SYNTHETIC AND REACTION STUDIES OF
STRAINED SMALL RING CARBOCYCLICS

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SUMMARY

1-Methoxy-2,3,3-trimethylcyclopropene, the methyl enol ether of 2,3,3-trimethylcyclopropene has been synthesized. An improved procedure for the synthesis of 1-methoxy-3,3-dimethyl-2-phenylcyclopropene is also reported. The syntheses of 1-benzylxoy-3,3-dimethyl-2-phenylcyclopropene, 1-methoxy-3,3-dimethylcyclopropene and 1-t-butoxy-2,3,3-triphenylcyclopropene are discussed. The key intermediates for the preparation of the above compounds were the p-toluenesulphonylhydrazones of α-alkoxy-α,β-unsaturated ketones.

An approach towards the synthesis of an enolate anion of cyclopropanone via 1-acetoxy-3,3-dimethyl-2-phenylcyclopropene is described.

The chemistry of both 1-methoxy-2,3,3-trimethylcyclopropene and 1-methoxy-3,3-dimethyl-2-phenylcyclopropene has been studied. Acid hydrolysis of both enol ethers gave products consistent with an intermediate cyclopropanone hemiacetal which underwent ring cleavage to give α-hydroxyketones.

Attempts to convert the above two ethers to bicyclobutanes with a bridgehead oxygen function failed. The addition of methylene carbenes did not give any of the desired products. Both ethers failed to undergo 1,3-dipolar cycloaddition with diazomethane or diphenyldiazomethane.

Approaches towards the synthesis of tricyclo(2.2.0.0^2,5) hexane via the key intermediate 2-benzoylbicyclo(1.1.1)pentane are reported. Attempts to convert 2-hydroxy-2-phenylbicyclo(1.1.1)pentane to 2-benzoylbicyclo(1.1.1)pentane via degradation of the aromatic ring with ruthenium tetroxide were thwarted by the instability of the bicyclopentanol. Removal of the hydroxyl function by catalytic hydrogenolysis or Birch reduction were unsuccessful with acyclic products predominating.
The hydroxyl group was successfully protected by conversion to its tetrahydropyranyl ether but conversion of this compound to 2-benzoylbicyclo(1.1.1)pentane has yet to be achieved.

The attempted preparation of 2-benzoylbicyclo(1.1.1)pentane via a Wolff rearrangement of 3-diazo[bicyclo(2.1.1)hexan-2-one or a quasi-Favorskii rearrangement of 3-bromobicyclo(2.1.1)hexan-2-one was also unsuccessful due to the low reactivity of bicyclo(2.1.1)hexan-2-one.