACTION OF BENZOCYCLOPROPENE WITH NITRILE OXIDES: A SYNTHETIC ENTRY INTO A BRIDGED OXAZONIN SKELETON

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It is known that tricyclo[4.3.1.0]deca-2,4,7-triene (A) reacts with sodium methylsulfinyl anion in dimethyl sulfoxide to afford bicyclo[4.3.1]decatetraenyl anion (B). This finding clearly indicates that the incorporation of negative charge into (A) makes more favorably the opened 10-pi-electron delocalized structure (B) rather than the closed tricyclo[4.3.1.0]deca-2,4,7-trienyl anion. The similar relation may be expected between 9-oxa-8-azatricyclo[4.3.1.0]deca-2,4,7-triene (C) and 9-oxa-8-azabicyclo[4.3.1]deca-1,3,5,7-tetraene (D). The heterocyclic analogue (C) having a lone pair electron on oxygen atom might also be the bridged oxazonin (D) rather than norcaradiene type tautomer (C). In this study we investigated the cycloaddition reaction of benzocyclopropene with arylnitrile oxides. Since benzocyclopropene is known to undergo cycloaddition reaction with various dienes, it might be a promising precursor for synthesizing the skeleton of (C) and then (D).

The solution of benzocyclopropene (8 mmol) with benzonitrile oxide (4 mmol) in diethyl ether at 0° for 1 week aforded mono-adduct Ia (7-phenyl-9-oxa-8-azatricyclo [4.3.1.0]deca-2,4,7-triene), mp 64-5°, in 10 % yield and three bis-adducts; IIa (mp 162-3°, 47 %), IIIa (mp 143-4°, 4 %), IVa (mp 203-4°, 2 %). When the mixture of benzocyclopropene (8 mmol) and mesitonitrile oxide (4 mmol) in 10 ml methylene chloride was refluxed for 5 days we could obtain mono-adduct Ib (mp 95-6°) in 27 % yield along with four bis-adducts; IIb (mp 189-190°, 10 %), IIIb (mp 193-4°, 22 %), IVb (mp 122-4°, 9 %), Vb (mp 160-1°). The structures of mono-adducts Ia and Ib were deduced from the spectral properties and were clarified that the closed norcaradiene type tautomers (C) were preferable to the opened bridged oxazonin type tautomers (D) in the range of 25°-120°. However, heating Ib at 130-135° caused isomerization to azirine derivative. Futhermore cycloaddition reaction of acetonitrile oxide with benzocyclopropene was also investigated. These results of cycloadditions and thermal behaviours of mono-adducts including the mechanistic aspect will be presented.