

INTRAMOLECULAR CARBENOID INSERTIONS: FORMATION OF 2,2,4,4-

TETRAMETHYLBICYCLO[1.1.0]BUTANE

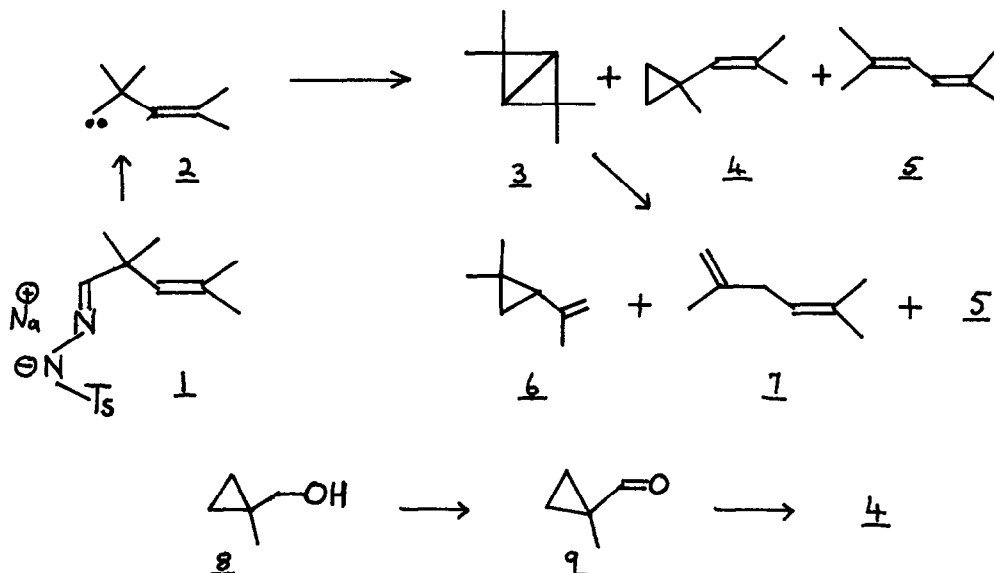
By D.P.G. Hamon* and H.P. Hopton

(Organic Chemistry Dept., University of Adelaide, Adelaide, Australia, 5000)

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In connection with other work in these laboratories we anticipated the need to produce a 2,2,4,4-tetramethylbicyclobutane derivative by carbenoid insertion into a double bond. Although bicyclobutanes have been prepared in this manner¹, no examples with the substitution pattern we required have been reported. Therefore we chose to study, as a model system, the formation of tetramethylbicyclo[1.1.0]butane (3)² by intramolecular insertion of the carbene 2. Because of the interest in this particular carbene^{3,4} with respect to transition-metal promoted rearrangements we have chosen to publish these results at this time.

The *p*-tosylhydrazone of the known aldehyde⁵ was converted to the sodium salt 1 by sodium methoxide in methanol. Upon heating the dry sodium salt 1 at 175° and atmospheric pressure, nitrogen was evolved and a liquid (ca 50% yield) distilled from the reaction flask. This liquid consisted of a mixture of the isomeric compounds[#] 3, 4 and 5 in the approximate relative ratios 6:5:4 respectively. The identity of these compounds was established in the following manner. Separation by vapour phase chromatography (VPC) on a base treated column (all glass system 6 ft. x ¼ in. 20% SE30 5% NaOH on Chromosorb W) gave two major components A and B in order of retention times. By a comparison of spectral data with those in the literature⁶, component B was shown to be 2,5-dimethylhexa-2:4-diene (5). Component A was a mixture of the two compounds 3 and 4 from which the vinylcyclopropane 4 could be obtained by VPC on a column containing the normal acid-washed support (36 ft. x ¼ in. 25% Apelizon M on Varaport-30) because the bicyclobutane decomposed⁷ under these conditions into the isomeric compounds 6, 7 and 5⁸ of differing retention times to 4. The identity of the vinylcyclopropane was proved by independent synthesis. (1-methylcyclopropyl)methanol (8)⁹ was oxidised to the known aldehyde¹⁰ 9 using the modified procedure¹¹ for the Collins oxidation. Treatment of this aldehyde with isopropylidene-triphenylphosphorane gave the vinylcyclopropane 4 identical in all respects with the compound obtained above. The difference between the nmr spectrum[†] of component A and that of vinylcyclopropane 4 is three peaks in the ratio 3:3:1 at $\delta = 1.22, 1.05$ and 0.90 which are in close agreement with those reported for authentic 2,2,4,4-tetramethylbicyclo[1.1.0]butane² (3). This data, coupled with that of the rearrangement¹² to the compounds 5, 6 and 7, gives us the confidence to claim that the bicyclobutane



3 is the other compound in the component A.

These three products of the pyrolysis reaction can be considered to have arisen by carbenoid insertions of the carbene **2** into various bonds. The difference between these results and those of Gassman³ and of Masamune⁴, probably reflects the cationic contribution to the resonance hybrid of transition-metal complexed carbenes.

^δ Correct combustion analysis was obtained
[†] in CCl₄/TMS

[#] also present were two minor components (<5% total) with the same retention times as E and Z, 2,5-dimethylhexa-2:4-diene, two trace components (unidentified) and a much less volatile crystalline component (as yet unidentified).

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